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Volume III

Colorimetric Determination of Traces of Metals

Second Edition, Revised and Enlarged

by E. B. SANDELL

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COLORIMETRIC DETERMINATION of TRACES of METALS

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Professor of Analytical Chemistry
University of Minnesota

Second Edition
Revised and Enlarged

1950

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PREFACE TO THE SECOND EDITION

Although hardly any new colorimetric reagents of importance have been introduced since the first edition of this book in 1944, there has been a flood of papers on further applications of previously known reagents. This mass of material has made necessary extensive additions in the present edition; in a few cases it has made possible the elimination of older procedures. The objectives and plan of the book remain the same as before.

E. B. SANDELL

September 1950

PREFACE TO THE FIRST EDITION

The colorimetric determination of traces of elements, especially of metals, has made great advances in recent years and it seemed to the writer that it would be useful to have available a collection of modern methods in this field of analysis. This book is the result of an attempt in this direction. It is not intended to be an encyclopaedia of methods for the colorimetric determination of small amounts of metals. The aim has been rather to present a limited number of methods which at the present time appear to be best suited for dealing with traces of metals. No one reagent is necessarily the best for the determination of an element in all kinds of samples or under all conditions, and consequently two or three methods are sometimes described in greater or less detail for a number of the metals. A few fluorimetric methods are included. The treatment is to a considerable extent based on the experience of the writer in testing or using various methods.

Anyone who surveys the methods of colorimetric trace analysis must experience a feeling of satisfaction arising from the many sensitive reactions available and, on the other hand, of something close to dismay at our imperfect knowledge of the application of these reactions. The effect of foreign elements on a particular color reaction is frequently poorly known and the prevention of the interference of foreign substances has, for the most part, been incompletely studied. Methods for the separation of traces are but poorly developed or even non-existent for many elements. The user of this book is likely to find many of his questions in this phase of trace analysis unanswered in the present treatment. It is to be hoped that the

workers of the future will be willing to devote as much of their energies to this prosaic aspect of the subject as to the more inviting one of searching for new reagents.

I am greatly indebted to Professor I. M. Kolthoff for reading the manuscript and offering suggestions; I also wish to thank Messrs. Arthur Anderson, George Matsuyama, Robert W. Perlich, and Leo Safranski, for reading and commenting on portions of the manuscript.

E. B. SANDELL

Minneapolis, Minn.
February 1944

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GENERAL PART

COLORIMETRIC TRACE ANALYSIS

CHAPTER I

TRACE ANALYSIS

On the basis of their relative amounts, the constituents of a sample can be divided into the *macro* and the *micro* as shown in the lower part of Fig. 1. A macro constituent is here defined as one making up more than 0.01 per cent of the sample, and a micro constituent as one occurring to the extent of 0.01 per cent or less. A micro constituent may also be called a *trace* constituent.

Originally *trace* in the chemical sense meant a quantity of a constituent so small that it either could not be determined, or was thought not worth determining. Today the term has a rather different meaning, and in its general sense signifies a minute amount of a constituent which usually can be determined, and which it frequently is necessary to determine with some degree of accuracy. Just how low the percentage of a constituent must be before it can be called a trace is a matter of somewhat arbitrary definition. In this connection a statement made by Hillebrand[1] with reference to rock analysis is of interest. He says: "It may be said with regard to the use of the word 'trace' that the amount of a constituent thus indicated is supposed to be below the limit of quantitative determination in the amount of sample taken for analysis. It should in general, for analyses laying claim to completeness and accuracy, be supposed to indicate less than 0.02 or even 0.01 per cent." Since 0.01 per cent more or less marks the lower limit of gravimetric or volumetric methods as commonly applied, we may take this figure as indicating the approximate upper limit of a trace constituent. There is no necessity for making the boundary a rigid one. It is sometimes convenient to consider as a trace constituent one that occurs to the extent of a few hundredths of a per cent. Thus in silicate rocks copper usually falls in the range 0.001 to 0.05 per cent, and it is permissible to speak of copper as a trace constituent in this class of material.

To lessen the abruptness of transition from micro to macro constituents, it is convenient to subdivide the latter into a major and minor class. A minor macro constituent may be assigned the range 0.01 to 1 per cent. It

[1] W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Survey Bull.*, **700**, 32 (1919). *Cf.* W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Wiley, New York, 1929, p. 659.

has, at least in its lower range, a certain similarity to a micro constituent, and methods used in trace analysis are often applied in its determination.

The content of a major or minor constituent in a sample is ordinarily expressed in weight percentage. The same unit is often used for a trace constituent but there is some advantage in using parts per million (p.p.m.) instead, especially for contents below 0.001 per cent.

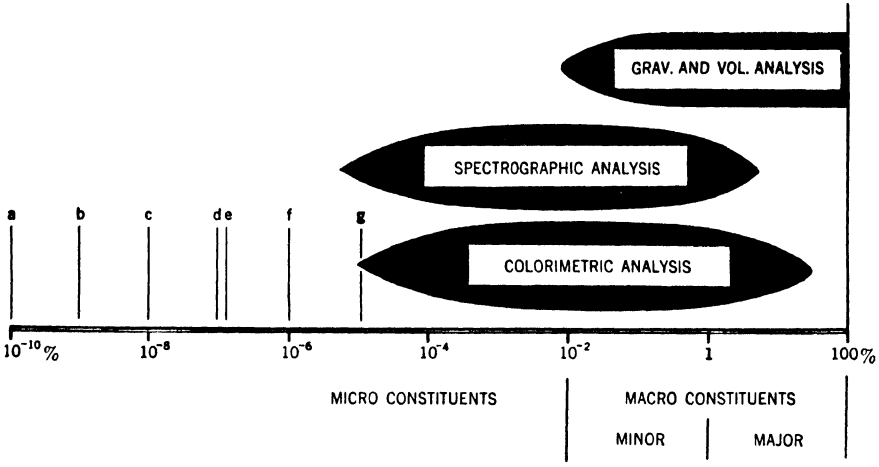


Fig. 1. Diagram showing classification of constituents on the basis of concentration in the sample, the useful ranges of various quantitative techniques, and the sensitivity of some methods for the determination of minute traces of elements.

a. Approximate gold content of some samples of sea water as determined by the microscopical measurement of the bead of the gold isolated from two liters of sample (Haber).

b. Percentage of iron in water that can be determined colorimetrically after concentration by zeolitic exchange from a sample of 5 liters. (Abrahamczik.)

c. Limit of detectability of lead as chromate nephelometrically. (Böttger.)

d. Approximate limit of determination of selenium in 1 kg. of soil by distillation as bromide followed by reduction to selenium which is determined colorimetrically in colloidal suspension. (Robinson, Dudley, Williams, and Byers.)

e. Limit of determination of beryllium in aqueous solution by fluorescence with morin.

f. Approximate limit of determination of iodine in aqueous solution by catalysis of the reaction between quadrivalent cerium and arsenite.

g. Limit of colorimetric determination of palladium in a 1 g. sample of sulfide mineral.

The lower limit of a trace constituent is zero, but the lower limit of a trace analysis is set by the sensitivity of the method. In a good many cases the sensitivity and specificity of a trace method are sufficiently high to meet rather exacting demands. For example, it may be necessary to determine amounts of iron as small as 10^{-5} mg. per liter ($1:10^{11}$) of water

in hydrobiological investigations (Fig. 1), and this has been accomplished. As little as 10^{-6} per cent of the platinum metals has been determined in a 2 g. sample of silicate rock.[2]

The essential feature of a trace analysis is not the determination of a minute quantity of a substance, but the determination of such a quantity in the presence of an overwhelming quantity of other substances which may seriously affect the reaction involving the trace constituent. A trace analysis has the characteristics of both macro and micro analysis. The size of sample and sometimes the preliminary steps of a trace analysis are similar to those of macro analysis. Frequently a trace analysis requires a

TABLE 1

ABUNDANCE OF SOME OF THE RARER ELEMENTS

(All figures are in p.p.m.)

	Igneous rocks[a]	Primary sulfides[b]		Igneous rocks[a]	Primary sulfides[b]
Ag	0.1	10	Mo	2.5	20
As	5	60	Ni	80	31400
Au	0.005	0.2	P	800	
B	3		Pb	15	100
Ba	250		Pd	0.01	4
Be	6		Pt	0.005	2
Bi	0.2	2	Rb	310	
Cb	20		Re	0.001	0.02
Cd	0.15	20	S	520	
Ce	46		Sb	1(?)	1
Cl	480		Sc	5	
Co	23	2100	Se	0.09	200
Cr	200	20	Sn	40	50
Cs	7		Sr	150	
Cu	70	10900	Ta	15(?)	
F	300		Te	0.002(?)	2
Ga	15	2	Th	11.5	
Ge	7	10	Ti	4400	
Hf	4.5		Tl	0.3	1
Hg	0.5	0.02	U	4	
I	0.3		V	150	40
In	0.1	0.7	W	1	2
La	18		Y	21	
Li	65		Zn	80	8500
Mn	1000	800	Zr	220	

[a] Figures are mostly from V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente, IX. Die Mengenverhältnisse der Elemente und der Atom-arten," *Skrifter Norske Vidensk.-Akad. i Oslo I. Mat. Natur. Klasse*, No. 4, 99 (1937). The values for Cd, Cu, Mo, Ni, Pb, and Zn are from estimates by E. B. Sandell and S. S. Goldich, *J. Geol.*, 51, 181 (1943); for W from Sandell, *Am. J. Sci.*, 244, 643 (1946).

[b] Values found by I. and W. Noddack, *Z. physik. Chem.*, A154, 232 (1931), on a composite sample of 35 pyrrhotites, 10 pyrites, 8 pentlandites, and 14 nickel-pyrites.

[2] G. Lunde and M. Johnson, *Z. anorg. allgem. Chem.*, 172, 167 (1928).

larger sample (>1 gram) than is used in macro analysis. In special cases, samples weighing several hundred kilograms have been taken. The final step in a trace analysis may be more micro than the usual micro analysis, in which 1 γ is usually the limit of accuracy striven for. Many colorimetric methods enable 1 γ or less of a constituent to be determined with an accuracy of 5 or 10 per cent, and the same is true of spectrochemical determinations.

A consideration of the distribution of trace elements in nature lies beyond the scope of this book but it may be of interest to give a table of the abundance of the rarer elements in igneous rocks and in primary sulfides (Table 1). The average content of the elements in the earth's crust is for most elements the same as their abundance in the igneous rocks. Many of the so-called rare elements are as abundant as those which are usually considered common. Germanium is as abundant as arsenic, gallium as abundant as lead, cerium as abundant as zinc, scandium more abundant than mercury or bismuth, etc. From the igneous rocks the rarer elements find their way by a longer or shorter route into plant and animal matter, and many are markedly enriched in the living material in the process. The important role played by trace elements in life processes is now well realized and their determination is of practical as well as of scientific interest.

I. Methods of Trace Analysis

A list of the methods which are or have been used in trace analysis would be a list of the methods used in general chemical analysis. Traces of elements have been determined even by gravimetric methods. For example, less than 0.001 per cent of gallium in aluminum has been determined gravimetrically by taking a 50 g. sample.[3] Titrimetric methods can at times render good service in trace analysis (determination of iodine, silver, etc.), especially when the end point is found potentiometrically. The new technique of amperometric titrations may find application.[4] Extractive titration with an organic solvent solution of dithizone (p. 87) is sometimes used in determining traces of heavy metals. When it is necessary, however, to determine very small quantities of a constituent, methods other than the gravimetric or volumetric are usually preferred, and these will be briefly discussed.

The methods commonly applied in the determination of traces may be divided into those that are of general applicability, and those that can be used only for a more or less restricted number of elements at the present

[3] J. A. Scherrer, *J. Research Natl. Bur. Standards*, 15, 585 (1935).

[4] See Chapter XXXIII of I. M. Kolthoff and J. J. Lingane, *Polarography*. Interscience, New York, 1941.

time. In the latter class are methods based on measurement of catalytic activity,[5] and certain microscopical methods involving the measurement of the diameter of a precious metal bead[6] obtained by cupellation, or of a mercury globule.[7]

In the class of general methods we have colorimetry and photometry (spectrophotometry, nephelometry, and turbidimetry), optical and X-ray spectrography, and polarography.[8] Methods based on fluorescence may also be included here. At the present time there are comparatively few procedures for the determination of elements based on fluorescence, but it may be expected that in the course of time such methods will increase in number (*cf.* p. 80). Moreover, measurements based on radioactivity (particularly after neutron activation) enable extremely small amounts of a considerable number of elements to be determined with satisfactory precision.

Present-day trace analysis relies chiefly on colorimetry (using this term in its wide sense to include spectrophotometry) and spectrography, although polarographic methods are being applied to an increasing extent. A few words may be said about the comparative merits of colorimetry and emission spectrography in trace analysis. Spectrography can be applied to the determination of any element, although with widely varying sensitivity. For some elements there are no colorimetric methods, and for others the methods are not sufficiently sensitive for use in trace analysis; or even if a color reagent is available, there may be no satisfactory method for isolating the constituent from interfering elements. A great advantage of spectrographic methods is speed, at least when many analyses are to be run. The preliminary isolation of the constituent which is the rule in colorimetry is the exception in spectrography. The gain in speed is sometimes offset by lower reliability or accuracy in spectrography. The composition of the sample may have a great effect on the accuracy of a spectrographic method, whereas in a good colorimetric method the isolation of the constituent eliminates this variable. So far as the actual measurement

[5] The determination of the concentration of a substance exerting a catalytic effect on a reaction otherwise proceeding very slowly may often be effected through the agency of colorimetry, or more generally, photometry. An example is given on p. 517. Such catalytic methods may have extraordinary sensitivity. Thus as little as 10^{-4} γ Fe per ml. of saturated ammonium thiocyanate solution can be detected by the appearance of a pink color when the solution is exposed to sunlight (B. S. Sharma, *J. Soc. Chem. Ind.*, **48**, 336 T (1929). This concentration corresponds to 1 γ Fe in a cubic meter of solution.

[6] F. Haber, *Angew Chem.*, **40**, 303 (1927) (determination of the gold content of sea water).

[7] A. Stock, *Ber.*, **71**, 550 (1938).

[8] For the latter see I. M. Kolthoff and J. J. Lingane, *Polarography*. Interscience, New York, 1941.

is concerned, it is easier to obtain the optical density of a colored solution than that of a line on a photographic plate.

There is often less difference than usually supposed in the concentration sensitivity of spectrochemical and colorimetric methods. A small sample is ordinarily used in spectrography and this tends to increase the lowest percentage of the element that can be determined, even though the absolute sensitivity is high. In a colorimetric determination the size of the sample taken can be 100 times as large as in an ordinary spectrographic determination, and thus the higher relative or concentration sensitivity of a colorimetric method may counterbalance the higher absolute sensitivity of a spectrographic method. If the amount of sample available is limited, the relative sensitivity of a spectrochemical method may, of course, greatly exceed that of a colorimetric method, but the situation is frequently reversed if a gram or two of sample is available.

Some comparisons between spectrochemical and colorimetric methods as regards sensitivity may be interesting. Owens[9] has given the following values for the average absolute sensitivity of various types of excitation:

Direct current arc	10^{-5} to 10^{-4} mg. metal on electrode
Cathode layer of direct current arc	10^{-6} to 10^{-5} mg.
High-voltage, alternating current arc	10^{-6} to 10^{-5} mg.
Direct current condensed spark	10^{-6} to 10^{-4} mg.

The practical sensitivity of some delicate color reactions corresponds to 10^{-4} mg. or less (for example, dithizone as reagent for Cu, Pb, Zn, Cd, etc.). *Cf.* Table 107, p. 648.

Owens gives the following figures for the lower limits of determination of certain metals in 25 per cent sodium hydroxide (one drop of solution corresponding to 12 mg. NaOH evaporated on electrodes):

Al	$5 \times 10^{-5}\%$
Ca	$4 \times 10^{-5}\%$
Mg	$3 \times 10^{-5}\%$
Cr	$2 \times 10^{-5}\%$
Cu	$1 \times 10^{-5}\%$
Fe	$1 \times 10^{-5}\%$
Ni	$8 \times 10^{-5}\%$
Pb	$2 \times 10^{-5}\%$
Sr	$1 \times 10^{-5}\%$

By using 10 ml. of solution, these limits can be equaled or exceeded by colorimetric methods for copper, nickel, and lead and possibly some of the other metals. Traces of calcium and strontium cannot be determined at all by colorimetric methods. A great advantage of a spectrographic

[9] J. S. Owens, *Ind. Eng. Chem., Anal. Ed.*, 11, 61 (1939).

method in an analysis such as this is the possibility of determining all of these elements (and others) at one and the same time.

Hess, Owens, and Reinhardt[10] have described a spectrographic procedure for traces of metallic impurities in organic materials, in which a 0.4 g. sample is wet-ashed and 0.03 ml. of solution corresponding to 30 mg. of sample is evaporated on an electrode and the residue arced with high-voltage alternating current. The lower limit was 0.0001 per cent for Al, Ca, Cu, Fe, Pb, Mg, Mn, Ni, Sr, Sn and 0.0005 per cent for Zn. The errors ranged from 0 to 50 per cent (latter with Zn) in the range 0.0005 to 0.005 per cent metal, with an average error of 12 per cent. For the metals Cu, Fe, Pb, and Ni comparable results can be obtained by colorimetric methods, and better results should be possible for zinc, but of course with a larger sample and a greater expenditure of time.

Arc spectrography is commonly applied in the determination of trace elements in silicates. The spectral sensitivity in p.p.m. for various metals is as follows (different figures for the same element from different authors): Ag 1; Be 10, 1, 4; Cd 300; Co 2, 10; Cr 1, 1, 0.2; Ga 5, 10, 5; Ge 15; Mo 1, 5; Ni 2, 5; Pb 30, 10, 10; Zn 350, 100. With the exception of silver, all of these can be determined colorimetrically or fluorimetrically with a sensitivity of 1 p.p.m.

TABLE 2

COMPARISON OF RESULTS IN SPECTROGRAPHIC, COLORIMETRIC, AND POLAROGRAPHIC DETERMINATION OF TRACES OF CADMIUM[a]

Cadmium added, γ	Cadmium recovered, γ		
	Spectrographic method	Polarographic method	Colorimetric method
0	1.0	2	1.2
1	2.5	—	2.2
2	3.0	3.5	3.2
5	7	6.5	6
10	11	12	11
50	48	50	48

[a] Determinations made on 100 ml. of urine. Data of J. Cholak and D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, 16, 333 (1944). Di-β-naphthylthiocarbazone used as reagent for the colorimetric (actually spectrophotometric) determination.

By a special technique involving fractional distillation, certain relatively easily volatile metals such as zinc, cadmium, mercury, indium, thallium, germanium, antimony, and bismuth may be detected spectrographically in amounts of the order of 10^{-6} per cent when 1 to 3 g. of silicate sample is

[10] T. M. Hess, J. S. Owens, and A. G. Reinhardt, *Ind. Eng. Chem., Anal. Ed.*, 11, 646 (1939).

taken.[11] As yet only cadmium has been determined in such low concentrations colorimetrically.

A few comparative studies have been made of the determination of trace constituents in materials of bio origin by various methods and it is interesting to compare the agreement that can be obtained (Tables 2 and 3).

TABLE 3

COMPARISON OF RESULTS IN SPECTROGRAPHIC, COLORIMETRIC, AND POLAROGRAPHIC DETERMINATION OF TRACES OF MOLYBDENUM[a]

Sample	Percentage of Mo in ash		
	Spectrographic method	Colorimetric method	Polarographic method
Woody peat	Trace	0.00065	0.0004
Peat	None	0.0003	Trace
Peat	0.0015	0.0011	0.0009
Muck	0.0022	0.0019	0.0014
Dallis grass	0.0035	0.0031	0.0025
Sugar cane leaves	0.0028	0.0023	0.0020

[a] Partial data of M. L. Nichols and L. H. Rogers,, *Ind. Eng. Chem., Anal. Ed.*, 16, 138 (1944).

When it is considered that colorimetric determinations can often be made with simple inexpensive apparatus usually available in most analytical laboratories, that the analyst requires no special training, that the sensitivity of modern colorimetric procedures is often very high, and that the accuracy is as good as, or even better than, that of any other applicable method, the conclusion may be drawn that colorimetry occupies an important place among the methods of trace analysis.

Limits of the Methods of Trace Analysis

In Fig. 1 the useful ranges of gravimetric, volumetric, colorimetric, and spectrographic methods are indicated. It will be understood that the diagram is a generalized representation of the limits of the methods mentioned, because obviously there can be no hard and fast boundaries. As already mentioned, gravimetric and volumetric methods have been used in trace analysis, but in the great majority of cases they are restricted to constituents in the range 0.01 to 100 per cent, and have a limited use in the range 0.01 to 0.1 or sometimes even in the range 0.01 to 1 per cent. There is nothing inherently impossible in the use of a gravimetric or volumetric method for determining a trace constituent, a micro technique being possible if the constituent can be separated from the macro constitu-

[11] E. Preuss, *Z. angew. Mineral.*, 3, 8 (1940).

ents, but the disadvantages of such a procedure often are so great that it is only occasionally applied.[12]

The useful range of a colorimetric method may be considered to extend from an upper limit of about 1 per cent (visual colorimetry) or 10+ per cent (spectrophotometry) down to about 10^{-5} per cent (or 0.1 p.p.m.). Naturally the lower limit varies with the sensitivity of the reaction, and may be much higher than 10^{-5} per cent, but for many metals and metalloids there are colorimetric methods which enable percentages as low as 10^{-5} to 10^{-4} to be determined. It is only rarely that colorimetric methods can be, or are, applied to the determination of traces below 10^{-5} per cent in a solid sample. For example, the practical limit of the colorimetric determination of palladium in sulfides is slightly less than 10^{-5} per cent, and of cadmium in silicate rocks 5×10^{-6} per cent. As little as 10^{-7} per cent of selenium, however, can be determined in soil.[13] Naturally the methods of separation available and the nature of the sample will in many cases be the deciding factors in the determination of the sensitivity of the method; in the presence of large amounts of interfering substances the lower limit of a colorimetric method may be raised by a factor of 10 or 100. In the simplest possible case, a dilute aqueous solution (for example, a natural water), the limit of a colorimetric method may lie at 10^{-8} or even 10^{-10} per cent after isolation of the constituent. In such a case the lower limit can be pushed indefinitely downward in many instances by taking increasingly larger samples, if a good method is available for the isolation of the constituent in question.

The useful range of spectrographic methods as generally carried out is nearly coincident with that of colorimetric methods, the upper limit being 1 per cent or slightly higher, and the lower limit approximately 10^{-5} per cent. With many elements a sensitivity of 10^{-5} per cent cannot be reached (with some not even 10^{-3} per cent), so that the limit indicated is attained only under favorable conditions as regards the nature of the sample and the element determined.

The determination of constituents occurring to the extent of 0.1 part or less per million is as a rule difficult or impossible by the usual methods of trace analysis and special procedures must in general be invoked. Fortunately the limit of most practical requirements of trace analysis lies above 10^{-5} per cent and often it is considerably higher. Thus in alloy analysis, constituents rarely have to be determined in amounts less than 10^{-3} to 10^{-4} per cent.

[12] An important exception to this generalization is the determination of gold and the platinum metals by dry assaying, in which the weight of the metal bead is obtained to within 0.01 mg.

[13] By a reconcentration procedure it is even possible to determine selenium down to 0.0001 p.p.m. (W. O. Robinson, private communication).

The determination of a trace substance occurring to the extent of less than 10^{-5} per cent in a sample will require, first, the isolation of the constituent, *i.e.*, its concentration in a small volume of liquid or solid, with or without complete separation from other constituents of the sample, and second, the determination of the constituent in the enriched phase by a method yielding a high absolute sensitivity. Spectrographic methods should be especially suitable for the purpose since they sometimes permit the detection of as little as 10^{-6} or 10^{-5} mg. of an element, or about $^1/_{100}$ as much as the most sensitive color method as ordinarily carried out, and, moreover, they are more specific than the latter.

Spectrographic detection and determination of elements after chemical enrichment have been applied in a number of cases, but up to the present time chiefly when the direct detection and determination were of low sensitivity. Thus Töpelmann[14] was able to detect 5×10^{-5} per cent of tellurium in bismuth, after precipitation of the tellurium from a 10 g. sample. The direct determination was sensitive to approximately 0.001 per cent tellurium. Germanium has been concentrated by distillation of the tetrachloride followed by sulfide precipitation[15]; in this way 2 γ of germanium could be detected in a 10 g. sample (2×10^{-5} per cent). Bayle and Amy[16] isolated minute amounts of various metals by electrolytic deposition on thin wires, and then detected the deposited metal spectrographically. It was possible in this way to detect 0.1 γ of copper in 1.5 g. of zinc. Urbain[17] determined minute quantities of gold after electrolytic isolation. The isolation of metals by preliminary electrolysis has also been used by others.[18] Preliminary volatilization of certain elements from a large sample as a means of increasing the sensitivity of their spectrographic determination has already been mentioned (p. 9).

Methods based on fluorescence, and possibly on catalytic activity of the constituent, should be applicable in some cases after enrichment, since they often have high absolute sensitivities. Such methods, however, are inferior to the spectrographic in that they are more subject to interference from foreign elements. When a good method of separation is available which permits a large sample to be worked up, a colorimetric method may be used in the final determination of the isolated constituent. As an illustration we have the determination of selenium in soils, mentioned above, in which distillation provides a simple means of separating the element from very large samples.

[14] H. Töpelmann, *Z. anal. Chem.*, **82**, 284 (1930).

[15] W. Geilmann and K. Brünger, *Z. anorg. allgem. Chem.*, **196**, 312 (1931).

[16] E. Bayle and L. Amy, *Bull. soc. chim.* [4], **43**, 604 (1927).

[17] P. Urbain, *Bull. soc. chim.* [4], **47**, 1183 (1930).

[18] A. Schleicher and J. Clermont, *Z. Elektrochem.*, **39**, 2 (1933); A. Schleicher and L. Laurs, *Z. anal. Chem.*, **108**, 241 (1937); A. Schleicher, *ibid.*, **105**, 393 (1936).

II. Precautions in Trace Analysis

The introduction of foreign substances during the preparation of the sample and in the course of the analysis may have more serious consequences in trace analysis than in any other type of analysis, and special attention must be paid to this source of error.

Great care must be taken to prevent possible gross contamination of the sample through accidental introduction of metal from common articles of the laboratory—iron from ring stands, nickel from crucible tongs, copper and zinc from burners, zinc from rubber, etc. If the sample requires sifting, a silk bolting cloth must be used instead of a metal sieve. The possible introduction of some of the alloying elements of steel must be considered when a Plattner (hardened steel) mortar is used to crush hard materials such as silicates.

The amounts of foreign metals which can thus be introduced under customary conditions of crushing are indicated in Table 4. Occasionally, some unexpected elements may be encountered. For example, columbium and tantalum have been found in the steel of a Plattner mortar.[19]

TABLE 4

AMOUNTS OF METALS INTRODUCED IN CRUSHING QUARTZ IN HARDENED STEEL (PLATTNER) MORTAR[a]

Nine grams of quartz crystal (up to 1 cm. in diameter) crushed with a total of 200 hammer blows; crushed material sifted through a screen with 0.7 mm. holes after every 20 strokes, and coarse material returned to mortar.

Metal	Fe	Mn	Cr	V	Ni	Co	Cu
Contamination, p.p.m.	280	1.8	0.4	<0.1	0.25	<0.1	0.35

[a] E. B. Sandell, *Anal. Chem.*, 19, 652 (1947). See this paper for further data. W. T. Schaller (private communication) found from 300 to 540 p.p.m. of introduced iron in beryl crushed to 100-mesh in a Plattner mortar under conditions similar to those in the above experiments.

It has been shown that serious contamination of plant material can occur in mechanical grinding.[20] Iron and copper were found to be introduced by grinding in Wiley and hammer mills. Jar mill grinding with flint balls resulted in contamination by iron, copper, zinc, cobalt, and sodium; the use of porcelain or mullite balls introduced these elements as well as calcium, sulfur, and phosphorus. Hand grinding with a porcelain mortar and pestle (Coors) did not result in appreciable contamination by iron, copper, zinc, boron, cobalt, manganese, molybdenum, calcium, sodium, magnesium,

[19] K. Rankama, *Bull. comm. géol. Finlande*, No. 133, p. 11 (1944).

[20] S. L. Hood, R. Q. Parks, and C. Hurwitz, *Ind. Eng. Chem., Anal. Ed.*, 16, 202 (1944).

phosphorus, sulfur, or potassium, and this is stated to be the only satisfactory method of plant sample preparation at present.

Small amounts of certain heavy metals may find their way into the sample from the glass ware and the platinum ware used in the analysis. Thus Pyrex may yield traces of arsenic, zinc,[21] and lead, and possibly other heavy metals. Platinum ware commonly contains iron, and will nearly certainly yield some of it to acid solutions brought into contact with it. The glaze of porcelain may contain heavy metals such as lead. Fused silica ware is frequently of great value in trace analysis because of its general freedom from heavy metals and its resistance to most acid solutions.

Glassware treated with dichromate-sulfuric acid cleaning solution tenaciously retains traces of chromium after thorough rinsing.[22]

Filter paper always contains small amounts of metals. Thus the following elements have been found in quantitative filter paper[23]: Al, Ba, Ca, Cr, Cu, Fe, Ge, K, Mg, Mn, Na, Ni, Pb, Sb, Si, Ti, V, Zn, Zr, and the rare earths (especially yttrium). Some of these occur in minute amounts, others in appreciable quantities. For example, Rankama found approximately 1 per cent PbO, 0.3 per cent ZnO, and 0.3 per cent SnO_2 in the ash of quantitative paper; larger amounts of calcium, magnesium, etc., are always present.

Certain volatile substances (*e.g.*, mercury) may be contributed by the atmosphere of the laboratory; they may be absorbed or adsorbed by liquids and solids (surfaces of vessels, filter paper, etc.). It hardly needs to be mentioned that care must be taken to exclude dust in the various stages of an analysis. Elements regarded as uncommon may occur in appreciable amounts in atmospheric dust. For example, as much as 300 p.p.m. of arsenic has been found in such dust.

On the other hand, losses of a trace constituent may sometimes result from interaction with the substance of the containing vessel. For example, in ashing samples of organic nature having a low ash content in a silica or porcelain dish, an appreciable fraction of the constituent may be fixed at the surface of the dish, probably by the formation of a silicate which may not be entirely decomposed by acids. The effect is more pronounced when old dishes with rough surfaces are used. The addition of an inert material to diminish surface contact helps to reduce such losses. In the use of platinum vessels at higher temperatures the possibility exists of reduction of a metal compound to metal and the alloying of the latter with the platinum, from which acid will fail to remove it entirely. Loss

[21] O. R. Alexander and L. V. Taylor, *J. Assoc. Official Agr. Chem.*, **27**, 325 (1944), found approximately 10 p.p.m. of zinc in Pyrex glass.

[22] F. J. Henry and E. C. Smith, *Science*, **104**, 426 (1946).

[23] K. Rankama, *Bull. comm. géol. Finlande*, No. 126, 14 (1939).

by adsorption in glass vessels is considered below. Filter paper may adsorb such metals as lead and copper from solutions, especially if these are neutral or only slightly acidic; inorganic filter media are in general preferable.

Insoluble material at any stage of a procedure must be regarded with suspicion. The residue may retain heavy metals, sometimes in large quantities. An example of this is afforded by the retention of iron and aluminum, and to a much smaller extent of manganese, by silica in the dry ashing of siliceous organic material (Table 5). Such insoluble material must be appropriately treated to recover any of the desired constituent it may contain.

TABLE 5

RETENTION OF IRON, ALUMINUM AND MANGANESE BY SILICA IN ASHING[a]

In each case 5 g. of sample were ashed as indicated; the ash was treated with dilute hydrochloric acid, the solution evaporated to dryness, and the residue extracted with dilute hydrochloric acid; iron, aluminum, and manganese were then determined in the washed residue after hydrofluorization. Samples as follows: No. 1, hay low in silica (0.4% crude SiO_2), No. 2, hay with normal silica (1.5%), No. 3, straw (2.4% SiO_2), No. 4, hay high in silica (*ca.* 4%).

Method of ashing	Sample No.	Amount of metal in silica					
		Fe_2O_3		Al_2O_3		MnO	
		mg.	% of total	mg.	% of total	mg.	% of total
Over Teclu burner	1	0.61	59	0.42	48	<0.005	< 3
	2	0.30	72	0.54	57	0.03	3.5
	3	0.95	73	1.10	56	0.04	6
	4	1.35	78	2.13	85	0.51	17
In electric muffle furnace	1	0.39	38	0.20	23	<0.005	<3
	2	0.17	40	0.29	30	0.01	1
	3	0.51	39	0.90	45	<0.005	<1
	4	0.98	56	1.59	63	0.09	3

[a] Selection of data from T. Wijkstrom, *Metoder för Undersökning av Fodermedels Mineralbeståndsdelar.* Svanbäck, Stockholm, 1935.

1. Reagents

In the determination of the more common heavy metals such as iron, copper, zinc, and lead, for example, it may be necessary to purify the reagents to be used. Special attention must be paid to the distilled water. The ordinary distilled water of the laboratory frequently contains such relatively large amounts of certain metals that its use in trace analysis is

out of the question.[24] Water sufficiently pure for most purposes can be obtained by simple redistillation from an all-glass (Pyrex) still.[25] Such water should not contain more than about 1 γ lead per liter. It may be stored in Pyrex or other resistant glass.

The common acids of reagent quality are as a rule very low in heavy metals,[26] but when it is necessary to use them in comparatively large quantities (as in the destruction of organic matter in samples of biological origin) they may have to be purified. Distillation in a Pyrex still usually suffices to give a product which is sufficiently pure for nearly all purposes.[27] Perchloric acid may be redistilled under reduced pressure. Hydrofluoric acid may be freed from lead by coprecipitating lead fluoride with strontium fluoride.[28] Pure ammonium hydroxide is most easily obtained by saturating redistilled water in a cooling bath with ammonia from a tank. Ammonium hydroxide is best kept in a ceresin-lined bottle.

Soluble solids may be purified by recrystallization for more or less successful removal of foreign substances in general, or by chemical treatment to remove specific impurities. The latter method is often adopted. A suitable reagent may be added to the solution to form a slightly soluble compound with the substance to be eliminated; it is advisable to use a collector, if possible one that forms mixed crystals with the insoluble body (see further, p. 22). Extraction methods are also useful. For example,

[24] See p. 28 for some typical figures for the metal content of distilled and redistilled water. Free chlorine may also be present in distilled water and can lead to difficulties in some trace determinations.

[25] A still with a fused silica condenser is even better but rarely necessary. See J. S. McHargue and E. B. Offutt, *Ind. Eng. Chem., Anal. Ed.*, 12, 157 (1940), for the description of a still for the production of large volumes of metal-free water (less than 1 part per billion of metal).

[26] Reagent-quality hydrochloric and nitric acids have been found to contain 0.01 to 0.03 p.p.m. of lead. From 0.4 to 1.5 p.p.m. of iron has been reported for some C.P. nitric acid. The iron content of analytical-reagent sulfuric acid is usually much less than this (0.1 p.p.m. has been reported). The copper content of some C.P. sulfuric acid has been found to be as high as 1 to 2 p.p.m. From 0.01 to 0.02 p.p.m. of cadmium has been reported for reagent-quality sulfuric acid (these figures seem high) and about one-tenth as much for nitric acid. Hydrofluoric acid may contain from 0.05 to 0.3 p.p.m. or even more of iron. Hydrochloric acid commonly contains appreciable traces of mercury.

[27] It has been claimed that nitric acid cannot be freed from zinc by distillation. Perhaps this is to be interpreted to mean that the distillate extracts zinc from the glass during distillation.

[28] I. T. Rosenqvist, *Am. J. Sci.*, 240, 358 (1942), adds 10 ml. of 10 per cent strontium chloride per kilogram of the concentrated acid, and repeats the precipitation in the same way. The precipitate is allowed to settle and the supernatant liquid is decanted through a filter in a hard-rubber or paraffined glass funnel. In this way the lead content of acid containing 2 p.p.m. can be reduced to 0.002 p.p.m. or less.

a number of heavy metals may be extracted in neutral or slightly basic medium with dithizone (p. 87).

2. Blanks

Every analyst knows the necessity for running blanks. A properly run blank takes account of the amounts of constituent contributed by the vessels and by the reagents. The aim in purifying reagents should be to reduce the quantity of the constituent in question to the point where it is small compared to that in the sample; if it is at all feasible the vessels used in the analysis should be of materials that will not yield any appreciable amounts of the constituent to the solutions treated in them. The blank determination should be carried through all the steps of the determination proper. A large blank value is naturally undesirable because it reduces the accuracy of the determination of the constituent in the sample. If it is known or there is good reason to believe that no appreciable amount of the constituent is being contributed by the vessels, it is advisable to run the blank on a larger quantity of reagents than used in the analysis of the sample in order to increase the accuracy.

It may be pointed out that a zero blank is not necessarily an indication that all is well. Such a result may be cause for suspicion in trace analysis. It may mean that a foreign substance in the reagents is combining with the desired constituent and preventing its reaction with the color reagent. For example, a trace of sulfide may lead to low results in the determination of various heavy metals with dithizone by forming sulfides that are inert toward the color reagent. The presence of such an interfering substance will be revealed if the standards are subjected to the same treatment as the sample.

3. Standard Solutions

Dilute solutions of metals used for the preparation of comparison solutions may undergo a serious loss in strength on standing as a result of adsorption or base exchange with the glass container. The loss is greatest in neutral or slightly basic medium (such as may result from attack of poorly resistant glass), but may occur as well, but to a smaller extent, in slightly acidic solution. Thus Leutwein[29] found that 0.001 per cent solutions of Mo, V, Ti, and Ni showed metal contents 0.2 to 0.4 of the original concentration after storage for 75 days in well-washed Jena glass bottles; 0.001 per cent solutions of Au, Pt, Pd, and Ru decreased to 0.1–0.3 of the original strength after 230 days in Jena glass. In fused silica containers only slight loss in strength was found, except in the case of palladium solu-

[29] F. Leutwein, *Zentr. Mineral. Geol.*, **1940A**, 129; *Chem. Abstracts*, **34**, 5776. For loss of mercury by adsorption see A. Stock, *Ber.*, **B72** 1844 (1939).

tion whose concentration decreased to 0.3 of the original after 230 days. According to the writer's experience losses in acid (*ca.* 0.1 *N*) solutions kept in Pyrex are much smaller for most metals than those found by Leutwein, but this source of error is not to be underestimated. It is usually best to prepare the standard solution in two stages. A moderately strong solution (*e.g.*, 0.1 per cent) is prepared in 0.1 to 1 *N* acid. This solution should be stable for a long time, especially if kept in Pyrex, and from it the more dilute standard solution (conveniently 0.001 per cent of metal) may be obtained by dilution. The latter solution should be made slightly acidic (0.1 *N* or so if permissible) and stored in Pyrex. It should not show any significant change in the course of a week or two.

Standard solutions may be prepared from pure metals or from pure salts of definite composition. If a good grade of "reagent-quality" salt is available it may as a rule be used without further purification for the purposes of colorimetry. Whenever possible anhydrous salts are used. These should be powdered and dried at 100° or higher to remove most of the vacuole water. Hydrated salts may in many instances be used with satisfaction if they are not deliquescent or markedly efflorescent. The crystals should be large enough to permit the picking out of clear uneffloresced individuals. Such air-dry crystals may contain a few parts per thousand of foreign water but this will rarely matter in trace analysis. It is a waste of time to weigh the standard substance too precisely. In preparing a liter of 0.1 per cent solution of sexivalent chromium one should take 3.73 g. of K_2CrO_4, not 3.734 g.

4. Sampling

A relatively large sample is usually taken in colorimetric trace analysis and the obtaining of a representative sample does not as a rule present any special difficulties.[30] The usual precautions should be observed.

Care should be taken that extraneous material does not accompany the sample proper. For example, serious errors may result in the determination of trace constituents in plants if the sample is contaminated with soil or dust.

[30] An illustration of an exception is afforded by the determination of gold in river waters (Haber) in which the particles consisting of, or carrying, gold are few in number so that 1–2 liter samples may give widely varying results, and an average value is not easily obtained.

CHAPTER II

METHODS FOR THE SEPARATION AND ISOLATION OF TRACES OF SUBSTANCES

Few colorimetric reagents are sufficiently specific to allow the determination of an element to be made directly in the presence of associated elements, especially when the ratios are unfavorable, as they are in trace analysis. Whenever possible, interfering elements are made harmless by such devices as the adjustment of the *p*H of the solution, addition of complex-forming agents, or oxidation or reduction to other valence states, but when such expedients fail recourse must be had to separations. Even when no interfering elements are present it is often necessary, especially when minute amounts of a constituent are being determined, to isolate the element in some way so as to bring it into a small volume of solution.

There are evidently two factors of importance in separations: the completeness of recovery of the substance being isolated, and the extent of separation from associated substances. The recovery factor for a given procedure is defined as

$$R_A = \frac{Q_A}{(Q_A)_0}$$

where $(Q_A)_0$ is the quantity of substance A in the sample and Q_A is the quantity isolated. If desired, this quotient may be multiplied by 100 to express the recovery in terms of percentage. A recovery of 90 per cent may sometimes be considered acceptable in trace analyses in which the percentage of constituent is 0.0001–0.001 or even 0.01; a recovery of 95 per cent would be considered satisfactory in most cases, although a higher recovery is always desirable.

The separation factor for B (the undesired constituent) with respect to A will be defined as the value by which the original ratio of B to A must be multiplied to give the final ratio:

$$\frac{Q_B}{Q_A} = S_{B/A} \frac{(Q_B)_0}{(Q_A)_0}$$

$$\therefore \quad S_{B/A} = \frac{(Q_A)_0}{(Q_B)_0} \frac{Q_B}{Q_A} \cong \frac{Q_B}{(Q_B)_0} \cong R_B$$

The degree of separation required depends, of course, upon the ratio of B to A in the original sample and upon the permissible value of Q_B/Q_A. If A and B react equally sensitively with the reagent used to determine A, Q_B/Q_A may be permitted a value 0.01 to 0.05, depending upon the accuracy required. Since $(Q_B)_0/(Q_A)_0$ may have a value of 100,000 or more, the separation factor in trace analysis may need to be 10^{-6} or even 10^{-7}.

I. Methods Involving Precipitation, Coprecipitation, Adsorption, and Related Processes

These methods all have the following common feature. The solution of the sample is subjected to some process by which two phases result, one a solution containing the macro constituents of the sample, the other a solid phase which is wholly or in part composed of the trace constituent. The general process may be represented as follows:

$$\text{Solution} \longrightarrow \overset{C}{\text{solution}} + \overset{c}{\text{solid}}$$

where C = phase containing the macro constituents (and any interfering micro constituents) of the sample, c = phase containing the micro constituent to be determined.

The processes by which the phase change represented above can be brought about are varied. The simplest one is a precipitation of the trace constituent, which leaves the macro constituents in solution. However, precipitation in its simple form is usually not applied when a trace constituent is present in very low concentration. Even if the precipitate has a very low solubility its separation may involve difficulties when the absolute amount is small. A colloidal suspension may be formed, or the solution may become supersaturated without precipitation occurring, etc. Therefore, a small amount of another substance forming a slightly soluble product with the precipitant is added to the solution. The precipitate produced from the added substance is called the *collector*, a term which describes its function rather well.

Sometimes the collector functions in a more or less mechanical way. Thus, when an aluminum salt is added to a solution of quadrivalent titanium so dilute that a reaction cannot be obtained even with thymol (p. 577) and precipitated with ammonium hydroxide, the aluminum hydroxide carries down the titanium hydroxide by entrainment, and titanium can be determined colorimetrically in the precipitate after it has been dissolved. In this way amounts of titanium of the order of 1 microgram per liter can be determined.[1]

[1] V. T. Chuĭko, *Zavodskaya Lab.*, **8**, 950 (1939).

Collectors are frequently used in the precipitation of sulfides. Copper sulfide has been employed as a collector for molybdenum,[2] zinc,[3] lead,[4] and other metals; lead sulfide has been used for copper,[5] silver sulfide for lead,[6] etc. In many cases the sulfide collector functions largely in a physical manner, but in others there is an additional effect due to operation of processes which are included in the term coprecipitation.[7] For example, there may be mixed crystal formation between the collector and the trace precipitate. Moreover, the collector may promote the precipitation of the micro constituent from its supersaturated solution.[8]

The completeness of separation of a particular metal by sulfide precipitation naturally depends to a large extent upon the solubility of its sulfide, especially if the collector does not form mixed crystals with the latter. As little as 0.02 γ of mercury can be isolated from a liter of solution by hydrogen sulfide precipitation (copper sulfide as collector).[9] On the other hand, lead sulfide, which has a solubility product equal to 3.4×10^{-28}, much greater than that of mercuric sulfide, may not be quantitatively precipitated from an acid solution, even if a collector such as silver sulfide is used (lead and silver sulfides are not isomorphous). It may be calculated that the solubility of lead sulfide in a 1 N acid solution saturated with hydrogen sulfide is 3×10^{-5} M, which corresponds to about 6 mg. Pb per liter. In 0.1 N acid, saturated with hydrogen sulfide, the calculated solubility corresponds to 0.06 mg. Pb per liter, which is still a rather large value from the viewpoint of the trace analyst. Actually the solubility may be greater than the calculations indicate because equilibrium in a metal–hydrogen sulfide system is attained with notorious slowness.[10] One of the functions of a collector is to hasten the attainment of equilibrium. Nevertheless, it is advisable in precipitation of traces of sulfides to let the solution stand overnight before filtration (*cf.* p. 295). Moreover, the

[2] G. von Hevesy and R. Hobbie, *Z. anorg. allgem. Chem.*, **214**, 380 (1933).

[3] R. E. Lutz, *J. Ind. Hyg. Toxicol.*, **7**, 273 (1925).

[4] R. L. Lucas and F. Grassner, *Mikrochemie (Emich Festschrift)*, **1930**, p. 203.

[5] R. Lucas and F. Grassner, *Mikrochemie (Emich Festschrift)*, **1930**, p. 199.

[6] G. von Hevesy and R. Hobbie, *Z. anal. Chem.*, **88**, 1 (1932).

[7] I. M. Kolthoff, *J. Phys. Chem.*, **36**, 860 (1932); *Chem. Weekblad*, **31**, 102, 230 (1934).

[8] *Cf.* in this connection, I. M. Kolthoff and E. Pearson, *J. Phys. Chem.*, **36**, 549 (1932).

[9] A. Stock, F. Cucuel, and H. Köhle, *Z. angew. Chem.*, **46**, 187 (1933).

[10] In addition it may be pointed out that too much reliance should not be placed on solubility values calculated from solubility products because the metal may be present in other than simple ionic form. Thus, W. D. Treadwell and F. Schaufelberger, *Helv. Chim. Acta*, **29**, 1936 (1946), found the molar solubility of mercury in 1 M perchloric acid saturated with hydrogen sulfide to be 3×10^{-7} (instead of the calculated value 10^{-31} M) because of the formation of H_2HgS_2.

acidity of the solution should be no higher than necessary to keep other metals in solution.

Occasionally a slightly soluble metal-organic complex is used to carry down traces of other metals forming insoluble compounds with the same reagent. Traces of zirconium, vanadium, and titanium occurring in mineral waters can be quantitatively recovered by collection in a precipitate of iron cupferrate produced by the addition of cupferron.[11] 8-Hydroxyquinoline has also been used to precipitate traces of various metals with ferric or aluminum quinolate as the gathering agent (*cf.* p. 274).

If the collector forms mixed crystals with the corresponding compound of the trace constituent, the precipitation of the latter may be virtually complete even though the same compound of the trace constituent alone in solution might not precipitate at all. This may be illustrated by the system lead sulfate–strontium sulfate, the components of which are isomorphous and form mixed crystals. If an excess of sulfate is added to a solution containing strontium ions and a trace of lead ions, practically all of the latter are removed from solution by incorporation in the strontium sulfate precipitate, the following relation holding approximately:

$$\frac{[Pb^{++}]\text{ crystals}}{[Pb^{++}]\text{ solution}} = K\frac{[Sr^{++}]\text{ crystals}}{[Sr^{++}]\text{ solution}}.$$

The distribution coefficient, K, ideally is equal to the ratio of the solubility products of the two components,

$$\frac{S_{SrSO_4}}{S_{PbSO_4}} = \frac{3 \times 10^{-7}}{10^{-8}} = 30.$$

The expression for the distribution of lead between precipitate and solution holds for equilibrium conditions; in the rapid formation of precipitate the relation is no longer fulfilled, and, moreover, the value of K is usually not very close to the calculated value.[12] These deviations, however, do not destroy the general usefulness of the equation for calculating the approximate amount of lead in the precipitate. It is not difficult to arrange matters so that 99 per cent of the added strontium is precipitated, and therefore lead must be strongly concentrated in the precipitate, even if K had a value of 1. Hahn[13] has shown that when 50 per cent of the strontium in a solution is precipitated as the sulfate, approximately 99 per cent of the total lead (as the isotope Th B) originally in the solution is found in the precipitate.

[11] L. W. Strock and S. Drexler, *J. Optical Soc. Am.*, **31**, 167 (1941).

[12] *Cf.* the system lead sulfate–barium sulfate, I. M. Kolthoff and G. Noponen, *J. Am. Chem. Soc.*, **60**, 197 (1938).

[13] O. Hahn, *Applied Radiochemistry*. Cornell Univ. Press, Ithaca, 1936, p. 105.

The lead in the strontium sulfate precipitate can be recovered by converting the sulfates to carbonates and dissolving the latter in acid. The isolation of lead by coprecipitation with strontium or barium sulfate is usually of slight practical importance in colorimetric trace analysis, because it is generally more advantageous to separate traces by extraction with dithizone in an organic solvent (p. 388).[14]

Foreign substances may have a marked effect on the separation of traces by mixed-crystal formation. For example, chloride has an inimical effect on the coprecipitation of lead with strontium sulfate. Thus, in a 1 *N* potassium chloride solution, 82 per cent of the lead is found in the precipitate when 50 per cent of the strontium is precipitated, and only 30 per cent of the lead is carried down when the precipitation is made in 2.5 *N* potassium chloride solution. The unfavorable effect of chloride may be attributed to the formation of a complex lead chloride which is not incorporated in the strontium sulfate lattice.[13]

Arsenic (V) can be coprecipitated with magnesium ammonium phosphate[15] and vanadium (V) with ammonium phosphomolybdate.[16] These are cases of mixed crystal formation.

The phenomenon of anomalous mixed crystal formation[17] may find application in the separation of traces of metals. For example, lead is enriched in certain alkali halides crystallizing from aqueous solution. When 18.4 per cent of potassium chloride in a solution is crystallized out at 0°, 98.8 per cent of the lead (as Th B) in the solution is incorporated in the crystals,[18] the distribution coefficient having the value 57. Likewise, lead is incorporated in sodium chloride crystallized from aqueous solution; for very low lead concentrations the distribution coefficient has a value of 60

[14] J. T. Rosenqvist, *Am. J. Sci.*, **240**, 356 (1942), has employed coprecipitation of lead sulfate with strontium sulfate for the isolation of lead in silicate rocks. He used samples of 50–300 g. and finally weighed the lead as the dioxide after electrolytic deposition. The object of this work was not only the determination of the percentage of lead, but also the separation of enough of the element to enable its isotopic composition to be determined.

[15] I. M. Kolthoff and C. W. Carr, *J. Phys. Chem.*, **47**, 148 (1943); *Anal. Chem.*, **20**, 728 (1948).

[16] J. R. Cain and J. C. Hostetter, *J. Ind. Eng. Chem.*, **4**, 250 (1912); *J. Am. Chem. Soc.*, **43**, 2552 (1921).

[17] When on chemical and crystallographic grounds no mixed crystal formation between two components is to be expected and yet, in spite of the non-fulfillment of the conditions of isomorphism, solid solutions apparently identical with mixed crystals are formed by them, the term *anomalous mixed crystal* formation is applied to the phenomenon. See O. Hahn, *Applied Radiochemistry*,[13] p. 98.

[18] O. Hahn, *Applied Radiochemistry*, Cornell Univ. Press, 1936, p. 103. H. Käding, *Z. physik. Chem.*, **A162**, 174 (1932). *Cf.* K. J. Murata and R. L. Smith, *Am. Mineral.*, **31**, 527 (1946).

but decreases as the lead concentration increases. In these cases it appears that lead is incorporated as chloroplumbite in the lattice of the alkali halide. Thallous chloride can be accumulated in potassium chloride crystals; crystallization of 5 per cent of the potassium chloride in an aqueous solution removes 99 per cent of the thallium.[19] These examples are a warning against the assumption often tacitly made that recrystallization of an easily soluble salt gives a product of greater purity.

Compound formation is sometimes involved in the carrying down of a trace constituent by a collector. Thus ferric hydroxide readily carries down arsenic (III and V) and phosphorus, slightly soluble ferric arsenite, arsenate, and phosphate being formed. The precipitation of the micro constituent may be more complete than would be expected from the solubility of the compound formed, because there is strong adsorption of ferric arsenate, for example, from its saturated solution by ferric hydroxide. Another case of compound formation in precipitation is encountered in the use of tellurium as a collector for gold, platinum,[20] and palladium. These metals are quantitatively carried down when a reducing agent such as sulfurous acid or stannous chloride is added to a solution containing them and a small amount of an alkali tellurite. It seems likely that the noble metals form tellurides under these conditions and are precipitated as such with the reduced tellurium. However, the precipitation of these metals would doubtless be just as complete if no compound formation occurred and they acted simply as crystallization centers for the elemental tellurium. The latter type of collection of a trace element is illustrated by the addition of an alkali stannite solution to a solution containing lead ions and a trace of bismuth. The reduced bismuth forms nuclei on which lead is speedily deposited; in the absence of bismuth the reduction of lead by stannite is very slow.[21] This particular case is of no great practical importance from the quantitative standpoint but analogous cases may find application.

The choice of a collector is governed by a number of factors, of which the first is naturally its ability to carry down the trace substance with sufficient completeness for the purpose. A good collector is one that will gather the trace element completely even when used in small amount. Limitation of the amount of collector is often of importance, since other substances in solution may be coprecipitated with it to a greater or less extent, and later lead to interference in the determination. An efficient collector can be used in minimum quantities and the coprecipitation of undesired constituents thus reduced in absolute amount to the point where they will do no harm. Preference is of course given to a collector which is more or less specific in

[19] P. Pringsheim, *Rev. Mod. Physics*, **14**, 132 (1942).

[20] S. K. Hagen, *Mikrochemie*, **20**, 180 (1936).

[21] F. Feigl, *Specific and Special Reactions*. Elsevier, New York, 1940, p. 75.

its action, but this is a desideratum which is rarely entirely satisfied. Collectors functioning by mixed crystal formation are the most satisfactory in this respect. The collector should be a substance which does not interfere in the final determination of the micro constituent. If this condition can-

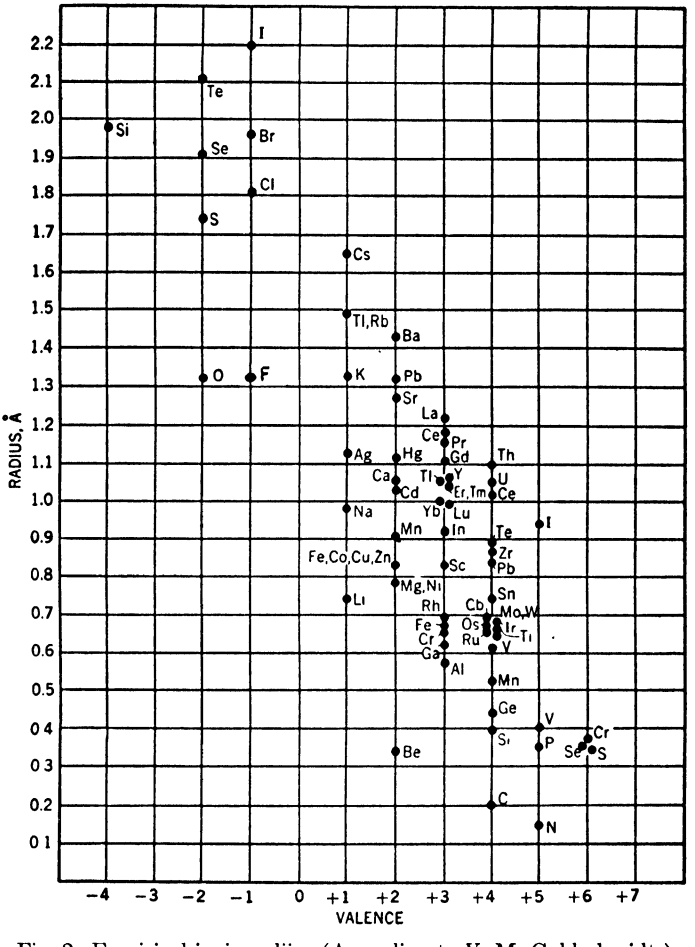


Fig. 2. Empirical ionic radii. (According to V. M. Goldschmidt.)

not be fulfilled the collector should be easily volatile so that it can be eliminated after it has served its purpose. In this respect mercuric and arsenic sulfides have advantages for collecting heavy metal sulfides, and the same is true for tellurium used to gather the precious metals.

As a guide in choosing collectors for coprecipitation by mixed crystal formation, ionic radii of the elements are given in Fig. 2.

Fractional precipitation. At times it is possible to arrange matters so that virtually all of a trace constituent and part of the major constituent are precipitated by a common precipitant. This is a kind of fractional precipitation, and for successful application of the method the trace component must evidently form a less soluble compound than does the major component with the precipitating agent. The precipitate of the major constituent functions as the collector. This method of concentration is applied as a preliminary step to another separation which might not be applicable if the ratio of foreign substance to trace substance were very unfavorable. Or, the fractional precipitation may reduce the concentration of the major constituent to the point where it no longer interferes appreciably with the direct determination of the trace constituent. This principle of concentration finds useful application in sulfide separations, as for example in isolating cadmium in the presence of much zinc (p. 239) and lead in the presence of much iron (p. 408).

1. Precipitation or Adsorption by a Solid

It is sometimes advantageous to use a slightly soluble solid as a precipitant or as an adsorbant for a trace constituent in solution. One cannot always distinguish sharply between the two effects; in either case the solid acts as a collector.

Clarke and Hermance[22] have shown that paper which has been impregnated with a slightly soluble solid may be used in isolating minute amounts of metal from large volumes of solution. For example, by passing a solution containing copper in very low concentration through a disk of filter paper impregnated with cadmium sulfide, copper is precipitated on the paper according to the reaction:

$$CdS + Cu^{++} \rightleftharpoons CuS + Cd^{++}$$

The solubility product of CuS, 9×10^{-45}, is so much smaller than that of CdS, 4×10^{-29}, that the above reaction can be made to run to practical completion from left to right under proper conditions of acidity and rate of flow. If necessary a number of impregnated disks can be used in series. In this way from 90 to 100 per cent of 20 to 50 γ of copper present in 500 ml. of a solution 0.01 *M* in sulfuric acid and 0.1 *M* in sodium acetate could be recovered. The paper disks can be ashed and the copper or other precipitated metal determined by any suitable colorimetric method, or the spot can be compared with standard spots obtained in a similar manner, after dissolving out the cadmium sulfide by immersion in warm 1 *M* hydrochloric acid. The method may be used to separate as little as 0.0001 per

[22] B. L. Clarke and H. W. Hermance, *Ind. Eng. Chem., Anal. Ed.*, **10**, 591 (1938); **9**, 292 (1937).

cent of copper from nickel, and also copper from lead. By the use of a zinc sulfide impregnated paper, traces of lead can be removed from a neutral solution.

Extremely minute amounts of gold, platinum, palladium, selenium, tellurium, and arsenic can be removed from acid solution by shaking the solution with mercurous chloride.[23] These metals are reduced to the elemental condition on the surface of the mercurous chloride and impart a strong color to it (p. 353).

Lead is strongly adsorbed on calcium carbonate, and can in this way be isolated from tap water. The strong adsorption is explained by the slight solubility of lead carbonate. It may also be mentioned that lead can be removed from water by filtration through a wad of cotton.[24] This method is of little practical importance for separating small amounts of lead, but this example of the strong adsorptive properties of cellulose serves as a warning against the inherent danger of partial or complete loss of a trace constituent when a solution is filtered through paper under some conditions.

The above examples indicate that a pre-formed, slightly soluble substance may be used effectively in a number of cases to separate a trace constituent. As a general rule, however, the separation is more complete and certain, or at least more rapid, if the solid phase is formed in the solution containing the trace constituent. Thus if the main concern of an analyst is to isolate a trace of gold from solution he would prefer to precipitate mercurous chloride in the solution rather than to shake the solution with added mercurous chloride. In the former case a greater effective surface of the mercurous chloride is available for the incorporation of gold in the precipitate and moreover the coprecipitation is more rapid than the adsorption. If it is desired, however, to determine gold in a solution by surface coloration on mercurous chloride the solid would of course be added preformed.

2. Ion-Exchange Adsorption

Some use has been made of ion-displacement adsorption on inorganic and organic zeolites in inorganic trace analysis. For example, a suitable synthetic resin, which has been treated with an acid and washed with water,

[23] G. G. Pierson, *Ind. Eng. Chem., Anal. Ed.*, 6, 437 (1934).

[24] G. Frerichs, *Apoth. Ztg.*, 17, 884 (1902). It may be added that oxycellulose has the property of fixing various heavy metals. G. Witz and F. Osmond, *Bull. soc. chim.*, [2], 45, 309 (1886), were able to detect 0.001 f vanadium in a liter of solution by adsorption on treated cotton fibers. The adso l vanadium was revealed by the catalytic formation of aniline black and a rough e ate of the amount could be made by comparison against a series of standards.

will have hydrogen ions on its large internal surface which can be replaced by cations:

$$nZ^-H^+ + M^{+n} \rightleftharpoons Z_n^-M^{+n} + nH^+.$$

The adsorption is usually carried out by the so-called chromatographic technique, *i.e.*, the solution containing the ions to be isolated is run slowly through a column of the material. Since the adsorption reaction is reversible, the adsorbed cations can be liberated by replacing them in turn by running an acid solution through the column. Since different cations will not be held equally strongly (such factors as valence and ionic radius play a role) it may be possible to effect more or less of a separation by eluting the column with a suitable solution; the less strongly held cation will be displaced first (as by hydrogen ions) and will be found in larger amounts in the first portion of effluent. More effective differential replacement may sometimes be obtained by the use of a substance forming complexes of different stabilities with the ions to be separated.[25] It will be evident that separations of cations from anions by ion-exchange will be easier than separations of cations from each other.

TABLE 6

REMOVAL OF HEAVY METALS FROM DISTILLED WATER BY PASSAGE THROUGH A COLUMN OF AMBERLITE IR-100[26]

	Amount of metal present, p.p.m.		
	Cu	Pb	Zn
Laboratory distilled water	0.2	0.055	0.02
Ion-exchange water, 1 passage	0.0035	0.0015	0.00
Ion-exchange water, 5 passages	0.0000	0.0010	0.00
Redistilled water (all-Pyrex still)	0.0016	0.0025	0.00

Some examples of the use of ion-exchange adsorbents in trace analysis may be given. First of all may be mentioned the purification of distilled water by passage through a synthetic cation-exchange resin.[26] Such metals as copper, zinc, and lead can be almost completely removed in this way (Table 6).

It has been suggested that the trace elements copper, cadmium, nickel,

[25] For a comprehensive treatment of this and other phases of ion-exchange separations, with particular reference to radioactive elements, see the series of papers in the November, 1947, number of *J. Am. Chem. Soc.*

[26] G. F. Liebig, Jr., A. P. Vanselow, and H. D. Chapman, *Soil Sci.*, **55**, 371 (1943). See this paper for tables showing concentration of the usual and rare constituents of tap water before and after ion-exchange.

zinc, and manganese be isolated from plant digests and separated from phosphate by passing the solution through a column of synthetic resin (Amberlite IR-100) and eluting with a 1 *N* solution of hydrochloric acid.[27] A high ionic strength has an unfavorable effect on the adsorption. The figures given show incomplete recovery of the metals.

Traces of copper have been isolated by the use of an ion-exchange resin (see p. 299). Complete adsorption of copper is stated to be obtained when the *p*H of the solution is 3.5–6.5. As much as 250 p.p.m. of calcium was found to be without effect on the recovery of copper.

Preferential adsorption of cations and anions on aluminum oxide by the chromatographic technique offers a possible method of separation or enrichment of inorganic trace constituents.[28] For example, ferric iron can be detected at a concentration of 10^{-4} *M* in 1 *M* cobalt or copper solutions, and 1 γ of copper can be detected in a molar solution of cobalt or cadmium.[29]

Abrahamczik[30] has shown that minute amounts of iron can be isolated by permutitic exchange. Ten liters of distilled water containing 0.0025 part per million of ferrous iron were run through a 50 × 450 mm. column of "neopermutite" (about 400 g.). One hundred ml. of warm saturated sodium chloride solution were then passed slowly through the column in the reverse direction, followed by 150 ml. of wash water. Iron was determined colorimetrically in an aliquot of the combined solutions, and 90 per cent of that added was found.

3. Electrolysis

The isolation of traces of metals from large volumes of solution may frequently be effected by electrolytic deposition. Among the metals which have been isolated in this manner are copper,[31] lead,[32] mercury,[33] zinc, silver, and gold (*cf.* p. 391).

The electrolytic separation of mercury has proved of great value in the determination of minute amounts of the element in connection with studies of mercury poisoning.

Von Hevesy and Hobbie[34] made use of the electrolytic deposition of lead

[27] J. P. R. Riches, *Nature*, **158**, 96 (1946).

[28] Regarding inorganic chromatography see G.-M. Schwab and K. Jockers, *Angew. Chem.*, **50**, 546 (1937); G.-M. Schwab and G. Dattler, *ibid.*, **50**, 691 (1937); **51**, 701 (1938). For the use of oxine in inorganic chromatography see H. Erlenmeyer and H. Dahn, *Helv. Chim. Acta*, **22**, 1369 (1939).

[29] G.-M. Schwab and K. Jockers, *loc. cit.*

[30] E. Abrahamczik, *Mikrochemie*, **25**, 230 (1938).

[31] R. Lucas and F. Grassner, *Mikrochemie* (*Emich Festschrift*), **1930**, p. 199.

[32] R. Lucas and F. Grassner, *Mikrochemie* (*Emich Festschrift*), **1930**, p. 201.

[33] See especially A. Stock, *Ber.*, **71**, 550 (1938).

[34] G. von Hevesy and R. Hobbie, *Z. anal. Chem.*, **88**, 1 (1932).

as the dioxide in the determination of the metal in silicate rocks. The deposited oxide was determined colorimetrically with tetramethyldiaminodiphenylmethane. The recovery of lead, however, was not quantitative and the true value had to be found by a radiometric method.

A special apparatus for the deposition of traces of metals from large volumes of solution has been described by Clarke and Hermance.[35] These authors worked with solutions having a volume of 250 ml. containing 5 or 10 g. of metal in which the trace constituent was to be determined. The deposited metal was determined gravimetrically or volumetrically, and it was possible to determine as little as 0.1 mg. of zinc in 5 g. of aluminum with an accuracy of 1 per cent, 0.1 mg. of lead in 10 g. of zinc with an accuracy of 4 per cent, and 0.1 mg. of copper in 5 g. of nickel with an accuracy of 3 per cent. There seems to be no reason why the weight of sample used cannot be much reduced and the deposited metal determined by a suitable colorimetric method instead of gravimetrically or volumetrically.

4. Separations in Which the Trace Constituent Is Left in Solution and the Macro Constituents Are Precipitated

This case is represented by:

$$\text{Solution} \xrightarrow{c} \text{solution} + \overset{C}{\text{solid}}.$$

In general it may be said that this method should be avoided so far as possible in trace analysis. In the first place, the precipitation of a large amount of substance involves the danger of greater or less loss of the trace constituent as a result of coprecipitation, and it must always be regarded with suspicion. If the coprecipitation is not extensive, a reprecipitation may result in a satisfactory separation. Each particular system of c and C must be tested. Even if a satisfactory separation can be effected in this way, the trace constituent is usually left in a large volume of solution and its subsequent determination may first require its isolation or concentration from this solution. Sometimes this method of separation must be applied for the lack of a better one.[36]

An exception to the statements made in the preceding paragraph is found in the use of electrolysis for separation of the major constituents.

[35] B. L. Clarke and H. W. Hermance, *J. Am. Chem. Soc.*, **54**, 877 (1932). For the use of a small mercury cathode to collect small amounts of certain metals, see N. H. Furman, C. E. Bricker, and B. McDuffie, *J. Wash. Acad. Sci.*, **38**, 159 (1948).

[36] In this connection it may be mentioned that small amounts of an interfering constituent which cannot be completely precipitated can sometimes be removed by coprecipitation. Thus scandium hydroxide is not completely precipitated by sodium hydroxide, but if a small amount of cobalt is present it is completely carried down in the cobalt hydroxide precipitate.

The electrolysis is usually carried out with a mercury cathode, so that this case does not strictly come under the above heading (see p. 144). In dilute sulfuric acid solution many metals such as iron, chromium, nickel, cobalt, zinc, cadmium, gallium, copper, tin, molybdenum, bismuth, silver, gold, and the platinum metals (except ruthenium and osmium) are deposited in the mercury, while such elements as aluminum, titanium, zirconium, phosphorus, vanadium, and uranium are quantitatively left in solution.[37] The method is chiefly valuable in the determination of the latter elements in metallurgical materials. Thus electrolysis with a mercury cathode provides an excellent method for the separation of interfering iron in a determination of aluminum in steel. It is not always easy to remove the last traces of the elements deposited. Microgram quantities may remain in solution, even when considerable care is taken. Similar quantities of mercury may be introduced into the solution.

II. Extraction by an Immiscible Solvent

$$\text{Solution 1} \xrightarrow{C} c\text{ solution 1} + c\text{ solution 2}$$

Extraction of a trace constituent from an aqueous solution by an immiscible organic solvent is frequently the ideal method of separating it from large amounts of foreign substances. The process is often very selective, and the isolation of the substance can be made as complete as desired in most cases by repetition of the extraction. Even when a separation from other substances is not involved, an extraction method can be of great value in isolating a minute amount of constituent from a large volume of aqueous solution and concentrating it in a small volume of an immiscible solvent, thus making the determination highly sensitive when the extracted compound is colored.

Occasionally inorganic compounds can be extracted as such (ferric chloride,[38] chloroauric acid, and other metal chlorides or chloro acids by ether (see p. 34), uranyl, thorium, and ceric nitrates from nitric acid medium by ethers and ketones, osmium tetroxide by carbon tetrachloride etc.), but usually in the case of metals one adds an organic reagent forming

[37] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Wiley, New York, 1929, p. 105; G. E. F. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis*, Wiley, New York, 1931, p. 94. For the removal of large amounts of heavy metals prior to the determination of such elements as aluminum, calcium, and sodium, see H. O. Johnson, J. R. Weaver, and L. Lykken, *Anal. Chem.*, **19**, 481 (1947); T. D. Parks, H. O. Johnson, and L. Lykken, *ibid.*, **20**, 148 (1948). These papers contain data on the quantities of the heavy metals left in solution.

[38] V. I. Kuznetsov, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 175 (1947); *Chem. Abst.*, **42**, 18 (1948), has found that ketones extract ferric chloride more readily than do ethers and esters.

an internal complex salt[39] which is often extractable by various organic solvents, the partition coefficient frequently being very favorable. Organic reagents are valuable in extraction procedures not only because they may be highly selective, but also because the metal complex formed may be colored, so that a metal can sometimes be separated and determined in one operation, as is illustrated by the use of diphenylthiocarbazone.

Extraction methods are of wide applicability, and there are few metals, with the exception of the alkalies and alkaline earths, which cannot be extracted as the internal complex salt of some organic reagent. The outstanding reagent for extraction separation of metals is diphenylthiocarbazone (dithizone) which is treated at length in Chapter IV, p. 87. Other reagents which give metal compounds extractable by organic solvents include cupferron (for iron and other metals), 8-hydroxyquinoline (for aluminum, iron, gallium, vanadium, etc.), sodium diethyldithiocarbamate (for copper, lead, zinc, etc.), potassium xanthate (for arsenic), dimethylglyoxime (for nickel), α-nitroso-β-naphthol (for cobalt, copper, etc.), thiocyanate (for iron, molybdenum, tungsten, and rhenium), and rhodamine B (for antimony).[40]

The distribution ratio of an extractable substance is independent of its initial concentration in a given aqueous solution, provided the molecular weight of the partitioning substance is the same in both phases, and no other complicating factors enter in. Thus Grahame and Seaborg[41] found that the distribution ratio of gallium chloride between ether and 6 N hydrochloric acid was the same within the experimental error whether the gallium concentration was 10^{-12} M (radioactive isotope of gallium) or 0.0016 M, being 17.5–18.1 in the first case and 16.9 in the second. Likewise the distribution of $(NH_4)_2Co(CNS)_4$ between amyl alcohol and an aqueous solution was found to be the same whether the initial concentration of cobalt was 10^{-12} M or 10^{-5} M.

If the extracted substance is associated or ionized to different extents in the two phases, the expression for the equilibrium constant of the reaction

$$xA_y \text{ (in phase 1)} \rightleftharpoons yA_x \text{ (in phase 2)}$$

[39] For a discussion of inner complex compounds see F. Feigl, *Specific and Special Reactions*. Elsevier, New York, 1940, p. 35.

[40] The rhodamine B complex of quinquevalent antimony provides an interesting example of the effect of the nature of the organic solvent on the extractability. Webster and Fairhall (p. 165) found that chloroform extracts the complex to give a fluorescent solution, whereas carbon tetrachloride and ether do not extract it. Solvents such as isoamyl alcohol extract both the complex and the excess reagent. Benzene, toluene, ethyl benzene, and xylene extract the complex, giving a non-fluorescent solution, without extracting the reagent.

[41] D. C. Grahame and G. T. Seaborg, *J. Am. Chem. Soc.*, **60**, 2524 (1938).

may be written

$$K = \frac{\{f_1[A]_1 (1 - \alpha_1)\}^x}{\{f_2[A]_2 (1 - \alpha_2)\}^y}$$

where f_1 and f_2 denote the activity coefficients of the substance in phases 1 and 2, and α_1 and α_2 are the degrees of dissociation of the substance in the two phases.[42]

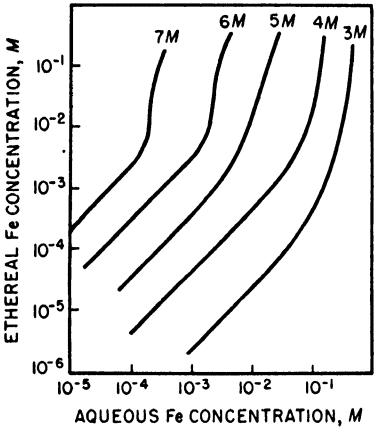


Fig. 3. Distribution of ferric iron between isopropyl ether and aqueous hydrochloric acid solution as a function of the concentration of the latter and of the iron concentration. (From N. H. Nachtrieb and R. E. Fryxell, *J. Am. Chem. Soc.*, **70**, 3557 (1948).)

Ferric chloride and gold (III) chloride show an anomalous behavior when extracted from an aqueous hydrochloric acid solution by ethyl or isopropyl ether. As may be seen from Fig. 3, proportionately more iron is extracted into the isopropyl ether phase at high iron concentrations. However, below a certain iron concentration, which depends on the hydrochloric acid concentration, the distribution coefficient is constant.[43] This example shows it is not always safe to assume that a substance will be extracted as easily at low concentrations as at higher ones.

[42] This expression is usually difficult to apply. It has been shown by J. A. Campbell, *Ind. Eng. Chem.*, **36**, 1158 (1944), that in the majority of distribution equilibria the following expression is applicable: $K' = [A]_1^s/[A]_2$. When log $[A]_2$ is plotted against log $[A]_1$, straight lines are obtained in many cases, and in others the deviation from linearity is usually slight; s is the slope of the line.

[43] N. H. Nachtrieb and R. E. Fryxell, *J. Am. Chem. Soc.*, **70**, 3552 (1948); Nachtrieb and J. G. Conway, *ibid.*, **70**, 3547 (1948). See also R. W. Dodson, G. J. Forney, and E. H. Swift, *ibid.*, **58**, 2575 (1936).

In nearly all extractions the acidity of the aqueous phase plays an important role, and there is generally an acidity range in which the extraction reaches a maximum. With certain organic reagents such as oxine and dithizone various separations of metals become possible by the adjustment of the *p*H.

TABLE 7

EXTRACTION OF VARIOUS METALS AS CHLORIDES WITH ETHER

An hydrochloric acid solution containing 1 g. of the metal as chloride in 100 ml. was shaken with an equal volume of ethyl ether saturated with water.

Metal	Percentage of metal in ether layer				
	1% HCl	5% HCl	10% HCl	15% HCl	20% HCl
Au (III)	84	98	98		95
Fe (III)	Trace	0.1	8	92	99
Sb (III)	0.3	8	22	13	6
Sb (V)	Trace	2.5	6	22	81
As (III)	0.2	0.7	7	37	68
Te (IV)	Trace	0.2	3	12	34
Sn (IV)	0.8	10	23	28	17
Hg (II)	13		0.4		0.2
Cu (II)	Trace		0.05		0.05
Zn	Trace		0.03		0.2
Ni	Trace		Trace		Trace
Pt (IV)	Trace		Trace		Trace
Ir (IV)	Trace		0.02		5
Pd (II)	Trace		0.02		

Data obtained by other workers (see W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Wiley, New York, 1929, p. 107) show that the following elements are also extracted from hydrochloric acid solution: As (V), very slightly; Ga, 97%: Ge, *ca.* 50%; Mo (VI), 80–90%; Tl (III), 90–95%; Sn (II), 15–30%. The following metals are not extracted appreciably: Al, Be, Bi, Ca, Cd, Cr, Co, Fe (II), Pb, Mn, Ni, Os, rare earths, Ag, Ti, Th, W, U, Zr. Vanadium (IV and V) appears to be extracted in traces. F. C. Edwards and A. F. Voigt, *Anal. Chem.*, **21**, 1204 (1949), found that the distribution coefficient of Sb (V) between isopropyl ether and 6.5 to 8.5 *N* hydrochloric acid was greater than 200, whereas that of Sb (III) was 0.016. For the ether extraction of some bromides see Table 89, p. 558.

The effect of foreign substances on the extraction or non-extraction of a substance is relatively slight as a rule if these do not alter the *p*H of the medium or react chemically with the given substance. An interesting example has been given by Grahame and Seaborg,[44] who found that on shaking a hydrochloric acid solution containing ferric chloride and cobalt chloride (as the radioactive isotope) in the ratio 10^8:1 with ether, the iron

[44] D. C. Grahame and G. T. Seaborg, *J. Am. Chem. Soc.*, **60**, 2527 (1938).

was nearly completely removed but no cobalt passed into the ether. The distribution ratio of cobalt chloride between ether and 5.5 N hydrochloric acid is of the order of 0.0001 at 20°, and is not significantly altered by the presence of ferric iron. This example is an illustration of the possibility of removing an interfering macro constituent from a solution by extraction in a case in which separation by precipitation would lead to serious loss of the micro constituent.

An example of increase in the extractability of a substance by another is afforded by the effect of ferric iron on phosphoric acid. The latter is hardly extracted at all from a hydrochloric acid solution by isopropyl ether when present alone, but if ferric iron is also present more than one-half of the phosphoric acid may be extracted under certain conditions, presumably because of the formation of a complex ferric phosphoric acid. On the other hand an extraneous substance may reduce or prevent the extractability of another substance by chemical reaction (reaction of fluoride with ferric iron to give complex fluoride, or reduction of ferric iron to ferrous).

Occasionally extractions are made to remove a major constituent from an aqueous solution (or to reduce its concentration to a small value) and leave the micro constituent therein. Thus large amounts of ferric iron can be removed by extraction as ferric chloride by ether as already mentioned. Some form of continuous extraction apparatus is usually preferable to separatory funnels in such a separation. This method for the removal of a major constituent is as a rule much superior to precipitation with its attendant errors.

Rationale of separations by extraction with immiscible liquids. If two substances, A and B, are to be separated by shaking their aqueous solution with an immiscible solvent, the procedure is simple enough if A has a favorable extraction coefficient[45] and B is virtually non-extractable. Then it is only necessary to extract the aqueous solution with a few portions of the immiscible solvent. The number of extractions required to provide a specified recovery can be found if the extraction coefficient is known.

The following relation between the concentrations of A in the two solvents holds (at least approximately) in many cases:

$$\frac{\sum[A]_2}{\sum[A]_1} = E_A,$$

[45] It seems desirable to distinguish between extraction coefficient, on the one hand, and partition or distribution coefficient on the other. The latter term strictly refers to the ratio of concentrations of the same species in two immiscible solvents at equilibrium, whereas the former refers to the ratio of all species of the same substance in the respective phases. Thus an extraction coefficient can refer to the ratio of the concentration of a metal-organic reagent complex in an organic solvent to the concentration of metal ions in an aqueous phase.

where subscript 1 refers to the original (aqueous) solution and 2 refers to the organic solvent, and E_A is the extraction coefficient. Assume for simplicity that the volumes of the two liquids are equal. The recovery of A, expressed as the fraction of the original amount, after n extractions is then:

$$(R_A)_n = \frac{(Q_A)_n}{(Q_A)_0} = 1 - \left(\frac{1}{E_A + 1}\right)^n,$$

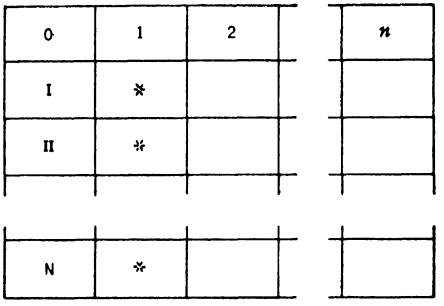
or approximately, if $E_A >$ *ca.* 10 and r is small,

$$\frac{E_A^n}{E_A^n + 1}.$$

If the volume of solution 1 is V_1 and the volume of each portion of liquid 2 is V_2, the expression becomes:

$$(R_A)_n = \frac{(Q_A)_n}{(Q_A)_0} = 1 - \left(\frac{V_1}{E_A V_2 + V_1}\right)^n.$$

If both A and B are extracted, but to different extents, a separation can still be effected, but a more complex procedure is needed, such as is represented schematically in the adjoining diagram. The horizontal row I,1...n represents the extraction of liquid 1 (water), in which A and B are dissolved, by n successive portions of liquid 2 (each equal in volume to that of liquid 1), which are combined with each other.



The combined extracts are now treated in some suitable way to remove A and B and transfer them to a portion of solvent 1. (For example, the extracts might be shaken with an acid aqueous solution.) The resulting aqueous solution (II,0) is now shaken with successive portions of solvent 2 under the same conditions as before. The sequence is repeated as many times as may be required. The general problem is to find the amounts of A and B in the combined n extracts of solvent 2 of the Nth row.

It is evident that in this sequence of operations the only ones resulting in a separation of the desired constituent (A) from the other (B) are I1, II1, ...N1. The others are made to obtain a satisfactory recovery of A. The former kind of extraction may be called *multiple*, the latter kind *consecutive*. The two types are necessarily antagonistic in greater or less degree. It can readily be shown that the amount of A in the combined extracts at stage N,n is:

$$(Q_A)_{N,n} = (Q_A)_0 \left\{1 - \left(\frac{1}{E_A + 1}\right)^n\right\}^N.$$

The recovery factor for A at this stage is therefore:

$$(R_A)_{N,n} = \frac{(Q_A)_{N,n}}{(Q_A)_0} = \left\{1 - \left(\frac{1}{E_A + 1}\right)^n\right\}^N \cong \left(\frac{E_A^n}{E_A^n + 1}\right)^N \qquad (1)$$

The expression for the recovery factor for B is analogous to this, and when E_B is small (*ca.* 0.1) and n is also small it becomes approximately equal to $(nE_B)^N$.

$$\therefore S_{B/A} = \frac{(Q_B)_{N,n}}{(Q_A)_{N,n}} \frac{(Q_A)_0}{(Q_B)_0} = \frac{(R_B)_{N,n}}{(R_A)_{N,n}}$$

$$= \frac{\left\{1 - \left(\frac{1}{E_B + 1}\right)^n\right\}^N}{\left\{1 - \left(\frac{1}{E_A + 1}\right)^n\right\}^N} \cong (nE_B)^N. \qquad (2a)$$

If the volume of liquid 1 is V_1 in each step and the portions of liquid 2 each have the volume V_2, the expression becomes:

$$S_{B/A} = \frac{\left\{1 - \left(\frac{V_1}{E_B V_2 + V_1}\right)^n\right\}^N}{\left\{1 - \left(\frac{V_1}{E_A V_2 + V_1}\right)^n\right\}^N} \qquad (2b)$$

These equations enable us to find the number of extractions (N and n) required to effect a specified recovery and separation. The denominator in equations 2a and 2b can usually be set equal to 1.

Sometimes E_A and E_B can be varied by changing the hydrogen ion concentration and the reagent concentration (*cf.* p. 91). When the substance to be extracted is a complex of a metal and an organic reagent, it is almost always found that the pH of the solution exerts a very strong effect on the extractability. Dithizonates, hydroxyquinolates, and cupferrates are ex-

amples. When such is the case, the value of the extraction coefficient can be changed by altering the pH. If the metals are of the same valence, the ratio of coefficients may remain approximately constant. It is evident that by proper choice of conditions, the values of E_A and E_B can be made such that the desired degree of recovery and separation can be had with the minimum numbers of operations. The value of E_A should not be made unnecessarily great, else the separation factor will be unfavorably affected.

It may not be necessary to resort to multiple extraction, which is a more or less time-consuming operation, for an effective separation. Instead, the device of retrograde extraction may be applied after A has been brought into solvent 2 with more or less of B, provided the extraction is reversible.[46] If the latter solution is now shaken with successive portions of solvent 1 (aqueous solution), the concentration of B in solvent 2 is rapidly decreased in geometrical progression. It is of course necessary that most of A remain in solvent 2. By adjusting the pH of the aqueous phase and the excess of reagent present, it may be possible to increase the value of E_A (if it is not already large enough) to the point where there will be no significant loss of A.

By way of example of direct and retrograde extraction, consider a case in which the ratio of E_A to E_B is constant and the value of E_A/E_B is 1000. For the sake of simplicity, assume A and B to be present in equal amounts in the aqueous solution at the beginning. Adjust the pH and concentration of reagent so that $E_A = 10$ and $E_B = 0.01$. Make two successive extractions of the aqueous solution with solvent 2 (each portion equal in volume to solution 1). The amount of A in the combined extracts (solvent 2) will then be 0.992 of the original amount and that of B will be 0.02 of the original (from equation 1, $N = 1$, $n = 2$). Now alter the conditions to make $E_A = 100$ and $E_B = 0.1$, and shake the solution in solvent 2 with three successive portions of aqueous phase (equal in volume to liquid 2) and discard these extracts. The amounts of A and B remaining in phase 2 will then be 0.96 and 0.000014 of the original, respectively (from equation 1, $N = 3$ and $n = 1$). Thus, in five extractions a separation factor of about $1/70{,}000$ has been attained. Practically, it would be difficult, if not impossible, to adjust conditions to obtain the precisely desired values of the extraction coefficients. This difficulty becomes smaller as the difference between E_A and E_B becomes greater, so that the principle can be applied in practice. For example, in acidic medium the extraction coefficients of copper and zinc dithizonates have a ratio of about 10^8, so that very close adjustment of the E's is not necessary.

[46] *Cf.* in this connection, M. T. Bush and P. M. Densen, *Anal. Chem.*, **20**, 121 (1948), and the comprehensive investigations of L. C. Craig and coworkers.

Even if retrograde extraction is not intentionally applied, the factors involved may have to be considered when the separated phases are washed with the other solvent to remove entrained droplets.

It is evident that if the constituent to be eliminated has the greater extraction coefficient, it may be possible to remove it by extracting the aqueous solution and leave the desired constituent in the latter as already mentioned. This procedure may not be feasible if the constituent to be eliminated occurs in such large amount that an inordinately large volume of solvent 2 would be required.

Full use of the principles outlined requires a knowledge of the extraction coefficients of the various separation forms, and these are mostly unknown at the present time. When they have been determined, it will be possible to specify the best conditions for extraction separations, which at present rest largely on an empirical basis.

The extraction coefficient is obtainable from the equilibrium constant of the extraction reaction. If the cation M^{+m} reacts with an organic reagent HC to give the extractable compound MC_m:

$$M^{+m} + mHC \rightleftharpoons MC_m + mH^+,$$

the following relation exists ideally (*cf.* dithizone, p. 91):

$$\frac{[MC_m]_o}{[M^{+m}]_{H_2O}} = K \frac{[HC]_o^m}{[H^+]_{H_2O}^m}$$

(Subscript o denotes immiscible organic solvent.) K is the equilibrium constant for the reaction. This relation is most readily applied in an acidic medium. However, even in such a medium, M will usually be present in the aqueous phase in various forms, *i.e.*, complex ions, undissociated molecules, etc., in addition to simple ions.

Sometimes $[M^{+m}]_{H_2O}$ can be replaced by the term $\sum[M]_{H_2O}$, the sum of the concentrations of all forms of M in the aqueous phase, with a change in the value of K. This will be the case, if, for example, M forms a series of complexes with a univalent ion, such as chloride ion: MCl^{m-1}, MCl_2^{m-2}, ... Then it can be shown that

$$[M^{+m}]_{H_2O} = \Sigma[M]_{H_2O} \times \text{constant},$$

if the concentration of the complex-forming substance is large compared to $\sum[M]_{H_2O}$ so that the concentration of the former is essentially constant.

Under these conditions, we obtain the analytically useful expression:

$$\frac{[MC_m]_o}{\Sigma[M]_{H_2O}} = K' \frac{[HC]_o^m}{[H^+]_{H_2O}^m}$$

K' is ideally a constant for a specified concentration of the complex forming substance. Its value will depend to some extent upon the concentration of indifferent electrolyte present.

$[MC_m]_O/\sum[M]_{H_2O}$ is the extraction coefficient, which gives the distribution of M in all its forms between the two phases. It will be essentially constant if M is not associated either actually or virtually in either phase. This means that the various species of M may contain only one atom of M per molecule.

1. Dry or Fire Assaying

This is a high temperature extraction process which is of great importance in the isolation of gold, silver, and the platinum metals. A mixture of the sample, lead oxide, flux, and reducing agent is heated to a high temperature. The precious metals present dissolve in the molten lead which sinks to the bottom of the crucible. The lead is removed by cupellation, the molten lead oxide being absorbed by the cupel, while the precious metal globule is not, and after appropriate treatment to remove silver, the bead of gold can be weighed or its diameter measured microscopically.

2. Extraction of Solid Mixtures

Another type of extraction process of lesser importance that may be considered here for convenience involves treatment of a solid mixture with a solvent (usually organic) which will dissolve the compound of the trace constituent but not the compounds of the macro constituents to any appreciable extent. This process finds occasional application in trace analysis. For example, lithium chloride may be dissolved out of a mixture of the other alkali metal chlorides by various organic solvents. In such a process there is danger that the large amount of insoluble material will occlude some of the soluble and prevent its complete extraction. For this reason it may be preferable to use a precipitation process instead. Thus in the Palkin method for the separation of lithium, the solution of the alkali chlorides in as small a volume of water as possible is poured into a mixture of absolute alcohol and ether; sodium and potassium chlorides are precipitated and lithium chloride remains in solution. Extraction of potassium iodide by alcohol is important in the determination of traces of iodine, which must first be separated from the bulk of other salts obtained in the preliminary treatment of the sample.[47]

The reverse application of extraction of solid mixtures—dissolving the compounds of the macro constituents and leaving the compound of the micro constituent undissolved—must be regarded as a dubious procedure because of the great effect of solubility loss even if the absolute solubility of the micro compound is extremely small. The isolation of very small amounts of sodium chloride occurring in lithium chloride by solution of the

[47] See, for example, T. Fellenberg and G. Lunde, *Norsk Geol. Tids.*, 9, 48 (1926).

latter in an anhydrous organic solvent can hardly be considered a feasible procedure.

III. Methods Involving Evolution of a Gas, Distillation, and Volatilization

These processes are based on the following transformations:

$$\text{Solution} \xrightarrow{C} \text{solution} + \text{gas}\ \overset{c}{(\text{vapor})} \tag{1}$$

$$\text{Solid} \xrightarrow{C} \text{solid (liquid)} + \text{gas}\ \overset{c}{(\text{vapor})} \tag{2}$$

The process represented by (1) is of more general applicability than that represented by (2). The former process involves evolution of a gas and distillation, and the latter volatilization. All of the non-metallic elements can be transformed into compounds which can be separated as a gas or vapor. A considerable number of the metals and metalloids, including germanium, arsenic, selenium, tin, antimony, ruthenium, osmium, and rhenium, can be separated by distillation from aqueous solution after conversion into suitable compounds (Table 8).[48] Less often, in the case of metals, evolution methods find application, as for instance in the evolution of arsenic as arsine. Mercury as the metal or as a compound can of course be volatilized easily by heating a solid sample and this method has been applied in the isolation of extremely small amounts occurring in rocks.

Very sharp separations are often possible by the use of evolution, distillation, and volatilization methods. As a rule large amounts of foreign material do not hinder the separation of traces by these processes, and consequently methods based on them give admirable results, which sometimes could not be obtained at all by other methods.

The converse process, in which one or more major constituents are volatilized, is illustrated by the use of hydrofluoric acid in the decomposition of silicates which leads to the expulsion of SiF_4, thus eliminating a constituent that could not readily be removed in any other way. Tin, in tin alloys, can be volatilized by evaporation of the sample with a mixture of bromine and hydrobromic acid. Chromium can be volatilized as chromyl chloride from hot perchloric acid medium by the addition of chloride.

[48] Organic reagents hardly ever find use in these separations. An illustration of an exception is provided by methyl alcohol, which is employed for the isolation of boron by distillation as methyl borate. In this way as little as 0.1 p.p.m. of boron in a silicate rock can be satisfactorily separated and subsequently determined colorimetrically with curcumin (K. Landmark, *Bergens Museums Årbok*, No. 5 (1944)).

TABLE 8

VOLATILIZATION OF METALLIC COMPOUNDS FROM PERCHLORIC AND SULFURIC ACID SOLUTIONS AT 200–220°[a]

Procedure 1 ($HClO_4$–HCl): 15 ml. of 60% $HClO_4$ added to metal chloride or perchlorate solution in a Scherrer distilling flask. Distillation made in a stream of CO_2. Temperature raised to 200°, and hydrochloric acid then added at such a rate that temperature remained at 200–220°. Distillation stopped after 15 ml. HCl had been added over a period of 20–30 minutes.

Procedure 2 ($HClO_4$–HBr): As in (1) except 40% HBr used in place of HCl.

Procedure 3 ($HClO_4$–H_3PO_4–HCl): As in (1) except 5 ml. 85% H_3PO_4 added to flask before distillation.

Procedure 4 ($HClO_4$–H_3PO_4–HBr): As in (3) except HBr substituted for HCl.

Procedure 5 (H_2SO_4–HCl): As in (1) except H_2SO_4 (sp. gr. 1.84) substituted for $HClO_4$.

Procedure 6 (H_2SO_4–HBr): As in (2) except H_2SO_4 substituted for $HClO_4$.

Approximate Percentage of Element Volatilized from 20–100 mg. Portions by Distillation with:

Element	HCl-$HClO_4$ Proc. 1	HBr-$HClO_4$ Proc. 2	HCl-H_3PO_4-$HClO_4$ Proc. 3	HBr-H_3PO_4-$HClO_4$ Proc. 4	HCl-H_2SO_4 Proc. 5	HBr-H_2SO_4 Proc. 6
As(III)	30	100	30	100	100	100
As (V)	5	100	5	100	5	100
Au	1	0.5	0.5	0.5	0.5	0.5
B	20	20	10	10	50	10
Bi	0.1	1	0	1	0	1
Cr(III)	99.7	40	99.8	40	0	0
Ge[b]	50	70	10	90	90	95
Hg(I)	75	75	75	75	75	90
Hg(II)	75	75	75	75	75	90
Mn	0.1	0.02	0.02	0.02	0.02	0.02
Mo	3	12	0	0	5	4
Os[c]	100	100	100	100	0	0
P	1	1	1	1	1	1
Re	100	100	80	100	90	100
Ru	99.5	100	100	100	0	0
Sb(III)	2	99.8	2	99.8	33	99.8
Sb(V)	2	99.8	0	99.8	2	98
Se(IV)	4	2–5	2–5	2–5	30	100
Se(VI)	4	5	5	5	20	100
Sn(II)	99.8	100	0	99.8	1	100
Sn(IV)	100	100	0	100	30	100
Te(IV)	0.5	0.5	0.1	0.5	0.1	10
Te(VI)	0.1	0.5	0.1	1	0.1	10
Tl[d]	1	1	1	1	1	1
V	0.5	2	0	0	0	0

The following elements are not volatilized in any of the procedures: Ag, alkalies (Li, Na, K, Rb, Cs), Al, Ba, Be, Ca, Cb, Cd, Co, Cu, Fe, Ga, Hf, In, Ir, Mg, Ni, Pb, Pd, Pt, rare earths, Rh, Si, Ta, Th, Ti, U, W, Zn, Zr.

[a] J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, 22, 465 (1939).

[b] H_2SO_4 and $HClO_4$ solutions heated to 200° before admitting HCl or HBr.

[c] At 200–220°, no O_3 is volatilized from H_2SO_4, but at 270–300° it is completely volatilized.

[d] No Tl distils if it is univalent (reduction with SO_2).

CHAPTER III

COLORIMETRY AND SPECTROPHOTOMETRY IN TRACE ANALYSIS

The wide use of colorimetric and spectrophotometric methods in analytical chemistry is based on the possibility of converting the constituent to be determined into a substance whose solution (or suspension) is strongly colored. Such a solution shows differential absorption of light of different wave lengths. When the percentage of light transmitted by the solution is plotted against the wave length, a *transmission curve* is obtained, which in most cases shows one or two pronounced maxima or minima, but which

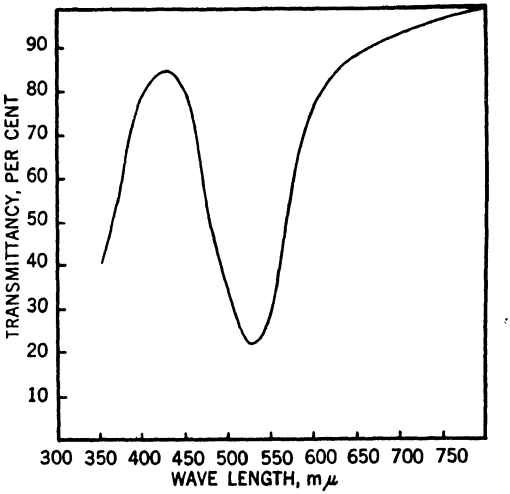


Fig. 4. Transmission curve of potassium permanganate solution (approximately 0.002 per cent Mn) with a band width of 30 mμ.

sometimes may be more complex (Figs. 4, 5, and 6). Instead of plotting the transmittancy against the wave length, the percentage of light absorbed may be plotted and an *absorption curve* is then obtained.[1]

[1] Other methods of plotting are sometimes employed. Thus, extinction is occasionally plotted against the wave length. If light transmission varies strongly with wave length, it is advantageous to plot the logarithm of the extinction (or of the molar extinction coefficient) versus wave length. For example, a logarithmic plot is practically a necessity in the case of chromate ion (Fig. 30).

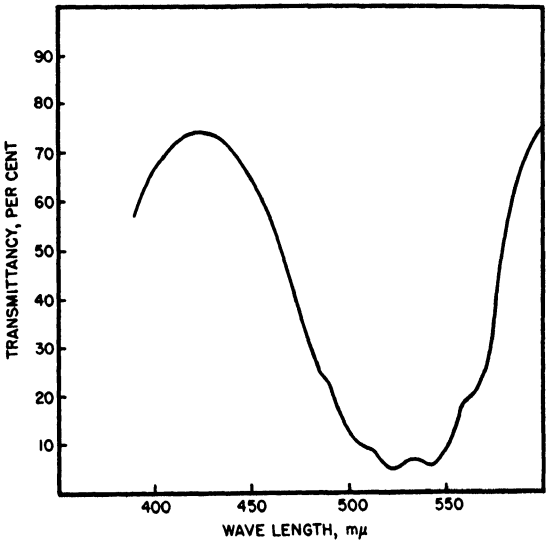


Fig. 5. Transmission curve of potassium permanganate solution (approximately 0.002 per cent Mn, in 1.3 cm. cell) with a band width of 5 mμ. Note the presence of small absorption bands which are not visible when the slit width is greater (Fig. 4). (From data of R. W. Geiger.)

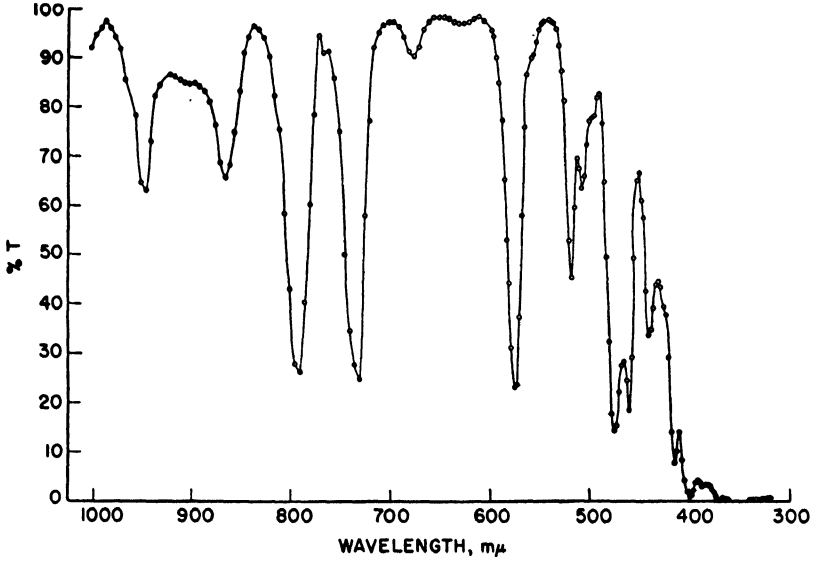


Fig. 6. Transmission curve of samarium chloride solution. (According to W. C. Miller, G. Hare, D. C. Strain, K. P. George, M. E. Stickney, and A. O. Beckman, *J. Opt. Soc. Am.*, **39**, 377 (1949).) Measurement made with Fery prism spectrophotometer.

In the great majority of cases in which dilute solutions are involved, the following relation (which can be derived *a priori*) between the intensity of the incident and the transmitted monochromatic light (Fig. 7) in terms of the concentration of the colored substance in the solution and the depth of the solution is found to hold closely:

$$I/I_0 = 10^{-kcl}, \qquad (1)$$

in which I_0 = intensity of the incident light beam,
I = intensity of the transmitted light beam,
k = a constant, the extinction coefficient (also called the specific extinction), whose value for specified units depends upon the solvent and the temperature as well as upon the wave length of the light,
c = concentration of the colored substance,
l = depth of solution traversed by the light.

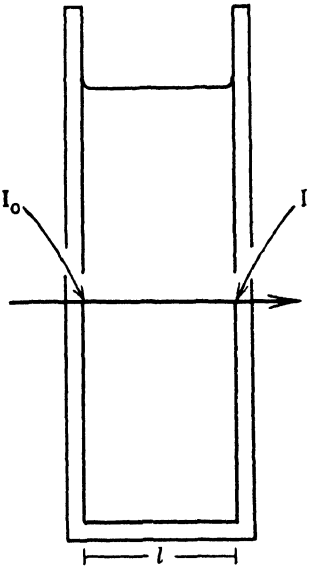


Fig. 7. The solution of the colored substance is contained in a glass cell having plane parallel walls, and the light beam impinges perpendicularly on the face of the cell. Light is lost by reflection at the air-glass and glass-solution interfaces. If I_0 is the intensity of the light beam entering the stratum of solution and I the intensity on leaving, the *transmittancy* of the solution is I/I_0. In practice the light transmitted by the cell containing the solution is compared against that transmitted by an identical cell containing water or a blank solution of the reagent. Alternatively the light transmitted by the cell filled with water is determined and subtracted from the light transmitted by the same cell containing solution.

This relation is known as the law of Lambert-Beer or Bouguer-Beer.[2]

If the concentration is expressed in moles per liter and the depth in centimeters, k becomes the *molar (or molecular) extinction coefficient*, usually designated ϵ.

Equation (1) may be written:

$$\log_{10} I/I_0 = -kcl$$

or

$$\log_{10} I_0/I = kcl \qquad (2)$$

[2] The law of Beer gives the relation between I and I_0 at constant depth and variable concentration, that of Lambert the relation between I and I_0 at constant concentration and variable depth.

Log I_0/I is called the *extinction*[3] (designated by E) or the *optical density* of the solution. It is evident that a plot of extinction (at constant l) against concentration gives a straight line if Beer's law is followed. This line passes through the origin, since any absorption due to the solvent is cancelled out in the usual method of making the measurement (Fig. 7).

Classification of Methods

Two fundamentally different techniques are applied in determining the concentration of a colored substance in solution based on its absorption of light.[4] The simplest method involves duplication of the color, *i.e.*, matters are so arranged that the color of the sample solution is the same as that of a standard solution containing a known quantity of the constituent being determined.[5] This will be the case when the two solutions contain the same amount of colored substance in a column having the same cross section normal to the direction of examination (Lambert-Beer's law followed). The term *colorimetry* is usually applied to this technique, but it is a misnomer since no measurement of color is involved. However, since the word is commonly used by chemists to describe the process of color duplication or comparison it will be used in this sense here, and also as a general term to include any method for the determination of a substance by its color in solution. The second technique involves measurement of the absorption of light by a solution (or liquid or gas) and may be called *absorptiometry*, but is generally known as *spectrophotometry* since light consisting of a restricted band of wave lengths is advantageously used.

[3] The term extinction is employed here in preference to others for the designation of log I_0/I because of its unequivocal meaning and world-wide usage.

[4] In this connection it may be mentioned that sparing use is made of colorimetry or photometry by *reflection* in the determination of traces. This technique usually involves the formation or the collection of a colored precipitate on a disk of filter paper, or other medium, having a constant diameter. An important application of the principle is made in the determination of less than 1 γ of arsenic by the Gutzeit method; the circular stain produced by arsine on paper impregnated with mercuric bromide is compared visually or with the aid of a photoelectric cell against a series of standards prepared photographically. Small amounts of selenium in a large volume of solution may be determined by reducing to the element and filtering off the colloidal precipitate on a mat of barium sulfate on a disk of filter paper. With a disk 20 mm. in diameter, comparisons can be made in the range 5 to 150 γ of selenium with a precision of 1 to 10 γ as shown by K. W. Franke, R. Burris, and R. S. Hutton, *Ind. Eng. Chem., Anal. Ed.*, **8**, 435 (1936). For other applications see pp. 195 and 353 of this book, and H. Yagoda, *Ind. Eng. Chem., Anal. Ed.*, **9**, 79 (1937); *Mikrochemie*, **24**, 117 (1938). For the use of reflectance spectrophotometry in the determination of carbon monoxide see J. Sendroy, Jr., and W. C. Granville, *Anal. Chem.*, **19**, 500 (1947).

[5] Usually it is the intensity of color that is duplicated, but sometimes it is the *hue* (see, for instance, the mixed-color dithizone methods).

Colorimetric and spectrophotometric methods may be subdivided as follows:

I. Colorimetric

White light is ordinarily used for illumination and the condition of equal transmission of light by the standard and sample solutions is found in either of two ways:

A. Subjective

The observer relies upon his judgment of color intensities or hues; comparison tubes or cells, or a Duboscq colorimeter are used. See, further, p. 50.

B. Objective (Photoelectric colorimetry)

The photoelectric cell replaces the eye of the observer.

II. Spectrophotometric

Light consisting of a narrow band of wave lengths (ideally a "single wave length") is used, and the fraction of the incident light transmitted by the solution is measured by either of two methods:

A. Subjective

The intensity of the light which has passed through the solution is duplicated in a comparison beam by reducing the intensity of the latter in some suitable manner (use of a variable diaphragm, neutral wedge, etc.). The observer must match two halves of a field.

B. Objective (Photoelectric spectrophotometry)

A photoelectric cell (or cells) is used to measure the light transmission of the solution.

Sensitivity

In colorimetric or spectrophotometric trace analysis, a knowledge of the sensitivity of the color reaction employed is of paramount importance, and it is necessary to have a simple method available for the expression of the sensitivity. The sensitivity of a color reaction may be defined as the smallest weight of substance that can be detected in a column of solution having a unit cross-section. The weight may conveniently be expressed in micrograms and the area in square centimeters. This method of stating the sensitivity is based on the assumption that the law of Lambert-Beer holds to indefinitely low concentrations, so that the actual concentration of the colored product is immaterial. This assumption holds for the great majority of reactions in which the colored substance formed is soluble.

There are evidently two factors involved in the sensitivity thus defined, first, the intrinsic sensitivity which is proportional to the extinction coefficient of the solution of the colored product, and second, the ability of the

observer, directly or indirectly, to detect small differences in the light transmission of a solution. For comparative purposes the sensitivity could be described or defined in terms of the extinction coefficient of the solution for the wave length of maximum absorption, but such definition would be of small value in applied analysis.

The sensitivity of a color reaction according to the above definition will depend upon the method of color comparison or of transmission measurement. Two important cases, corresponding to IA and IIB of the classification above, will be considered.

Visual Colorimetry

The sensitivity is usually determined by using flat-bottomed tubes, one containing the blank solution, and the other variable amounts of the substance yielding the colored product together with the reagent. White light (daylight reflected from a white surface) is used for illumination. Such factors as the acidity, the excess of reagent and the time of standing must be specified. The quantity of substance (γ/cm.^{2}) required to give a perceptible difference in appearance from the blank can be defined exactly only on the basis of probability. Thus the minimum amount might be defined as that which allows a detectable difference in appearance from the blank in 90 out of 100 comparisons. The determination of the limit thus defined would be laborious, and a less exactly defined and somewhat larger limit may be taken for all practical purposes, namely that which in practically every case will show a difference from the blank. A few such values are given in Table 107.

For low values of mass/cm.^{2}, the sensitivity determines the precision of the visual color duplication. The probability is great that the error of a single color duplication will not exceed $(s/q) \times 100$ per cent (where s is the sensitivity and q is the weight of substance in micrograms per square centimeter cross-section of solution) as long as q is less than 15 or 20 s. When q/s is greater than 15 or 20 the law of Weber applies and the precision remains constant over a wide range of q values.[6] *Cf.* Fig. 8. In

[6] Weber's law states that the increase or decrease in stimulus required to produce a just noticeable difference in the resulting sensation bears a constant relation to the original stimulus, or expressed symbolically:

$\Delta r/r$ = constant, where r = magnitude of stimulus. $\therefore \Delta q/q$ = constant.

In comparing color intensities in tubes according to the procedure described above, the value of $\Delta q/q$ is usually found to be 0.05–0.07. See, for example, J. H. Yoe and F. H. Wirsing, *J. Am. Chem. Soc.*, **54**, 1866 (1932). R. C. Wells, *J. Am. Chem. Soc.*, **33**, 504 (1911), found $\Delta q/q$ to equal 0.065 in the determination of titanium with hydrogen peroxide. D. W. Horn and S. A. Blake, *Am. Chem. J.*, **36**, 202 (1906), obtained the respective values 0.07 and 0.08 for potassium chromate and copper sulfate in the favorable concentration range.

other words no useful purpose is served in working under conditions such that q/s is larger than about 20. It has been stated that smaller absolute differences can be detected between two faintly colored solutions in an optimum concentration range than between a very faintly colored solution

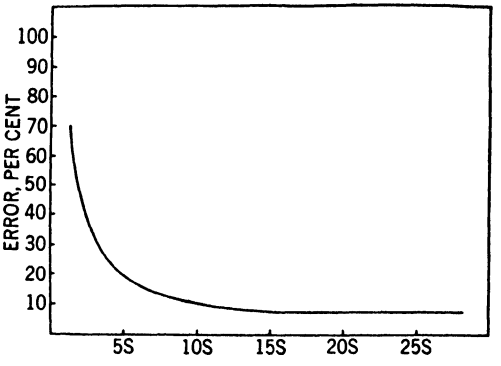


Fig. 8. Maximum error in color comparison by the standard series method as a function of the amount of colored substance in a column of unit cross-section in terms of the sensitivity s of the reaction (page 48). The error becomes constant at approximately 15 s.

and water. It is difficult to see why this should be true, and the experimental evidence on this point is not convincing.

Photoelectric Spectrophotometry

The minimum amount of a colored substance that can be detected by photoelectric spectrophotometry usually does not depend upon the sensitivity of the light-measuring apparatus, but instead upon the reproducibility of the measurement of the transmittancy of the faintly colored solution (this includes the precision of reading a scale or making a pointer setting). As a reasonable basis for the expression of the sensitivity it may be assumed that a difference of 0.001 in extinction can be detected with certainty. This value corresponds to a difference of 0.2 per cent in the transmittancies of the blank and sample solutions. Instruments in common use permit the attainment of a precision of 0.2 per cent in transmittancy determination without much difficulty.[7]

Spectrophotometric sensitivities of a number of reactions, calculated

[7] Much better precision is attainable with specially constructed instruments. See B. Chance, *Rev. Sci. Inst.*, 18, 601 (1947). According to Kortüm, extinction measurements can be made to 0.1 per cent with a barrier layer cell and to 0.01 per cent with a gas-filled alkali metal cell.

from data in the literature, are given in Table 107.[8] The values represent the number of micrograms of element, converted to the colored product, which in a column of solution having a cross-section of 1 square centimeter shows an extinction of 0.001. The smallest amount of an element detectable in the most sensitive color reactions by photoelectric spectrophotometry usually lies in the range 0.001 to 0.01 γ/cm.^{2} Very exceptionally it may lie below 0.001 γ/cm.^{2}, as in the reaction between heptavalent manganese and benzidine or similar oxidizable compounds, the basis of an indirect colorimetric method for manganese. It may be noted that the upper limit of the molar extinction coefficients of the most strongly colored substances used in color methods seems to lie at about 100,000. Thus, ϵ for zinc di-β-naphthylthiocarbazonate in chloroform is slightly greater than 100,000 at 560 mμ (ϵ for di-β-naphthylthiocarbazone itself is about 46,000 at 645 mμ). Most molar extinction coefficients will have values smaller than 35,000.[9] Organic reagents of high molecular weight provide the greatest sensitivity, other factors being the same.

The spectrophotometric sensitivity as defined above is roughly 5 or 10 times the visual sensitivity for most substances having broad absorption bands in the part of the visible spectrum in which the eye is not too insensitive.

Sensitivity values such as those given in Table 107, p. 648, enable one to adjust the concentration or the length of column of solution to furnish the required precision in a determination, and to predict the precision under specified conditions.

I. Colorimetry

Although the practice in the quantitative use of color methods greatly favors the application of spectrophotometry over colorimetry, the latter technique can still render good service in trace analysis, and indeed sometimes offer some advantages. The apparatus required in colorimetry is simple and inexpensive, the sensitivity and precision are frequently satisfactory, and if only an occasional determination is to be run less time may be required than in a spectrophotometric method which will often necessitate the preliminary construction of a standard curve.

As already mentioned, the essential feature of colorimetric methods is the matching of the color of the sample solution with that of a comparison solution, so that when duplication is attained both solutions contain the same amount of the colored substance in columns of equal cross-section:

[8] If the molar extinction coefficient of the colored compound is known, the sensitivity as here defined is given by M/ϵ where M is the molecular weight (in grams) of the compound. Expressed in terms of an element, the sensitivity is nM/ϵ where n is the number of atoms of the element in a molecule of the compound.

[9] H. A. Liebhafsky and E. H. Winslow, *Ind. Eng. Chem., Anal. Ed.*, 11, 189 (1939).

$$c_x l_x = c_s l_s,$$

where c_x = concentration of sample solution,
l_x = depth of sample solution (in line of sight),
c_s = concentration of standard solution,
l_s = depth of standard solution.

Since c = mass/l^3, the dimensions of cl are mass/l^2 or mass per unit cross-section.

If $c_x l_x$ is fixed, there are evidently three ways in which this product can be duplicated if one starts with a standard solution of concentration c_s (Fig. 9):

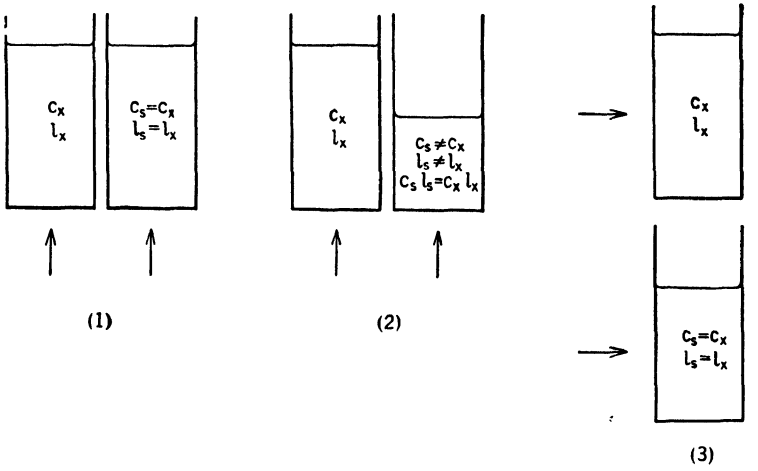


Fig. 9. Schematic representation of methods used in arriving at the state of equi-coloration in colorimetry.

	Vary	Keep constant
Method (1)	c_s, l_s	—
Method (2)	l_s	c_s
Method (3)	c_s	l_s

Method (1) includes (*a*) the standard series method, and (*b*) the colorimetric titration or duplication method. In the standard series procedure a number of known solutions is prepared, each having the same volume as the sample solution and contained in identical tubes with flat bottoms. The sample and comparison solutions are treated with reagent at as nearly the same time as possible. This method of color comparison is the most sound in principle, because Beer's law need not hold, error from fading or slow development of color is reduced to a minimum, and any effect of variable concentration of reagent is eliminated. The method is not as convenient

as some others to carry out, however, for a comparatively large number of standards may have to be prepared. Sometimes the amount of constituent in the sample solution is roughly determined with a preliminary series (or by a colorimetric titration) and then more exactly by the use of a second series in which adjacent members differ by smaller increments.

Nessler tubes are generally less convenient to use in color comparisons in trace analysis than shorter and somewhat narrower tubes such as the one illustrated in Fig. 10. These tubes are provided with ground glass stoppers to permit their use in procedures involving extraction with immiscible solvents, and to facilitate mixing by inversion. It is convenient to have available two sizes of these tubes, namely 1.8 × 15 cm. (25 ml.) and 1.2 × 8 cm. (5 ml.).

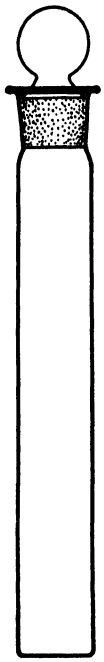


Fig. 10. Tube for color comparisons.

Comparison of the solutions should be made in daylight by examining the tubes axially against a white background such as that obtained by inclining a white card at an angle of about 45 degrees in front of a window receiving light from the sky, but not directly from the sun. When layers of immiscible solvents are to be compared, the tubes are viewed at right angles to their axes against a white vertical background. The tubes should be interchanged during the examination when the colors are very similar, because to some observers the tube on one particular side will always appear a little more strongly colored than that on the other when the color intensities are actually the same.

An observer can usually differentiate without hesitation between two solutions when the amounts of colored substance in columns of equal cross-section differ by about 1/15 (or 7 per cent) in the optimum range where Weber's law applies. As a rule no useful purpose is served in having adjacent members of the standard series differ by less than 10 or 15 per cent. As a matter of fact, standards differing by 20 per cent will serve satisfactorily. With such a series an experienced observer can usually find the content of the sample within 5 per cent. Suppose X (the sample) contains 11.2 γ of constituent, and the two adjacent standards contain 10 and 12 γ. The observer will probably have difficulty in deciding whether X is closer to one or the other of the standards, or at least will see that it is very close to being midway between the two, and he will call the content 11 γ. If X contains 11.6 γ he probably will be unable to distinguish X from the 12 γ standard and will call the amount of constituent present 12 γ, and the error will still be less than 5 per cent. If the amount of constituent is very small, then the standard

solutions may contain respectively 0, 2*s*, 4*s*, 6*s*, 8*s*, and 10*s* micrograms of the constituent per square centimeter of cross-section (*s* is the sensitivity as defined on p. 48).

Sometimes a series of artificial standards, prepared from a substance, or more generally a mixture of substances, as similar as possible in transmission characteristics to the constituent being determined is used for comparison in place of standards prepared from the constituent itself. Such artificial standards are convenient when natural standards are difficult to prepare, as for instance in the determination of free chlorine in water, and in certain routine work. As a rule, the use of such standards is best avoided. They need rarely be used in the trace determination of metals and will not be considered further here.

In the colorimetric titration method a standard solution of the constituent being determined is added to a tube or other suitable vessel containing water and reagent until the color is the same as that of a second tube containing the sample solution which has been treated with reagent. The tubes are examined axially. The standard solution of suitable strength is conveniently added from a microburet subdivided to 0.01 ml. The volume of the two solutions should be approximately the same at the end. A difference of 10 per cent or so is usually of no importance. The tubes should be checked for equal diameter. The tubes mentioned above may be used to advantage in colorimetric titrations if the volume of solution is not too great. Mixing may be accomplished simply by shaking the tubes or, if necessary, by the use of a glass rod. It is hardly necessary to slip a cylinder of black paper around the tubes to exclude extraneous light as sometimes recommended.

In order that this method may yield accurate results it is necessary that the manner of mixing the reagent and the solution of the reacting constituent have no effect upon the color. Moreover the color development must be very rapid,[10] and the colored product must be stable. Thus the colorimetric titration method is not to be recommended for the determination of iron by the thiocyanate method, because the color of the thiocyanate complex fades fairly rapidly on standing. Even if the conditions mentioned are not entirely fulfilled, the colorimetric titration technique may at times be used to advantage in connection with the standard series method. The approximate amount of the constituent in the sample solution can first be found by colorimetric titration, and then a series of standards covering a narrow range can be used to fix the amount more precisely, a new aliquot of the sample solution being used if necessary. The titration technique is

[10] This requirement can often be circumvented by using a standard solution containing the constituent in the form of the colored product. Thus in determining manganese as permanganate, a solution of potassium permanganate can be used as the standard.

generally to be preferred to the standard series method whenever it is applicable and only one or two analyses are to be made.

The following procedure is advantageously followed in finding the amount of constituent required for equicoloration in colorimetric titration. The standard solution is added to tube S (standard) until it is seen that the color intensities are nearly the same. The standard is now added in small increments with comparison after each addition, and the amount noted which corresponds to the last definite difference between X and S. The addition of standard is continued until S is definitely stronger in color than X. If a_1 is the amount of standard for which S is just weaker than X, and a_2 is the amount for which S is just stronger than X, the amount of constituent in the sample solution is taken to be $(a_1 + a_2)/2$. The error should not exceed 5 per cent.

Method (*2*), usually called the balancing method, is the one used with the Duboscq colorimeter. The chief advantage of the method lies in the ease with which l_s (or l_x) can be varied and exactly measured to arrive at the state of equicoloration. Beer's law is assumed to be obeyed.

The Duboscq colorimeter is of restricted value when a very low concentration of substance is to be determined, because the value that can be given the product $c_x l_x$ is limited by the height of the cups (about 5 cm). Frequently in trace analysis the sample solution will have a comparatively large volume, and in such a case color comparison tubes must be used instead. It may also be noted that the Duboscq colorimeter cannot be employed when the reagent or solvent is appreciably colored. The absorption of light by water in layers a few centimeters thick is too small to have any effect.

In using a colorimeter the following precautions should be taken. It should be ascertained whether each scale reads zero when the plunger touches the bottom of the cup. Cups must not be changed from one side to the other. Cups and plungers must be scrupulously clean. The optical perfection of the instrument should be tested by filling both cups with a standard solution of the colored substance being determined, setting one cup at a height which gives a suitable color intensity and permits the depth to be read with small percentage error, then moving the other cup until the two halves of the field appear the same, and repeating the balancing until a total of about 10 readings has been obtained. The average reading should agree with the setting of the stationary cup within 1 or 2 per cent. If this is not the case the reading of the unknown solution can be corrected with the aid of the ratio that has been determined. Alternatively, if the optical perfection of the instrument is in doubt one can proceed in the following manner. One of the cups, say L (the left), is filled with standard solution and set at a convenient height. Cup R is filled with the same standard

solution and the average of 10 settings of R found; cup R is emptied, rinsed with the unknown (sample) solution, and then filled with the latter. The point of balance is found by moving R and averaging a sufficient number of readings. The concentration of the unknown solution then is $c_x = R_s/R_x \times c_s$, R_s and R_x being the average readings given by the standard and unknown solutions in the right-hand cup, the other cup being kept stationary.

Either daylight or artificial light of proper color quality may be used for illumination. The white glass plate beneath the cups should be set at the angle giving the optimum illumination when daylight is used; this plate must be kept clean or else the two halves of the field may appear of different color intensities when a balance should exist, or it may be impossible to match two solutions because of a difference in hue. The same difficulties may be encountered if any other surfaces in the optical paths become dirty or dusty.

TABLE 9

PRECISION OF COLOR INTENSITY DUPLICATION WITH THE DUBOSCQ COLORIMETER

Solution	Q, γ/cm.^{2}	Average deviation of a single setting, %
K_2CrO_4	10 Cr	6
	20	2.5
	60	1.1
	100	0.8
	300	1.8
$Bi^{+++} + I^-$	2 Bi	2.6
	4	1.4
	6	0.9
	8	1.1
	12	1.0
$Fe^{+++} + CNS^-$	10 Fe	0.8
$NiCl_2$	35,000 Ni	0.6
$Cu^{++} + NH_4OH$	100 Cu	1.0

The precision of color comparison with a Duboscq colorimeter may be described by giving the average deviation of a single setting of a cup. Table 9 contains some data on the precision of comparison for solutions of different colors and, in the case of potassium chromate and the bismuth iodide complex, for different concentrations. The second column of the table shows the quantity of the element in a column of solution having a cross-section of 1 square centimeter. The average deviations given in the third column of the table were obtained in each instance from a series of 10 settings. Daylight (cloudy western sky in the afternoon) was used for illumi-

nation. So far as these results permit generalization, it may be concluded that the hue of the solution plays a minor role in the precision of matching. This is in accord with observations of others.[6] At suitable color intensities the average deviation is substantially the same for red, yellow, green, and blue colors, and is slightly less than 1 per cent on the average. It should be pointed out that the brightness of the field is an important factor in the precision of matching. At low light intensities the average deviation becomes greater. For this reason the use of filters with a Duboscq colorimeter in the comparison of faintly colored solutions is of dubious value.

At sufficiently low color intensities (below the range in which Weber's law applies) the average deviation corresponds to a constant amount of the colored substance which is related to, but obviously smaller than, the sensitivity s that has already been referred to (p. 48).[11] For potassium chromate this constant amount is approximately 0.5 γ Cr per cm.^{2} This quantity is important since it is an index of the precision with which small amounts of a constituent can be determined with a Duboscq colorimeter. In obtaining the net precision of the comparison of an unknown solution against a standard solution it must be remembered that it is actually necessary to make two comparisons, namely the standard against a fixed solution (standard) and the unknown against the same solution, to avoid error due to differences in the two halves of the instrument. Suppose one desires to know what precision may be expected in determining 20 γ of Cr as chromate in 10 ml. of solution by the use of the Duboscq colorimeter. Assume for simplicity that the solution fills the colorimeter cup to a height of about 5 cm., the maximum possible. Then $q = 10\ \gamma/\text{cm.}^2$ and the average deviation of a setting is 6 per cent according to Table 9. If ten settings are made of standard against standard, and of unknown against standard, the net average deviation (error) of the ratio standard/unknown will be $\sqrt{2} \times 6/\sqrt{10}$ or 2.7 per cent. By referring to a probability table, it may be found that the probability of the average lying within 5 per cent of the truth is 0.86, a figure which does not carry much conviction. But the probability that the average is in error by less than 10 per cent is 0.997. This figure is sufficiently favorable to allow the expectation that the precision of the comparison will correspond to an error of less than 10 per cent.

[11] It may have occurred to the reader that the quantity s (p. 48) may be obtained from the average deviation in the comparison of two very faintly colored solutions of the substance in question. If q' is the amount of material in a column of solution of unit cross-section corresponding to the average deviation, it is readily shown that a deviation as large as twice the average deviation will be encountered only once in 10 observations on the average, or in other words in 9 times out of 10 the stronger solution will appear more strongly colored to the observer and $2q'$ might be taken as defining s. The s so obtained might not be quite the same as the s for color comparison tubes because of the different conditions of comparison.

As the value of q becomes greater the relative error of the comparison becomes smaller, until in the optimum range the average deviation of the ratio derived from the mean of 10 readings becomes equal to approximately 0.4 per cent ($\sqrt{2}/\sqrt{10}$). This means that in the most favorable range the measured mean is likely to lie within 1 per cent of the true mean. Whether the same *accuracy* can be obtained will depend upon such factors as the stability of the colored compound, the reproducibility of the color system,

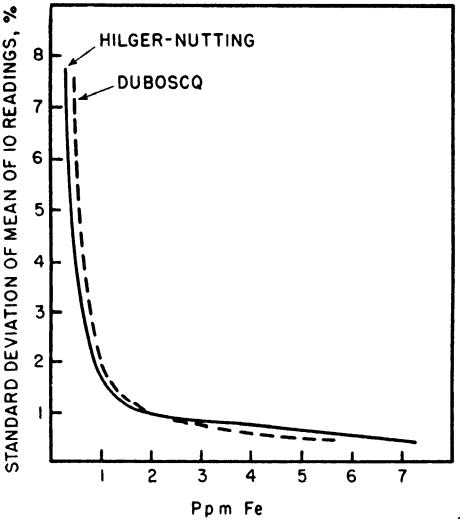


Fig. 11. Illustration of precision of readings with a Duboscq colorimeter and a visual (Hilger-Nutting) spectrophotometer on a green solution of the ferric complex of 8-hydroxyquinoline-5-sulfonic acid. (From data of J. Molland, *Archiv. Math. Naturvid.*, **B43**, 67 (1940).) Stratum thickness not reported.

and its adherence to Beer's law, to say nothing of the effect of foreign substances. Moreover, the accuracy may depend upon the relative thicknesses of the standard and sample solutions at the balance point.

Method (*3*), sometimes called the dilution method, has found little use in colorimetry, but can be applied to advantage at times (*cf.* p. 63) in the colorimetry of traces. Application may be made of it in extraction methods if the reagent is colorless (or is not extractable if colored). For example, the aqueous solution can be shaken with a small volume of the immiscible solvent in a glass-stoppered tube, and more of the solvent then added from a buret until the layer of the organic solvent shows the same

color intensity as that in the unknown tube when the tubes are examined at right angles to their axes.

Since the concentration of the reagent is not the same in the sample and standard solutions at the point of balance, the concentration of the constituent may not be the same in the two solutions in spite of the equal color intensities if the excess of reagent has an effect upon the color intensity. This method must therefore be used with caution.

Photoelectric Colorimetry

The photoelectric cell may be used instead of the eye to determine the point of equi-coloration. Two of the methods mentioned on p. 47 have been applied in photoelectric colorimetry, namely (2) and (3). A photoelectric colorimeter on the principle of the Duboscq visual instrument has been described.[12] If optical difficulties in the construction of such an instrument are surmounted, it should have definite usefulness. Such an instrument is in theory superior to a photoelectric filter photometer working at constant depth of solution in one respect, namely that heterochromatic light will not cause apparent deviations from Beer's law. Practically this is true if the two photocells have equal spectral sensitivities. Since filters are commonly used to supply a restricted band of wave lengths this condition should not impose any serious obstacle.

A double photocell filter photometer may be used as a photoelectric colorimeter as described on p. 63 and such a procedure sometimes possesses definite advantages in trace analysis.

II. Spectrophotometry

Spectrophotometric methods have a number of advantages over the colorimetric. The sensitivity may be increased by measuring the absorption of a solution at the wave length of minimum transmission. If a photoelectric cell is used, measurements may be made in the ultraviolet or infrared.[13] It is possible to avoid or minimize the effect of foreign colored substances by working at suitable wave lengths. Higher precision can be obtained in photoelectric spectrophotometry than in ordinary colorimetry. Moreover, when many determinations are to be made, objective spectro-

[12] A. Goudsmit, Jr., and W. H. Summerson, *J. Biol. Chem.*, 111, 421 (1935); G. Bernheim and G. Revillon, *Ann. fals.*, 29, 5 (1936).

[13] A few inorganic substances have pronounced absorption bands in the near infrared. According to G. Berraz and E. Virasoro, *Anales inst. investigaciones cient. technol. (Univ. nacl. litoral, Santa Fé, Argentina)*, 12/13, 147 (1943); *Chem. Abst.*, 38, 6225, the ions Cu^{++}, Fe^{++}, Ni^{++}, and Co^{++} absorb strongly in the region 800–1200 mμ and may be determined with the aid of a thallous sulfide photocell which is sensitive to near infrared radiation. *Cf.* H. H. Willard and G. H. Ayres, *Ind. Eng. Chem., Anal. Ed.*, 12, 287 (1940).

photometric methods are more rapid and less fatiguing than the subjective colorimetric.

A detailed account of the instruments used in spectrophotometry is beyond the scope of this book, and the discussion here will be limited to brief, general considerations, with special reference to the methods of measurement, particularly as these bear on trace analysis.

As the name indicates, a spectrophotometer is an instrument for measuring the intensity of the light of various wave lengths transmitted (or reflected) by a solution (or other medium). It consists essentially of a device (usually a monochromator of diffraction grating) for furnishing "monochromatic light," one or more absorption cells for holding the sample and reference solutions, and a photometric arrangement for the subjective or objective measurement of the intensity of the transmitted light. Instead of a monochromator, color filters may be used to furnish more or less narrow bands of wave lengths from a continuous light source. Such an instrument is called a *filter photometer*, or sometimes an *abridged spectrophotometer*. Occasionally a mercury arc with suitable filters is used to furnish monochromatic light; the choice of wave lengths is of course limited.

Visual Instruments[14] and Methods

Briefly, these instruments (frequently filter photometers) function in the following manner. Two beams from the same light source, one passing through the solution whose transmittancy is being measured, the other usually passing through a comparison cell containing water or a solution of the colored component, are brought together in such a manner that the observer sees two halves of a field illuminated by each. The amount of light in the comparison beam is reduced by one of the following methods so that it becomes equal to that in the other beam, and the two halves of the field of view show the same color intensity:

1. The aperture is varied by means of a diaphragm or slit.[15]
2. The light passes through two polarizing prisms, one of which can be rotated to vary the amount of light transmitted.
3. A neutral light-absorbing wedge, movable in the direction of its

[14] For a brief account see R. H. Müller, *Ind. Eng. Chem., Anal. Ed.*, **13**, 706 (1941); T. R. P. Gibb, Jr., *Optical Methods of Chemical Analysis*, McGraw-Hill, New York, 1942, pp. 79 and 141; W. R. Brode, *Chemical Spectroscopy*, 2nd ed., Wiley, New York, 1943; M. G. Mellon, *Colorimetry for Chemists*, G. F. Smith Chemical Co., Columbus, Ohio, 1946, pp. 24, 90.

[15] C. Pulfrich, *Z. Instrumentenk.*, **45**, 35, 61, 109, 521 (1925). For applications see: C. Urbach, *Stufenphotometrische Absorptionsbestimmungen in der medizinischen Chemie*, E. T. Haim, Vienna, 1932; L. Heilmeyer, *Medizinische Spectrophotometrie*, G. Fischer, Jena, 1933; S. E. Q. Ashley, *Ind. Eng. Chem., Anal. Ed.*, **11**, 72 (1939).

length, is used (in combination with a compensating wedge to furnish uniform density).[16]

These instruments may be graduated to read transmission, absorption, or extinction. An advantage of these instruments over some photoelectric filter photometers employing barrier-layer cells is the possibility of using highly selective filters, which would not transmit sufficient light for use with the latter.

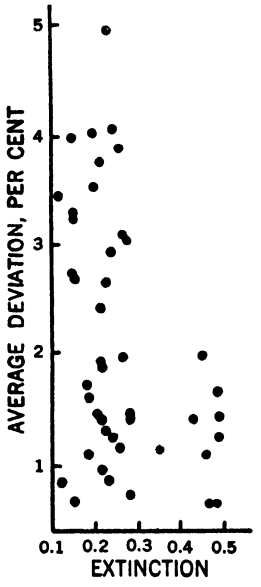


Fig. 12. Error in visual photometry of various solutions as a function of extinction. (Partial reproduction of a figure given by Ashley, *Ind. Eng. Chem., Anal. Ed.*, 11, 75 (1939).)

It is usually necessary to prepare a standard curve in using an instrument of this type for determining the concentration of the unknown. If the solution of the colored component follows Beer's law and if the light transmitted by the filter is sufficiently "monochromatic," a plot of extinction against concentration gives a straight line (see p. 46). The precision attainable in the favorable range of extinction is governed by Weber's law. Under the most favorable conditions, a difference of approximately 1 per cent in the brightness of the two juxtaposed fields can be detected by a trained observer. The error in concentration determination as a function of the extinction is given by:

$$\frac{dc}{c} = -\frac{0.43}{E}\frac{dI}{I}$$

If Weber's law held for very low light intensities and there were no instrumental limitations, the accuracy would be greater the larger the extinction. Actually, visual spectrophotometers give the most precise results when the transmittancy is 10 to 20 per cent, and from the preceding expression it is seen that an error of 1 per cent in determining the transmittancy in this range causes a corresponding error of about 0.5 per cent in the calculated concentration. When the transmittancy is 90 per cent the error in concentration should be about 10 per cent on the same basis. Naturally the precision can be increased by making a number of readings and taking the average, as is done in the use of the Duboscq colorimeter. The precision attained in practice is graphically represented in Figure 12 above.

[16] The so-called absolute colorimetry of Thiel, in which a "gray solution" is used, is a variant. See A. Thiel, *Absolutkolorimetrie*, De Gruyter, Berlin (1939).

Photoelectric Spectrophotometric Methods

In recent years the use of photoelectric cells in photometry has attained great popularity. There are numerous photoelectric photometers for colorimetric analysis on the market. Many of these are filter photometers. Some instruments employ barrier layer photocells, others the emission type. A detailed description of the various instruments with discussions of their use may be found in the literature.[17] It should be noted that instruments with photo-emission cells are superior to those with photovoltaic cells, in that the intensity of the light can be lower for the former, and therefore more selective filters can be used. Moreover, the volume of the solution can be less with the former type, since the light beam can be made narrow. This is often an important consideration in trace analysis.

Photoelectric methods applied in colorimetric analysis may be classified as follows:

1. Single photocell methods
   a. Ordinary

      A cell containing water or diluted reagent solution is placed in the path of the light beam, which impinges on a photoelectric cell. The photocurrent produced is measured by some suitable arrangement (a low-resistance microammeter may, for example, be used with a photronic cell), and its magnitude is a measure of the light intensity I_0. An identical cell containing the solution of the colored component is now substituted for the blank cell and the intensity, I, of the beam measured. If the response of the photocell is linear, the respective photocurrents give the transmittancy I/I_0. The chief requirement to be fulfilled in this method is constancy of the light source during the interval the two photocurrents are measured. Linear response of the photocell is desirable, but not essential if a standard curve is used in finding the concentration of the sample solution, as is generally the case.

   b. Flicker

      By a suitable device a light beam is sent rapidly alternately through the reference and sample solutions, and the resultant beams are balanced, as indicated by the absence of a pulsating photocurrent. The complete transmission curve of a solution can be recorded automatically with an instrument based on this principle.

[17] For a comprehensive account of photoelectric methods in analytical chemistry, with many references, see R. H. Müller, *Ind. Eng. Chem., Anal. Ed.*, **11**, 1 (1939); also see G. Kortüm, *Angew. Chem.*, **50**, 193 (1937). Refer also to the books mentioned in footnote 14.

2. Double photocell methods

In these methods the difference in intensity of two light beams is measured. Fluctuations in the light source are automatically compensated if a circuit of proper design is employed.

a. Two light beams from the same source are passed respectively through the reference and sample solutions and allowed to strike the respective photocells. The net response of the cells is a measure of the light absorbed by the sample solution, if the cells were adjusted for equal response initially. The current of the opposed cells may be measured directly by deflection, or one photocell may be balanced against the other by a suitable circuit arrangement, the galvanometer then being used as a null instrument. Both photocells must show linear response, and should have identical color sensitivity if the light is not monochromatic.

b. The arrangement is the same as in (*a*) except the amount or intensity of light in the reference beam is reduced by means of a variable diaphragm or other device until the net response of the photocells is zero.

Some observations may be made on some of these methods. One well-known instrument frequently used, especially in clinical work, utilizes the system mentioned in 1 *a* (1) above. It is a filter photometer with a barrier-layer cell, and a microammeter for reading the photocurrent. A constant-current transformer feeds the tungsten lamp. The absorption cells are placed in a sliding carriage movable at right angles to the path of the beam of light from the lamp to the photocell. Briefly, the following procedure is used in determining the transmittancy of a solution. A suitable filter is put into place in front of the photocell, and two parallel-walled absorption cells are respectively filled with the solution of the colored component and the blank or reference solution (either water or reagent solution having the same concentration as in the unknown). These cells are placed next to each other in the carriage, with the reference cell in front of the photocell. The light is switched on and the microammeter put into the circuit. The iris diaphragm between the light source and the reference cell is adjusted so that the microammeter reads approximately 100. The reading will be found to decrease quite rapidly at first, but after a few minutes the ammeter needle becomes virtually stationary, and the iris diaphragm is then carefully adjusted so that the meter reads 100.0 (corresponding to 100 per cent transmission). The carriage is now quickly moved to bring the colored solution in front of the photocell, and the microammeter read immediately (to 0.1 division by estimation). The value obtained is the percentage transmittancy. The reading is repeated as many times as the required

precision calls for, the reference solution transmission being adjusted to 100 each time. If the line voltage does not show too great fluctuations, readings can be reproduced in most cases to 0.2 scale division. Under constant illumination the current given by the photocell slowly decreases as a result of "fatigue," but the change is so slow that no appreciable error results if the reference and sample solutions are read within a few seconds of each other.

With one of the common types of double cell photometer there are a number of ways in which a measurement can be made:

1. Deflection Method. Both absorption cells are filled with water, and one or both iris diaphragms are adjusted until the galvanometer shows no deflection. One of the photocells (say the right) is shaded and the resistances adjusted so that the ammeter reads 100 (meaning 100 per cent absorption). The solution whose absorption is to be measured is placed in the right-hand cell and illuminated. The reading obtained is the percentage absorption.

2. Compensation Method. The absorption cells are filled with water, and one of the iris diaphragms (left) is opened so that it reads zero. The opening of the other iris diaphragm is varied until the galvanometer gives no deflection. The solution being measured is substituted for the water on the right side, and the galvanometer restored to null by varying the opening of the right-hand diaphragm. The reading of the latter gives the absorption.

3. Duplication Method. This method is really a colorimetric one, but it is included here for the sake of convenience. One may proceed in one of two ways:

a. Duplication by substitution. The null point of the instrument is obtained as in the deflection method, the sample solution is placed in the right cell, and the resistance is altered to give a reading of 100 or other large value. A cell containing a measured volume of reagent solution is substituted for the sample solution and a standard solution of the constituent is added from a buret until the deflection is the same as with the sample solution. If V is the volume of the reagent solution, v the volume of standard solution required for duplication, and c its concentration, the concentration of the sample solution is $cv/(V + v)$.

b. Duplication by direct comparison. The zero point of the instrument is obtained at full sensitivity, one absorption cell is filled with the sample solution treated with reagent and the cell on the other side is filled with a known volume of diluted reagent solution. A standard solution of the constituent being determined is added to the latter until the galvanometer again reads zero. If the spectral sensitivity of the two photocells is not

the same, the initial zero point adjustment must be made with the colored solution of the sample in both absorption cells.

Before considering the relative merits of the various methods involving the use of photocells, a few words may be said in general about the relation between the error in the measurement of transmittancy or absorption and the resulting error in concentration.[18] The error in concentration arising from a given error in the determination of the transmittancy of the solution may be calculated from the expression given on page 60, which shows that the former error is a function of the extinction of the solution. If the error in the transmittancy is 1 per cent absolute, the corresponding error in concentration is as follows:[19]

I per cent	dc/c, per cent
90	10.7
80	5 6
70	4.0
60	3.3
50	2 9
40	2 7
30	2.8
20	3 2
10	4.3

The most favorable transmittancy range is 20 to 60 per cent, over which the error remains nearly constant. In trace analysis the analyst is frequently forced to work with solutions having transmittancies greater than 80 per cent. The concentration error (in per cent) in the range 80 to 100 per cent is for all practical purposes given by $100\ dI/(100 - I)$.

The deflection method with double photocells requires a constant light source, just as does the ordinary single cell method. With a properly designed balancing circuit this requirement is eliminated, or at least reduced to the extent that small variations in source intensity are without appreciable effect. Under favorable conditions the error in reading the scale becomes the major one. The error in setting the microammeter needle at 100 and making the transmittancy or absorption reading should not exceed 0.2 scale division (0.2 per cent), which represents an error of 0.6 per cent in concentration at 50 per cent transmittancy, if it is assumed that the standard curve is not in error. At 95 per cent transmittancy the corresponding concentration error will be 4 per cent.

[18] For a further discussion see R. H. Hamilton, *Ind. Eng. Chem., Anal. Ed.*, **16**, 123 (1944).

[19] These values hold only when the relation between concentration and extinction is linear. If Beer's law is not followed, the error in concentration corresponding to a given error in transmittancy must be found with the aid of a curve in which absorption is plotted against log c. See A. Ringbom, *Z. anal. Chem.*, **115**, 332 (1938/39).

In the compensation method, slight fluctuations in the source have little effect and the limiting factor is likely to be the accuracy of the compensating device and the precision with which it can be read, provided proper attention is paid to overshooting and fatigue phenomena of the barrier-layer photocells. A sufficient length of time must be allowed to elapse before final adjustment of the compensating device, and unnecessary alteration in the illumination of the compensating photocell is to be avoided. In general practice this method has no advantage over the deflection method if a constant light source is available.

Duplication methods have certain advantages. Real or apparent deviations of the color system from Beer's law do not matter. When only a few determinations are to be made, the duplication technique has the advantage that a standard curve need not be constructed. In duplication by substitution (3*a*) slight variations in source intensity may have a marked effect. In contrast to all the other methods, the method of direct comparison between sample and standard (3*b*) permits use of the full sensitivity of the photocells, which is a fact of importance in trace analysis. Moreover, in this method small variations in the intensity of the source have hardly any effect. Ringbom has recommended this procedure and given results of its use. When using a yellow filter and a clear 5-watt lamp, Ringbom found that his instrument (a barrier-layer cell photometer) at full sensitivity gave a deflection of 9 scale divisions for a 1 per cent change in absorption. In other words, if the scale error in the color duplication is 0.5 division (the error in careful work), the error in the transmittancy will be about 0.05 per cent, and this corresponds to an error of approximately 0.15 per cent in the concentration when the transmittancy is 50 per cent. If the transmittancy of the solution is 0.95, the concentration should be determinable to 1 per cent or thereabouts, provided the reproducibility remains approximately the same at low extinction values. Naturally this deduction rests on good reproducibility and stability of the colored product (*cf.* p. 76), but the result indicates what may be expected under favorable conditions. For other than yellow filters the sensitivity becomes smaller, since the barrier-layer cell shows decreased sensitivity at other wave lengths. Ringbom gives the following figures for some other filters (values are deflections in scale divisions for 1 per cent absorption):

Green	5 0
Blue-green	4 6
Red	4.0
Blue	1.1
No filter	9.4

It may be pointed out that it is not possible to increase the differential sensitivity of two photocells by using a more intense light source or a more

sensitive meter, because there is a limit to the constancy of the current yielded by them. The current becomes more variable at high light intensities and the zero point shifts. The results are more reproducible when light filters are used to cut down the intensity of the illumination, and when the solution absorbs fairly strongly. From the standpoint of trace analysis a study of the limits of the measurements of slight differences in transmittancy by this method is desirable.

Absorption Cells

In trace analysis it is obviously important to have as much as possible of the colored substance in the column of solution traversed by the light beam. With constant cell thickness the volume must be kept as small as possible; with constant volume the cell depth must be increased as far as practicable, the amount of substance remaining constant in both cases. A limit is imposed in either case by the cross-sectional area of the column, which cannot be decreased below a certain minimum which depends upon the photometer used for the transmittancy measurements. Since the volume of solution is likely to be comparatively large in trace analysis, absorption cells of great depth are the more useful. Cells of 5 or 10 ml. capacity with a stratum thickness of 2.5 to 5 cm. and a photometer which will give extinction readings reproducible to 0.001 are desiderata in trace analysis.[20]

Cases will arise in which cells of smaller capacities are desirable. A number of workers have described such special cells. Quartz cells with the inner dimensions 2 × 10 × 25 mm. and 1 × 10 × 25 mm. respectively have been constructed[21]; the light path is 10 mm. long and the volumes needed for measurement are 0.05 and 0.03 ml. respectively. The light beam passing through the solution is circular in cross-section with a diameter of 1 to 1.4 mm. Teflon (an opaque fluorinated hydrocarbon inert to most liquids) has been used for the construction of capillary absorption cells having diameters of 4 and 2 mm., lengths of 50 mm., and capacities of approximately 1 and 0.2 ml. respectively.[22] It appears that absorption measurements with these cells can be made with essentially the same precision as in conventional cells. Emission type photocells are required;

[20] The filter photometers commercially available in the U. S. A. are not particularly designed for trace analysis. Thus, the cells usually have too large a volume and too small a thickness. A filter photometer well adapted for trace analysis is described by P. Krumholz, *Mikrochim. Acta*, 1, 205 (1937). The cells have a capacity of 5 ml. and a stratum thickness of 2.5 cm. They are constructed like a volumetric flask so that the solution can be made up to volume directly in them.

[21] O. H. Lowry and O. A. Bessey, *J. Biol. Chem.*, 163, 633 (1946).

[22] P. L. Kirk, R. S. Rosenfels, and D. J. Hanahan, *Anal. Chem.*, 19, 355 (1947).

barrier layer photocells, without amplification, are not sufficiently sensitive. Standard deviations of 0.001 to 0.002 in extinction readings at 870 mμ have been obtained in the determination of phosphorus by the molybdenum blue method when micro absorption cells were used.[21] Sensitivity values such as those given in Table 107 (Appendix) are of direct aid in estimating the probable precision of the measurements. The problem in the use of these small cells in trace analysis, as compared to micro analysis, is getting the constituent into such a small volume of solution.

If the colored substance can be extracted by an immiscible solvent, the final volume can often be kept small, and if at the same time a long absorption tube can be used, remarkably small quantities of a substance can be determined with good precision. For example, 0.03 γ of cobalt has been determined with an average deviation of about 5 per cent by extracting its nitrosocresol complex with approximately 4 ml. of ligroin and measuring the transmittancy in a 10 cm. tube having a diameter of 5 mm. or less (p. 279).

Filters

Except when there are good reasons to the contrary the transmittancy of a weakly colored solution should be determined at the wave length of minimum transmittancy, in order that maximum sensitivity may be obtained. When a spectrophotometer is used, the wave length, or rather a narrow band of wave lengths, can be selected at will with the aid of a monochromator. This is the ideal arrangement but it is possible to obtain good results by the use of a filter photometer. It is a fortunate fact that solutions of most of the determination forms used in colorimetric analysis show broad absorption bands, and with such solutions suitable filters will in many cases yield practically the same results as a monochromator. The filters used with a filter photometer are commonly glass,[23] but gelatin filters (stained gelatin films mounted between glass[24]) are also useful. Suitable solutions placed in cells find occasional application.[25] Gelatin filters are sensitive to heat, and the transmission characteristics of some may be

[23] See Corning Glass Works, *Glass Color Filters*; Fish-Schurman Corporation, *Jena Colored Optical Filter Glasses*; Hodgman and Lange, *Handbook of Chemistry and Physics*: *International Critical Tables*, Vol. 5, p. 271 (1929). For a series of filters suitable for use with a neutral wedge photometer see P. A. Clifford and B. A. Brice, *Ind. Eng. Chem., Anal. Ed.*, **12**, 218 (1940). The newly developed interference filters provide relatively narrow spectral bands, even narrower than that (35 mμ) supplied by some spectrophotometers.

[24] Eastman Kodak Company, *Wratten Light Filters.*

[25] Formulas for the preparation of selectively absorbing solutions may be found in *International Critical Tables*, Vol. 7, p. 160 (1929), and in a paper by E. J. Bowen, *J. Chem. Soc.*, **1935**, p. 76.

markedly changed on continued exposure to strong light. With some exceptions glass filters are stable to the action of light. As already mentioned, highly selective filters cannot be used with some types of photoelectric photometers because of the small amount of light transmitted by such filters.

Apparent deviation from Beer's law may occur if the light used in absorptiometry is not monochromatic. If the principal wave lengths of the illuminating light are restricted to one side of an absorption band as illustrated in Fig. 13, a linear relation between extinction and concentration will not be obtained, even if Beer's law actually holds.[26] Yellow solutions sometimes do not appear to obey Beer's law because the blue or violet filters used may not be sufficiently selective. Even when a monochromator is employed, deviations from linearity may occur if the absorption maxima are very sharp and the slit width is too great or there is stray or scattered light in the emergent beam. On the other hand, it is usually possible to obtain a close approximation to linearity between extinction and concentration if the absorption band is broad and it does not occur at the ends of the visible spectrum, because suitable filters can then be obtained without much difficulty. Thus in the case of potassium permanganate solutions, which have a broad absorption band in the green, a green filter whose transmission curve is more or less inversely symmetrical to those of the permanganate solutions will give a straight line relation or a very close approximation thereto. Deviation from linearity is less likely to be encountered in trace analysis than in general colorimetric analysis because of the lower concentrations involved in the former.

If the transmission curve of a colored solution is available, the proper wave length of illuminating light for use with a spectrophotometer can usually be chosen with exactness. When a filter photometer is used, and a number of filters are available, the one which gives the lowest transmittancy with a given solution (referred to a blank) is usually the most suitable one.[27]

[26] For a thorough analysis of the effect of stray light in photoelectric photometers see M. N. States and J. C. Anderson, *J. Opt. Soc. Am.*, **32**, 659 (1942). A related error is the *fluorescence error*, to which attention has been drawn by K. S. Gibson and H. J. Keegan, *J. Opt. Soc. Am.*, **28**, 180 (1938). In recent spectrophotometers the arrangement is such that the radiant energy is dispersed before it reaches the sample and only a narrow band of wave lengths is incident on the latter. In this way undue heating of the sample and possible resultant change in transmittancy are avoided. However, this arrangement may introduce a significant error if the sample is activated to fluorescence by this narrow band, since the fluorescent light is added to that normally transmitted. Thus, a sample illuminated with green light may show a red fluorescence and the transmittancy in the green will then be erroneously high, especially if the photocell is highly sensitive to red light, as is often the case.

[27] Sometimes the best filter on this basis may be less desirable than one giving a higher transmission, because it transmits so little light that sensitivity is impaired.

It is not always possible to choose the best filter from several whose transmission curves are known, on the basis of the transmission curve of the solution, because the sensitivity of the photocell and the distribution of energy in the light source will also play a role.[28] A rough choice of filter may be made by selecting one whose color is as close as possible to the complementary color of the solution.

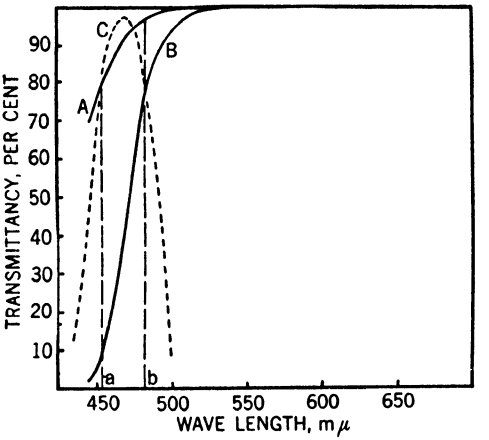


Fig. 13. Illustrating the apparent failure of Beer's law when a blue filter is used in determining the transmittancy of potassium chromate solutions. *A* is the transmission curve of *ca.* 0.5 p.p.m. Cr solution, *B* the curve of *ca.* 5 p.p.m. Cr solution and *C* the transmission curve of the filter. Suppose the light transmitted by the filter to consist of two wave lengths *a* and *b*. Evidently the sum of transmitted *a* and *b* will be greater for *B* than it should be in comparison with *A* because the difference in transmittancy between the two solutions is greater for *a* than for *b*. The situation is the same for any other two similar wave lengths transmitted by the filter. Consequently the extinction is less than it should be at the higher concentrations, and a plot of extinction against concentration will give a curve concave downwards. The extent of deviation from a straight line will depend on the sensitivity of the photocell for light of various wave lengths and the distribution of energy in the spectrum of the light source.

If the solution is colored by a foreign substance or if that substance develops a color when the reagent is added, it may be possible to find a wave length at which the compound of the constituent being determined absorbs strongly (not necessarily at the peak of the absorption curve) but at which the foreign substance absorbs only slightly; the transmittancy of the solution would then be measured at this wave length and the foreign substance would interfere only slightly.

[28] S. S. Cooper, *Anal. Chem.*, 19, 245 (1947), gives a thorough discussion of the factors involved and shows how the best filter can be selected without direct test from the characteristics of the light source, the photocell, the filter, and the solution.

If a solution contains two colored substances having considerably different absorption curves it may be possible to determine both substances by measuring the transmittancy of the solution at two suitable wave lengths and calculating the concentrations from the known extinction coefficients. The formula which applies may be obtained as follows:

Let λ_1 = a wave length at which constituent A, in the form of its colored compound, absorbs strongly, but at which constituent B absorbs only slightly.

λ_2 = a wave length at which B absorbs strongly, but A weakly.

K_1^A, K_2^A = extinction coefficient for the colored compound of A at wave lengths λ_1 and λ_2.

K_1^B, K_2^B = extinction coefficient for the colored compound of B at wave lengths λ_1 and λ_2. (The units of K can be made whatever desired. It is convenient to let K represent the extinction of a solution containing 1 γ of the constituent in 1 ml. of solution, *i.e.*, 1 p.p.m., and having a depth of 1 cm.)

C_A, C_B = concentration of A and B in the solution.

At wave length, λ_1, the extinction of the solution, E_1, will be the sum of the extinctions due to A and B:

$$E_1 = \log (I_0/I)_1 = K_1^A C_A + K_1^B C_B. \tag{1}$$

At wave length λ_2:

$$E_2 = \log (I_0/I)_2 = K_2^A C_A + K_2^B C_B. \tag{2}$$

From (1) and (2):

$$C_A = \frac{K_1^B E_2 - K_2^B E_1}{K_2^A K_1^B - K_1^A K_2^B}.$$

An analogous expression is obtained for C_B.

The values of the K's are obtained by constructing calibration curves (E *vs.* C) for the two constituents separately at the two optimum wave lengths. If Beer's law holds, as it must if the above formula is to be applied, a straight line will be obtained whose slope is $K = E/C$.

Obviously a monochromator is superior to filters in this method but the latter can sometimes be used with success. For examples, see p. 150 and p. 444.

Standard Curves

The common method of using the filter photometer or the spectrophotometer involves the construction of a standard curve (also called the analytical, reference, or calibration curve) for the constituent being determined. For this purpose suitable quantities of the constituent are taken and treated in exactly the same way as the sample solution for the development of the color and the measurement of the transmittancy at the optimum wave length.[29] The extinction ($\log I_0/I$) is plotted against the concentration of the constituent.[30] A straight line is obtained if Beer's law is followed and if there are no complications due to the heterochromaticity of the light. This curve may then be used in future determinations of the constituent under the same conditions. When extinction is directly proportional to concentration only a few points are needed to establish the line. A greater number of points will generally be required when the relation is not linear.

It is advisable to check the standard curve at intervals. This may be done sufficiently well in most cases by verifying the position of one of the points situated some distance from the origin. When a filter photometer is used, the characteristics of the filter and the light source may change with time and the standard curve may be altered. Moreover in certain procedures the color intensity will depend upon the concentration of the reagent and if the latter undergoes a change with time the standard curve may have to be checked at the time the determination itself is run.

Only the most sanguine user of a spectrophotometer will calculate the concentration of his colored solution from the observed extinction and the value of the extinction coefficient taken from the literature. Such a procedure demands the use of light of great spectral purity. It is very difficult to determine the absolute value of an extinction coefficient to within ± 1 per cent, whereas determination of the concentration of a solution by com-

[29] It may be mentioned that as a matter of convenience the transmittancies of the sample and standard solutions are usually obtained with respect to water in the reference cell. In plotting the standard curve it is customary to assign a transmittancy of 100 per cent to the blank solution (reagent solution plus water), which represents zero concentration of the constituent, in order that the curve may pass through the origin. In some instances it is advantageous to use the blank solution in the reference cell. This would, for example, be preferable in measuring the transmittancy of an acid solution containing iodide. The error due to slow liberation of iodine by air-oxidation would thus be cancelled out. In any event, the transmittancy of the blank solution should be obtained when the sample solution is measured if the reagent solution is unstable. If colored substances, not reacting with the reagent, are present in the sample, an aliquot of the latter without reagent is advantageously used as the reference solution (see Table 10). This procedure is all the more advisable if the optical density of the foreign colored substance shows a pronounced variation with temperature (*e.g.*, ferric salts).

[30] Semi-log paper may be used for the plotting in order to avoid converting transmittancies into extinctions.

parison against a similar standard can be made to within a few parts per ten thousand under the same conditions.[31]

As an example of the accuracy attainable with a photoelectric spectrophotometer when used with a standard curve, the results obtained by von Halban and Zimpelmann[32] in the determination of ferric iron with thiocyanate may be given. In spite of the shortcomings of this colorimetric reaction (particularly the fading of the color), iron in concentrations of 1:50,000 to 1:50,000,000 could be determined with an error of less than 1 per cent in all cases except one:

Iron present, mg.	Iron found, mg.	Error, %
0.938	0.938	0
0.762	0.760	−0.26
0.3050	0.3047	−0.1
0.1335	0.1338	+0.25
0.0405	0.0407	+0.5
0.01010	0.01002	−0.8
0.00401	0.00407	+1.5
0.00126	0.00127	−0.8

The thickness of the layer of solution in these determinations was 10 cm. and the volume 50 ml.

III. Sources of Error in Color Methods

The errors peculiar[33] to the determination of substances by color methods are of three kinds:

1. Those having their origin in the system *constituent + reagent → colored product.* These errors may be subdivided into those associated with:
   a. The reproducibility of the color, and the closely related factor.
   b. The stability of the color.
2. Those due to foreign substances, which may have a positive effect

[31] G. Kortüm, *Angew. Chem.*, **50**, 193 (1937). *Cf.* J. M. Vanderbilt, J. Forsyth and A. Garrett, *Ind. Eng. Chem., Anal. Ed.*, **17**, 235 (1945).

[32] H. von Halban and E. Zimpelmann, *Z. Elektrochem.*, **34**, 387 (1928).

[33] Naturally colorimetric methods are subject to other errors common to all quantitative methods, and sometimes these errors may have a large effect. For example, in an indirect colorimetric method in which a constituent is determined from the color given by another substance supposedly bearing a constant relation to the first such errors may determine the accuracy of the procedure. Thus in determining sodium colorimetrically, the metal must first be precipitated as the triple acetate (p. 552) and the uranium in the precipitate is then determined colorimetrically. The chief limitation of this method lies in the difficulty of obtaining the amount of uranium equivalent to the quantity of sodium because of incomplete precipitation of the triple acetate and solubility losses on washing.

(giving a color of their own) or a negative one (reducing the color given by the constituent being determined).

3. Those involved in the measurement or comparison of the color intensity.

Errors of (3) have already been considered in sufficient detail for our purpose, but those of (1) and (2) require some discussion. The conditions in a color reaction for quantitative purposes must be capable of control so that virtually constant amounts of the colored product will be given by constant amounts of the constituent being determined. The reaction between the constituent and the reagent may in the simpler cases be represented by an equation of the general type:

$$mC + nR \rightleftharpoons C_mR_n.$$

Sometimes a further equilibrium of the type

$$pC_mR_n \rightleftharpoons (C_mR_n)_p$$

may be involved, and moreover more than one colored species may be produced in the reaction. The latter appears to be the case in the reaction between cupric ions and ammonia, and also in that between ferric ions and thiocyanate. It is desirable but not necessary that practically all of the constituent be converted into the colored product. If a standard curve is constructed, all that is strictly necessary is the possibility of reproducing the color system without difficulty over a considerable range of concentrations of the constituent. If the reagent is used in large excess, as is generally the case, so that the quantity consumed in the reaction is small compared to that originally added, $[R]^n$ is very nearly constant in the equilibrium expression

$$\frac{[C_mR_n]}{[C]^m[R]^n} = K,$$

and therefore $[C_mR_n]/[C]^m$ is constant. If C and R are colorless, this means that the color intensity of the solution will be proportional to the total amount of the constituent present if $m = 1$, but not for other values, and Beer's law will be followed if there are no other disturbing factors.

The variables that may have to be controlled in a color reaction include the pH of the medium, the excess of the reagent, the time of standing before the color intensity is measured or compared, and the temperature required to develop the color. If these factors do not require too close control, the color should as a rule be reproducible, provided that the colored product is stable.

The stability of the products of color reactions varies over a wide range.

TABLE 10

GENERAL METHODS FOR THE PREVENTION OR THE MINIMIZATION OF ERRORS DUE TO FOREIGN SUBSTANCES IN COLORIMETRIC ANALYSIS

Type of Interference	Procedure	Remarks
I. *Positive*		
A. The foreign substance is colored but undergoes no change on addition of reagent.	1. Measure the transmittancy of the solution at a wave length at which the foreign substance shows practically no absorption, but at which the compound of the constituent absorbs strongly, or use method IB (1).	This procedure often successful.
	2. Measure the transmittancy of the solution before and after the addition of reagent.	The most generally applicable procedure.
	3. Measure the transmittancy of the solution after the addition of reagent against the original solution in the reference cell (both solutions at the same concentration), calling the transmittancy of the latter 100 per cent.	A variant of the preceding procedure. Used in preference to others when sufficient sample solution is available. Monochromatic light should be used.
	4. Add a reagent (usually a complex-forming agent) to destroy the color of the foreign substance.	A useful procedure in both spectrophotometric and colorimetric methods.
	5. After the transmittancy of the sample solution containing reagent has been measured, add a reagent which will discharge the color without affecting that of the foreign substance, and determine the transmittancy of the resulting solution.	In the determination of manganese as permanganate in the presence of iron, hydrogen peroxide may be used to destroy the permanganate.
	6. Add a solution of the foreign substance to the standards to duplicate the color of the sample before reagent is added.	For colorimetry by the series and colorimetric titration methods
	7. Extract the colored compound of the constituent being determined by the use of an immiscible solvent and measure the transmittancy of the latter.	Example: determination of cobalt in the presence of nickel by extraction of cobalt thiocyanate complex with amyl alcohol.
B. The foreign substance may or may not be colored, but it gives a colored product (or colorless precipitate) with the reagent.	1. Measure the transmittancy at two suitable wave lengths and calculate the concentration of the constituent, using two simultaneous equations involving the known extinction coefficients of the two colored substances, or use method IA (1).	Accuracy may not be great, especially when the foreign substance preponderates or gives a strongly colored compound. For an example, see p. 149.
	2. Convert the interfering substance into a non-reactant by (*a*) complex formation, or (*b*) oxidation or reduction.	A powerful method, convenient to use, which is frequently applicable.
	3. Make separations, preferably employing a method which effects a direct isolation of the constituent to be determined.	The method which is applied when others fail; applicable to most constituents; must be resorted to when minute traces are to be determined See Chapter II.

TABLE 10 — (*Continued*)

Type of Interference	Procedure	Remarks
II. *Negative* The foreign substance prevents or hinders the reaction between the constituent and reagent, thus reducing the color intensity. The interference may be due to the formation of a complex between the substance and the constituent or the reagent, destruction of the reagent, etc. Foreign substances may rarely increase the color intensity (see p. 269 for an example).	1. Increase the excess of reagent.	Of limited value. Helpful when the interfering substance forms a relatively weak complex with the constituent. Thus a large excess of thiocyanate reduces the error due to phosphate in the determination of ferric iron.
	2. Find the extinction, E_x, given by x g. of constituent in V ml. of solution. Add a g. of the constituent in a volume of v ml. and obtain the extinction E_{x+a} of the mixture (a should be comparable in amount to x and v should be small). If there are no complications, we have the relation $$\frac{E_x}{E_{x+a}} = \frac{x/V}{\frac{x+a}{V+v}}$$ and $$x = aV \frac{E_x}{E_{x+a}} \Big/ \left(V + v - V \frac{E_x}{E_{x+a}} \right).$$	This method is not often applied but it can be used with profit in checking the results obtained with solutions of unknown composition to avoid gross errors.
	3. Prepare a standard solution having the same composition as the sample solution.	Occasionally applicable, as for example in the determination of trace constituents in sea water or chemical reagents, or other samples having a known composition.
	4. As in IB 2.	
	5. Separate the constituent.	

On the one hand we have substances such as permanganate and chromate which in a suitable environment show no change in solution for months or even years, and on the other hand certain organic products, illustrated by the evanescent substance formed when benzidine is oxidized by permanganate and other strong oxidizing agents, which decompose in a matter of minutes or seconds. As a rule organic reagents give less stable products than do the inorganic, but in many cases the organic product is sufficiently stable to enable it to be used for quantitative purposes to give results of high accuracy.

The natural tendency of many colored substances to be transformed with time into others which are colorless or less strongly colored may frequently

be minimized or practically prevented if suitable precautions are taken. First of all, conditions of acidity, concentration of reagent, etc. may be found at which the stability of the product is a maximum. Light frequently hastens decomposition or produces it. For example, the ferric thiocyanate complex in aqueous solution is markedly sensitive to light; dithizone and the dithizonates in organic solvents decompose slowly on exposure to illumination. An increase in temperature may have an unfavorable effect on stability, especially if organic substances are involved. Solutions of dithizone and various dithizonates in carbon tetrachloride and chloroform may be kept for days without appreciable change if stored in an ice box, but may change quite rapidly at summer temperatures. Occasionally organic substances are fairly easily air-oxidized, and the stability of the color system is improved if a reducing environment can be maintained.

Instability is a characteristic of colloidal systems, and special attention must be paid to the time effect when the method involves the formation of a suspension of a slightly soluble substance (*cf.* p. 344).

Methods for avoiding to a greater or less extent the errors due to foreign substances are indicated in Table 10.

Failure of Beer's Law[34]

At this point we may consider briefly the reasons for the failure of Beer's law. In the first place, Beer's law as it is generally stated is actually the limiting case of a more exact relation

$$\log \frac{I_0}{I} = \frac{n}{(n^2 + 2)^2} kc$$

in which n is the refractive index of the solution.[35] Ordinarily n changes so little from one concentration to another that the coefficient $n/(n^2 + 2)^2$ may be disregarded.

A reason for true deviation of a color system from Beer's law lies in the interaction of the light-absorbing molecules or ions in the solution either with each other or with foreign substances ("neutral salt effect"). This leads to a change in the absorption curve. The effect is small, but by no means negligible, with most inorganic substances at low concentrations (*cf.* Table 11). Potassium dichromate shows greater deviations than do most salts. In trace analysis, in which very dilute solutions are usually being dealt with, serious error is not likely to arise from the operation of this effect. The effect of neutral salts may be more serious, since it is not un-

[34] The material in this section is based on a discussion by G. Kortüm and M. Seiler, *Angew. Chem.*, **52**, 687 (1939).

[35] G. Kortüm, *Das optische Verhalten gelöster Elektrolyte.* Enke, Stuttgart, 1936, p. 65.

usual for the sample solution to contain a comparatively high concentration of some salt, or perhaps base or acid.

An illustration of the effect of high concentrations of what may be called an indifferent substance on the optical density of a colored compound is provided by the system titanium-hydrogen peroxide-perchloric acid (Table 12). In this case the decrease in extinction with increasing perchloric acid concentration is due largely, if not entirely, to a shift in the absorption peak of "pertitanic acid."

TABLE 11

ILLUSTRATIONS OF DEVIATIONS FROM BEER'S LAW[a]

K_2CrO_4 in 0.005 *N* NaOH at 366 mμ		K_2CrO_4 in 0.005 *N* NaOH at 436 mμ		$K_2Cr_2O_7$ in 0.005 *N* H_2SO_4 at 366 mμ	
C (moles/liter)	ε	C (moles/liter)	ε	C (moles/liter)	ε
1.38×10^{-4}	4609	6.8×10^{-4}	320.0	2.38×10^{-5}	2581.6
4.92×10^{-4}	4608	1.87×10^{-3}	319.75	8.50×10^{-5}	2596.2
2.66×10^{-3}	4617	3.7×10^{-3}	319.5	2.25×10^{-4}	2629.9
		6.8×10^{-3}	319.15	4.59×10^{-4}	2687.1
		3.7×10^{-2}	317.55	8.04×10^{-4}	2751.2
				4.35×10^{-3}	3172.4

[a] From G. Kortüm, *Z. physik. Chem.*, **33B**, 243 (1936).

TABLE 12

EFFECT OF PERCHLORIC ACID ON THE OPTICAL DENSITY OF THE TITANIUM PEROXY COMPOUND[a]

(1 mg. of titanium and varying amounts of perchloric acid in 50 ml. of solution)

$HClO_4$, 70%, ml.	Optical density, 410 mμ, 1 cm.	Absorption peak, mμ
0	0.305	410
1	0.309	410
3	0.301	410
5	0.305	410
10	0.304	410
15	0.305	415
25	0.297	420
40	0.285	425
49	0.272	430

[a] Data of A. Weissler, *Ind. Eng. Chem., Anal. Ed.*, **17**, 696 (1945).

Apparent failure of Beer's law may result when the color system involves an equilibrium between the constituent, reagent, and the colored product, as we have just seen. Deviations from this cause cannot justly be included under failure of Beer's law, because this law simply states that the extinction is proportional to the concentration of the colored substance; it does

not state that the extinction must be proportional to the analytical concentration of the constituent which forms the colored substance. The apparent failure of Beer's law when light of insufficient monochromaticity is used has already been considered and nothing more need be said about it here. Another reason for apparent failure of Beer's law when photoelectric instruments are used may lie in the lack of proportionality between the response of the photocell and the light intensity.

IV. General Desiderata for Color Reactions for Trace Analysis

These may be summarized as follows:

1. High Sensitivity

This is the most important desideratum when minute amounts of substances are to be determined. Reproducibility and stability of the colored product can be sacrificed within limits to obtain sensitivity. It is better to be able to determine a minute amount of a constituent with an error of 25 per cent than not to be able to determine it at all. With a fixed minute quantity of substance the accuracy obtainable is directly proportional to the sensitivity of the reaction employed, other things being the same.

2. Specificity or Selectivity

Few if any reagents are strictly specific (reacting only with one substance) but they differ among themselves in the number of substances with which they will give a more or less sensitive reaction, a property which is described by the term *selectivity*. Strictly one should speak of the specificity or the selectivity of a reaction rather than of a reagent. Dithizone for example will react with nearly a score of metals, but by adjustment of the *p*H of the medium and the use of complex-forming agents it can be made to yield practically specific reactions for a number of metals. Although lack of selectivity does not necessarily exclude a reagent from use in trace analysis, selectivity is nevertheless a desirable property, for it generally permits a determination to be made with the expenditure of less time and effort.

3. Good Reproducibility and Stability of the Color

A certain latitude is always desirable in the variables (p. 73) that determine these properties.

4. Adherence to Beer's Law

This is the least important of the desiderata, but a desirable one nonetheless. A system following Beer's law is more convenient to use and permits greater accuracy than one which does not, other factors being comparable. As a matter of fact it is a little superfluous to specify that a color system

should obey Beer's law, for in the natural state of things it generally does so within close limits if the colored substance is soluble. Even when the colored substance is slightly soluble and a colloidal dispersion is obtained, color intensity is proportional to concentration in many cases; systems involving lakes are an exception (see p. 84). As pointed out above, the phrase "adherence to Beer's law" is frequently used, not in the strictly correct sense, but to signify proportionality between color intensity and analytical concentration of the substance being determined.

Organic Reagents

Colorimetric trace analysis would be sadly hampered without organic reagents. The property shown by many organic compounds of forming strongly colored internal complexes with metals is put to good use in colorimetric analysis, being especially valuable when minute quantities of metals are to be determined. Frequently organic reagents show good selectivity, which under the proper conditions can be made the basis of reactions having actual or virtual specificity.[36] The vast array of organic compounds and the ease with which a given compound can often be modified by the introduction of various groups to alter the solubility, color, etc. permit the hope that the number of useful organic reagents will be materially increased in the future.

From the standpoint of trace analysis, an important property of many of the metal-organic complexes is their extractability by organic solvents not miscible with water to give solutions that are more or less strongly colored.[37] Traces of metals can thus be isolated and separated from large amounts of other substances in many cases, and sometimes determined by the color of the organic solvent. Other advantages, besides increased sensitivity, offered by extraction methods are the avoidance of difficulties due to the color of foreign substances or sometimes the reagent itself, the increased stability of the colored product in some cases, and the avoidance of colloidal suspensions which may be formed in aqueous medium.

There are a few organic reagents which are important because they yield strongly fluorescent metal complexes, some of which can be extracted by immiscible solvents.

Although organic reagents play an important role in trace analysis, they do not monopolize the field, and a number of inorganic reagents or deter-

[36] For a discussion of atomic "specific" groupings in organic compounds see F. Feigl, *Specific and Special Reactions* (translated by R. E. Oesper), Elsevier, New York, 1940; *Qualitative Analysis by Spot Tests*, Nordeman, New York, 1939.

[37] A small number of inorganic compounds of strong color are extracted by certain organic solvents. Among these may be mentioned chloroplatinous acid, iodobismuthous acid and "molybdenum blue."

mination forms are the basis of some sensitive and reliable trace methods for metals, for example, manganese as permanganate, chromium as chromate, titanium with hydrogen peroxide, vanadium with peroxide or phosphotungstic acid, arsenic and other metals by the formation of molybdenum blue, bismuth and platinum with iodide, gold and tellurium as the colloidal metals, etc.

V. Fluorimetry

A number of elements can be determined with greater sensitivity and specificity by fluorimetric than by colorimetric methods, and the trace analyst should be familiar with the possibilities of fluorescence analysis. Only a brief outline of the subject will be given here.[38]

The concentration of a fluorescent substance in a solution is obtained by illuminating the latter with ultraviolet radiation and comparing or measuring the intensity of the light emitted. The intensity of the fluorescence is a function of a number of factors:

$$F = AI_0(1 - 10^{-kcl})$$

where F = fluorescence intensity,
I_0 = intensity of the incident radiation,
A = fraction of radiation absorbed,
k = a constant depending on the particular substance, solvent, wave length, etc.,
c = concentration of the fluorescing substance,
l = depth of the layer of solution.

If kcl is small, say less than 0.01, the above expression becomes

$$F = 2.3\, AI_0kcl$$

and F is then directly proportional to the concentration. The linear relation is usually found to hold in practice over a considerable range of concentrations; at higher concentrations a plot of F against c curves toward the c-axis.[39] It should be pointed out that a solution of a fluorescing substance shows maximum fluorescence at a certain concentration, above which the fluorescence decreases. Care should be taken to work with solutions

[38] The following works may be consulted for further information on fluorescence analysis, including more or less material on quantitative methods: M. Haitinger, *Die Fluoreszenzanalyse in der Mikrochemie*, E. Haim, Vienna and Leipzig, 1937. P. W. Danckwortt and J. Eisenbrand, *Lumineszenzanalyse im filtrierten ultravioletten Licht*, 4th ed., Akademische Verlagsgesellschaft, Leipzig, 1940. J. A. Radley and J. Grant, *Fluorescence Analysis in Ultraviolet Light*, 3d ed., Van Nostrand, 1939. For reviews of fluorescence analysis see C. E. White, *Ind. Eng. Chem., Anal. Ed.*, **11**, 63 (1939); *Anal. Chem.*, **21**, 104 (1949).

[39] *Cf.* F. Kavanagh, *Ind. Eng. Chem., Anal. Ed.*, **13**, 108 (1941).

whose concentrations lie below those near the flat maximum of the intensity-concentration curve.

Comparison or measurement of the fluorescence intensity of solutions may be made with a modified Duboscq colorimeter[40] or a Pulfrich photometer,[41] but more precise measurements can be made with properly designed photoelectric instruments. Such fluorophotometers may have either one or two photocells.[42] The essential features of two typical instruments are schematically represented in Fig. 15. A filter is used to isolate the desired wave lengths from the ultraviolet source. By the proper choice of exciting wave length it is sometimes possible to prevent the fluorescence of other substances in the solution. For the greatest fluorescence intensity the wave length of the ultraviolet radiation should be close to the wave length of maximum absorption shown by the solution. Another filter is placed in front of the photocell to absorb reflected or scattered ultraviolet light (a small amount of suspended material in the solution will then be without effect). In some instances the determination of a fluorescent substance may be made more specific by using a photocell filter which will largely absorb any fluorescent light emitted by a foreign substance in the solution. The fluorescence intensity of the unknown solution is referred to that of a comparison solution containing a stable fluorescing substance in suitable concentration. A solution of quinine sulfate or fluorescein is often used for this purpose. The concentration of the fluorescent substance is obtained by reference to a standard curve in which the concentration is plotted against the fluorescence intensity.

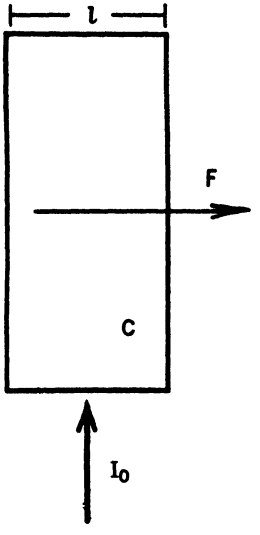


Fig. 14. Illustrating the principle of fluorescence measurements in solutions.

[40] B. Josephy, *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, **4**, 46 (1934); W. Koch, *Nature*, **154**, 239 (1944).

[41] See, for example, C. E. White and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.*, **12**, 229 (1940).

[42] For descriptions of one-cell instruments consult the papers of F. H. Cohen, *Rec. trav. chim.*, **54**, 133 (1935); D. B. Hand, *Ind. Eng. Chem., Anal. Ed.*, **11**, 306 (1939). A double-cell fluorophotometer has been described by F. Kavanagh, *Ind. Eng. Chem., Anal. Ed.*, **13**, 108 (1941). See also R. H. Müller, *ibid.*, **13**, 714 (1941). A description of an alternating current-operated fluorimeter with vacuum photocells is given by R. P. Krebs and H. J. Kersten, *ibid.*, **15**, 132 (1943). Regarding design of photoelectric fluorimeters see E. J. Bowen, *Analyst*, **72**, 377 (1947).

Fluorimetry by visual comparison is less exact than fluorophotometry, but nevertheless is capable of giving useful results. As a matter of fact visual comparison offers an advantage over the use of a fluorophotometer when the absolute amount of the fluorescing substance is very minute, since volumes of 1 ml. or less can be used in the former method whereas such volumes are not great enough for ordinary fluorophotometer cells.

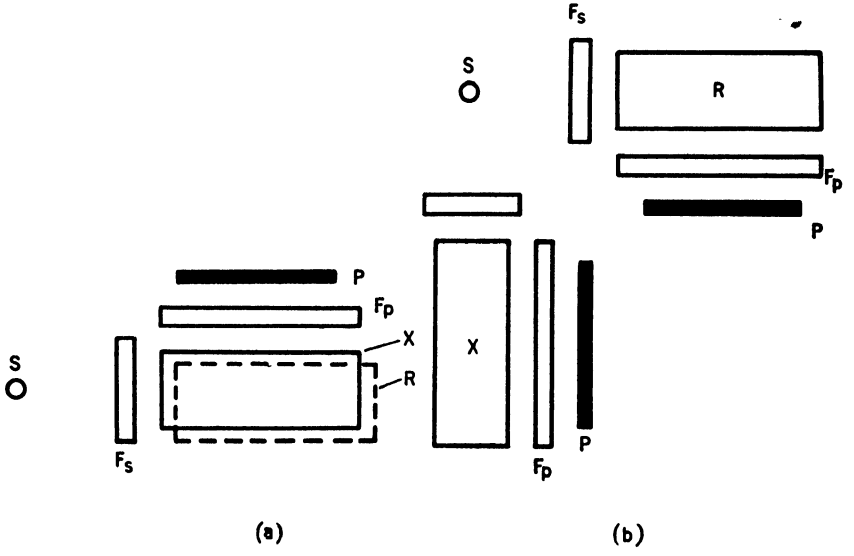


Fig. 15. Schematic representation of measurement of fluorescence of solutions with (*a*) single photocell, (*b*) double photocell. S = source of ultraviolet, P = photocell, X = cell holding sample solution, R = cell holding reference solution, F_s = filter for ultraviolet, F_p = filter for photocell.

For the determination of such elements as beryllium, aluminum, and gallium by methods which are described elsewhere in this book, the ultraviolet source need not be particularly strong and radiation in the near ultraviolet suffices. A G-5 type mercury glow lamp with a purple Corex shell may be mentioned as one satisfactory source of ultraviolet radiation in visual work.[43] It provides a relatively large area of radiation. In carrying out a comparison the tubes (p. 52) or vials containing the sample solution and one of the standard solutions are held vertically in juxtaposition close above the lamp in a dark room. It is important that visible light from the source be reduced to a minimum. The tubes should be interchanged before

[43] A narrow tubular form of lamp, approximately 20 cm. long, is particularly useful when relatively large volumes of solution are to be examined in 1.8 × 15 cm. tubes, which can be illuminated over their whole length.

deciding which shows the stronger fluorescence, in order to avoid error due to non-uniform radiation. Differences of 7 per cent (1:15) in fluorescence intensity can be distinguished in the optimum concentration range (*cf.* p. 48). The use of solutions giving too strong a fluorescence must be avoided, for then a concentration difference of 7 per cent and greater will be undetectable because of the imperceptible difference in fluorescence of two such solutions. The beginning of the optimum concentration range may be taken to lie at 10 times the concentration giving the minimum visible fluorescence.

The visual sensitivity of a fluorescence reaction can be described in the same manner as colorimetric sensitivity by stating the smallest quantity (γ) of the element in a column of solution of unit cross-section (1 cm.^{2}), in the direction of view, which suffices to give a perceptible fluorescence, or a fluorescence just perceptibly stronger than that of a blank. The conditions of observation, particularly the intensity and the wave length of the ultraviolet radiation, must naturally be specified. In some instances the intensity of the ultraviolet excitation is of subsidiary importance, because the blank may already give an appreciable fluorescence, due either to the solvent (organic liquids such as chloroform, alcohol, and acetone commonly show a weak fluorescence) or the reagent. Since the solvent may fluoresce, the fluorescence sensitivity unlike color sensitivity may not be independent of the depth of solution layer examined. Practically this limitation is of slight importance since the depth of layer examined is usually not greater than 1 or 2 cm. An example of the great sensitivity of fluorescence reactions is provided by the beryllium-morin reaction in basic solution, whose visual sensitivity is approximately 0.002 γ Be per cm.^{2} in ultraviolet light. This sensitivity is roughly one hundred times that of the more sensitive color reactions. Not all fluorescence reactions have such great sensitivity however. The sensitivity of the gallium-hydroxyquinoline reaction in which the gallium complex is extracted from an aqueous solution of *p*H 3.0 by chloroform and the latter examined in ultraviolet light is about 0.1 γ Ga per cm.^{2} Since 1 ml. of chloroform suffices for the extraction of 10–20 ml. of solution the concentration limit of this test is 1:10^8. The photometric sensitivity of fluorescence methods (analogous to the spectrophotometric sensitivity of colorimetry discussed on p. 49) depends principally upon the reproducibility of the measurements. Data on this point so far as inorganic fluorimetry is concerned are lacking.

The errors encountered in fluorimetry are to a great extent the analogues of the errors associated with colorimetry but some are peculiar to fluorescence phenomena. Foreign substances may have a profound effect on the fluorescence intensity of a substance. They may diminish the fluorescence by absorbing the ultraviolet radiation (chromate ion is an example), by

absorbing the emitted light and by direct action (quenching).[44] On the other hand the foreign substance may itself fluoresce. Not infrequently it is found that the fluorescent substance is rapidly destroyed by ultraviolet light, and the fluorescence intensity must then be determined quickly or successive readings extrapolated to zero time.

VI. Turbidimetry and Nephelometry

As a rule these methods are used more by necessity than by choice. In turbidimetry the amount of light absorbed by a suspension is determined, and in nephelometry the amount scattered by the suspension is determined. A colorimeter or photometer may be used in turbidimetric comparisons or measurements. On the other hand, a nephelometer does not differ in any essential respect from a fluorimeter except in the character of the illumination. Since nephelometry is rarely used in inorganic trace analysis at the present time, a description of nephelometers will be omitted here.[45]

The chief difficulty in turbidimetry and nephelometry lies in obtaining reproducible suspensions. Small variations in the manner of addition of the precipitant, in the temperature, and in the time elapsing before observation may have a great effect on the light absorption or scattering, because these factors influence the primary or secondary particle size of the precipitate. Moreover, electrolytes may exert a profound effect. Slightly soluble substances differ greatly in their suitability for use in turbidimetry and nephelometry. It is desirable that the precipitate be exceedingly slightly soluble, that it form rapidly, and that it be colored or opaque (the latter desiderata for turbidimetry). It is often found that the optical density of the suspension varies linearly with the concentration of the suspended substance over a wide range, particularly if the substance absorbs strongly. The relation fails at very low concentrations. Colloidal tellurium produced by precipitation with stannous chloride, colloidal gold (p. 344). silver diethylaminobenzylidenerhodanate, copper ferrocyanide, and many heavy metal sulfide dispersions show the linear relation over a considerable concentration range. Silver chloride suspensions give a more complex extinction-concentration curve (p. 550). In colorimetric determinations based on lake formation, in which the reagent (dye) is adsorbed on the surface of the precipitate with a change in color, a linear relation is frequently found between extinction and concentration at low concentrations. This is to be expected, since when the reagent is in large excess the surface of the precipitate becomes saturated with it, and over a limited range the color intensity is proportional to the concentration of the colloidal precipitate.

[44] A discussion of fluorescence quenching in solutions is given by E. J. Bowen, *Analyst*, 72, 379 (1947).

[45] See J. H. Yoe, *Photometric Chemical Analysis*, Vol. II. Wiley, New York, 1928.

When the ratio of reagent to precipitate decreases below a more or less fixed value the amount of dye adsorbed begins to decrease markedly and the extinction-concentration curve then tends to run parallel to the concentration axis. See, for example, p. 423.

Colorless suspensions are of minor value in trace analysis because of the low sensitivity afforded by them. In other words it is the light absorbing power rather than light scattering ability of a suspension that determines its value for use in analysis. Colored or opaque dispersions of slightly soluble substances have been made the basis of sensitive trace methods

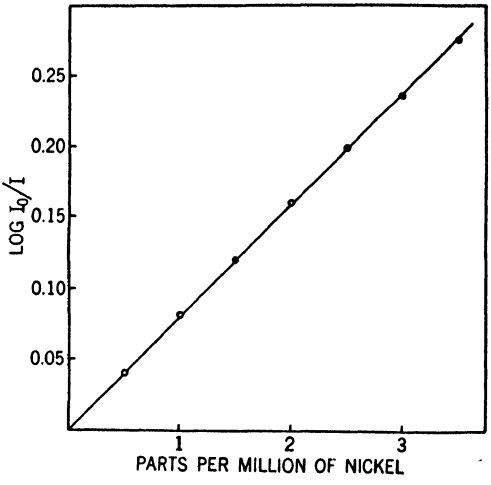


Fig. 16. Determination of nickel as colloidal nickel dimethylglyoxime in the presence of gelatin. (From data of Juza and Langheim, *loc. cit.*)

(Fig. 16).[46] A protective colloid such as gelatin is frequently added to obtain a more stable dispersion of the colloidal substance. If the concentration of the precipitated substance is low, however, such addition may be unnecessary. Sometimes it is difficult to distinguish between a true colorimetric and a turbidimetric method. For example, the lakes given by alizarin and other hydroxyanthraquinones may under some conditions be so finely dispersed that they are practically molecular. The time factor is

[46] See R. Juza and R. Langheim, *Angew. Chem.*, **50**, 255 (1937), for some examples of colorimetry with colloidal solutions. Many organic reagents yield slightly soluble products with metal ions in aqueous medium and determinations based on such reactions involve colorimetry or photometry of colloidal dispersions of strongly colored substances. However, the colored product can often be extracted by an immiscible organic solvent and any difficulties associated with the use of a suspension can thus be avoided.

important in all determinations involving the use of a suspension and readings must often be made a definite time after the addition of the precipitant.

It may be pointed out that turbidimetric, as well as colorimetric, measurements at high light transmittancies have an inherent weakness which decreases precision: the amount of light scattered or absorbed by the substance being determined must be found as the difference between the intensities of two light beams. Nephelometric (and fluorimetric) intensity measurements do not suffer from this limitation and therefore present the possibility of greater sensitivity and precision.[47] Of course other factors may prevent the exploitation of this advantage.

[47] See F. T. Gucker, Jr., H. B. Pickard, and C. T. O'Konski, *J. Am. Chem. Soc.*, **69**, 429 (1947), for a very sensitive photoelectric instrument for measuring low intensities of scattered light.

CHAPTER IV

GENERAL COLORIMETRIC REAGENTS

In this chapter some colorimetric reagents that can be used for the determination of more than one element are considered. Dithizone is the general heavy metal reagent par excellence and its importance in trace analysis calls for a fairly full discussion of its properties and uses. Other reagents are discussed more briefly.[1]

I. Dithizone

Diphenylthiocarbazone, or dithizone, $S{=}C\begin{matrix}\diagup NH\cdot NH\cdot C_6H_5\\ \diagdown N{=}N{-}C_6H_5\end{matrix}$ was first prepared by Emil Fischer,[2] who noted the reaction of the compound with heavy metals to give brilliantly colored products. No analytical use was made of the compound until 1925 when Hellmut Fischer[3] showed its great value for the detection and determination of various heavy metals. In an

[1] The following books on organic reagents contain more or less information on the use of organic compounds for qualitative and quantitative color reactions: F. Feigl, *Qualitative Analysis by Spot Tests* (translated by R. E. Oesper), Elsevier, New York, 1946. F. Feigl, *Specific and Special Reactions* (translated by R. E. Oesper), Elsevier, New York, 1940. C. J. van Nieuwenburg, W. Böttger, F. Feigl, A. S. Komarovsky, and N. Strafford, *Tables of Reagents for Inorganic Analysis*, Akademische Verlagsgesellschaft, Leipzig, 1938; P. E. Wenger and R. Duckert (editors), *Reagents for Qualitative Inorganic Analysis* (Second Report of International Committee on New Analytical Reactions and Reagents of International Union of Chemistry), Elsevier, New York, 1948; J. F. Flagg, *Organic Reagents Used in Gravimetric and Volumetric Analysis*, Interscience, New York, 1948; J. H. Yoe and L. A. Sarver, *Organic Analytical Reagents*, Wiley, New York, 1941; I. Mellan, *Organic Reagents in Inorganic Analysis*, Blakiston, Philadelphia, 1941; W. Prodinger, *Organic Reagents Used in Quantitative Inorganic Analysis* (translated by S. Holmes), Elsevier, New York, 1940. P. Von Stein, *Organic Reagents in Inorganic Analysis*, Chemical Publ. Co., Brooklyn, 1942. Research staff of Hopkin and Williams, *Organic Reagents for Metals and for Certain Acid Radicals*, Hopkin and Williams, London, 1943. F. J. Welcher, *Organic Analytical Reagents*, 4 vols., Van Nostrand, New York, 1947. F. Feigl (translated by R. E. Oesper), *Chemistry of Specific, Selective and Sensitive Reactions*, Academic Press, New York, 1949.

[2] E. Fischer, *Ann.*, **190**, 118 (1878); E. Fischer and E. Besthorn, *ibid.*, **212**, 316 (1882).

[3] H. Fischer, *Wiss. Veröffentlich. Siemens-Konzern*, **4**, 158 (1925).

extensive series of papers,[4] H. Fischer and his coworkers have given procedures for the detection and determination of traces of many heavy metals with dithizone. The reagent has proved highly valuable and there is now an extensive literature concerning its use. Although dithizone has been applied chiefly in the determination of traces of lead, it is no less valuable for the determination of small amounts of other metals. Without it, or its analogs, the determination of traces of zinc and cadmium in complex materials would be virtually impossible. The sensitivity of dithizone methods approaches or equals that of spectrographic methods. Dithizone is also useful for the isolation of traces of heavy metals (*e.g.*, cobalt) which finally may be determined with another reagent.

Dithizone is a violet-black solid which dissolves in most organic solvents to a greater or less extent. In hydrocarbons it is only slightly soluble. Its solubility in chloroform at room temperature is approximately 2 g. per 100 ml., and in carbon tetrachloride about 0.05 g. per 100 ml. These two solvents are used almost exclusively in the preparation of dithizone solutions for analytical purposes.[5] Dilute solutions of dithizone in carbon tetrachloride and chloroform are green, but more concentrated ones are dichroic (red in transmitted light, green in reflected light). In strongly polar solvents, such as nitrobenzene, dithizone is yellow.

When a solution of dithizone in an immiscible organic liquid is shaken with an aqueous solution of a reacting heavy metal, an internal complex salt—dithizonate—is formed, which generally is soluble in the organic solvent, to which it imparts a violet, red, orange, or yellow color, depending upon the metal involved. Dithizone and the dithizonates are virtually insoluble in neutral and acid aqueous solutions[6] (but some dithizonates are decomposed when their carbon tetrachloride or chloroform solutions are shaken with dilute acid).

In basic aqueous solutions dithizone dissolves with a yellow color to give the alkali metal dithizonate, which may be considered to be completely dissociated. When a solution of dithizone in an organic solvent is shaken with an alkaline aqueous solution, more or less of the dithizone is transferred to the aqueous phase as a consequence of the formation of dithizonate ions.

[4] For a review see H. Fischer, *Angew. Chem.*, **47**, 685 (1934); **50**, 919 (1937).

[5] N. Strafford, P. F. Wyatt, and F. G. Kershaw, *Analyst*, **70**, 232 (1945), employ a toluene solution of dithizone for the determination of lead. J. Cholak, D. M. Hubbard, and R. E. Burkey, *J. Ind. Hygiene Toxicol.*, **30**, 59 (1948), use a solution of dithizone in a buffer mixture containing citrate, ammonia, cyanide, and sulfite for the determination of lead in a rapid screening test. The aqueous solution can be kept for months without noticeable change in strength.

[6] When a carbon tetrachloride solution of dithizone is shaken with concentrated hydrochloric acid, dithizone partially passes into the acid layer and imparts a violet-red color to it. In 6 *N* hydrochloric acid dithizone is insoluble.

Dithizone behaves as a monobasic acid under these conditions.[7] In the aqueous phase the following equilibrium is assumed to exist:

$$Dz \rightleftharpoons Dz'^- + H^+,$$

where Dz designates undissociated dithizone and Dz'^- the monovalent (keto) dithizonate ion. Since

$$\frac{[H^+]_w[Dz'^-]_w}{[Dz]_w} = K_d \tag{1}$$

(acid dissociation constant; subscript d refers to dithizone and w to the aqueous phase) and

$$\frac{[Dz]_o}{[Dz]_w} = P_d \tag{2}$$

(partition coefficient for undissociated dithizone between organic solvent, o, and the water phase) it follows that

$$\frac{[Dz]_o}{[Dz]_w + [Dz'^-]_w} = \frac{[H^+]_w P_d}{K_d + [H^+]_w}$$

For basic solutions, in which $[Dz]_w$ and $[H^+]$ are small, the preceding expression may be written

$$\frac{[Dz]_o}{[Dz'^-]_w} = \frac{P_d}{K_d}[H^+]_w = F[H^+]_w \tag{3}$$

The ratio $[Dz]_o/[Dz'^-]_w$ gives the relative amounts of dithizone in the organic solvent and in the aqueous phase when equilibrium has been attained.

The value of F has been determined for carbon tetrachloride by a number of workers. The average is about 7×10^8 at room temperature. For chloroform the value 3.6×10^{10} has been obtained by Irving and collaborators.[7]

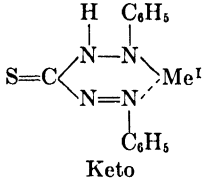
The value of K_d from measurements by the writer is 1.5×10^{-5}, and that of P_d for carbon tetrachloride-water is 1.1×10^4.

The dithizonates, like dithizone itself, are more soluble in chloroform than in carbon tetrachloride and still more soluble in strongly polar organic solvents.

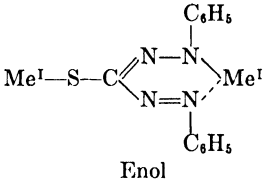
[7] K. Buch and F. Koroleff, *Finska Kemistsamfundets Medd.*, **54**, 98 (1945). However, it must be assumed that dithizone has a slight tendency to ionize as a dibasic acid in order that the formation of enol dithizonates can be accounted for (p. 96). The essentially monobasic character of dithizone up to a *p*H of 12 has also been demonstrated by H. Irving, S. J. H Cooke, S. C. Woodger, and R. J. P. Williams, *J. Chem. Soc.*, **1949**, 1847.

1. The Metal Dithizonates

Some heavy metals can replace either one or both hydrogen atoms of dithizone, thus forming two different salts. These have been termed keto and enol forms by H. Fischer. According to him, the hydrogen of the imide group of dithizone is replaced by the metal in the keto form, whereas in the enol form the hydrogen of the sulfhydryl group of the hypothetical enol dithizone is also replaced, so that the enol compound contains twice as much of the metal as the corresponding keto form. The formulas assigned by Fischer to the keto and enol dithizonates of a univalent metal are as follows:

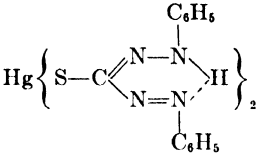


Keto



Enol

There is considerable doubt about the actual structure of the dithizonates. Justifiable objections have been raised against Fischer's formulas, especially of the enol compound of a divalent metal. Irving and coworkers[7] represent the structure of monobasic mercuric dithizonate (the keto form of Fischer) as



According to Fischer the "keto" forms of all metal dithizonates exist; the "enol" forms of many metals are not known. Copper, silver, and mercury readily form both monobasic and dibasic dithizonates. The monobasic complexes are preferentially formed in acidic solution, and the dibasic in alkaline medium or with a deficiency of dithizone. The dibasic dithizonate can be transformed into the monobasic by treatment with acid and dithizone or with acid alone:

$$Me^{II}Dz'' + Dz \overset{H^+}{\rightleftharpoons} MeDz'_2$$

$$Me^{II}Dz'' + 2H^+ \rightleftharpoons MeDz' + Me^{++}$$

In Table 13 the metals forming complexes with dithizone are indicated, and in Table 14 (p. 92) some data on the metal dithizonates are given. It will be noted that certain metals react only in one valence. Thus Fe^{II}, Sn^{II}, and Pt^{II} react, but not Fe^{III}, Sn^{IV}, and Pt^{IV}.

TABLE 13

METALS REACTING WITH DITHIZONE

(The enclosed elements yield dithizonates)

H																
Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—
—	Ra	Ac	Th	Pa	U											

2. *Metal-Dithizone Equilibria*

The over-all reversible[8] reaction between dithizone and a divalent metal ion in acidic medium can be represented by the general equation

$$(Me^{++})_w + (2\ Dz)_o \rightleftharpoons (MeDz_2')_o + (2\ H^+)_w,$$

in which Dz = dithizone and $MeDz_2'$ = keto dithizonate, and the subscripts w and o refer to the aqueous and organic solvent phases, respectively. On the basis of this equilibrium it is a simple matter to derive an expression for the extractability of the metal as the function of the hydrogen-ion concentration of the aqueous solution and the concentration of dithizone. The following relation exists:

$$\frac{[MeDz_2']_o}{[Me^{++}]_w} = K\frac{[Dz]_o^2}{[H^+]_w^2}. \tag{4}$$

Strictly, activities should be written instead of concentrations, and the more exact expression is:

$$\frac{[MeDz_2']_o}{[Me^{++}]_w} = K\frac{[Dz]_o^2 f_{Me^{++}}}{[H^+]_w^2 f_{H^+}^2}, \tag{5}$$

in which $f_{Me^{++}}$ and f_{H^+} are the activity coefficients of metal and hydrogen ions. If the acidity is such that the metal is present entirely as a simple ion (Me^{++}), this expression gives the ratio of the concentration of the metal in the organic solvent to that in the aqueous phase. Equation (4) has been tested in a preliminary way for zinc in a biphthalate buffer medium

[8] Not all metal—dithizone reactions are simply reversible. Thus cobalt and nickel do not react markedly with dithizone in dilute acid medium (*e.g.*, *p*H 2), but if either dithizonate has once been formed (in basic solution) it is not readily decomposed by dilute acids. The behavior of cobalt and nickel dithizonates in this respect is similar to the behavior of the sulfides. Cobalt dithizonate is more resistant than nickel dithizonate to the action of acids.

TABLE 14. THE DITHIZONATES[a]

K = keto *E* = enol *S* = soluble *I* = insoluble

Metal	Complex	Color (CCl_4)	Solubility in CCl_4 or $CHCl_3$	*p*H for extraction	Remarks
Bismuth	*K*	Orange-yellow	*S*	>2(CCl_4)	
	E	Orange-red	*S*	Basic soln.	See Reith and van Dijk, *Chem. Weekblad*, **36**, 343 (1939). Also reacts in presence of KCN (*p*H 7–8).
Cadmium	*K*	Red	*S*	Basic soln.	Stable when shaken with 1 *N* NaOH.
Cobalt	*K*	Violet	*S*	7–9 (optimum in CCl_4)	Organic soln. of dithizonate quite stable to dilute mineral acids.
	E?	Brownish	*S*	Strongly basic soln.	May be decomposition product.
Copper (I)	*K*	Violet	*S*	Dil. mineral acid soln. (*ca.* 0.1 *N*)	
(I)	*E*	Red-brown	*S*	Basic soln.	Only slightly soluble in CCl_4.
(II)	*K*	Violet-red	*S*	Dil. mineral acid soln.	
(II)	*E*	Yellow-brown	*S*	Basic soln.	Can also be formed in slightly acid soln. when copper is in excess of D_2.
Gold		Yellow	*S*($CHCl_3$)	Dil. mineral acid soln.	Red color first appears on shaking; this quickly changes to orange and then to yellow. Flocs in CCl_4. Au (III) probably reduced to Au (I).
Indium		Red	*S*	5–6 (CCl_4); 8.3–9.6($CHCl_3$)	Also reacts in presence of cyanide.
Iron (II)		Violet-red	*S*	6–7 (CCl_4)	Fe (III) does not form a complex but oxidizes D_2 in basic medium, especially in presence of cyanide.
Lead	*K*	Cinnabar red	*S*	8.5–11 (optimum in $CHCl_3$)	Cyanide does not prevent reaction.
Manganese		Violet-brown ($CHCl_3$)	*S*($CHCl_3$)	*ca.* 11	Solution very unstable. Brown flocs in CCl_4.
Mercury (I)	*K*	Orange	*S*	Dil. mineral acid soln.	
(I)	*E*	Purplish red	*S*	Basic medium	
(II)	*K*	Orange-yellow	*S*	Dil. mineral acid soln.	Can also be formed in weakly alkaline solution with an excess of D_2. Light sensitive.
(II)	*E*	Purplish red	*S*	Basic medium	Can also be formed in slightly acid solution with a deficiency of D_2.
Nickel		Brownish	*S*	Weakly basic medium	CCl_4 solution not easily decomposed by dilute mineral acids. From a strongly basic solution, CCl_4 extract is gray.
Palladium	*E*?	Brown-red ($CHCl_3$)	*S*($CHCl_3$)	Dil. mineral acid soln.	Partly soluble in CCl_4 (dark violet). Reaction is slow.
	K	Brownish green ($CHCl_3$)	*S*($CHCl_3$)		By addition of D_2 to solution of enol compound. Stable toward 6 *N* NaOH and 6 *N* H_2SO_4.

[a] Based on data of H. Fischer and others. *K* and *E* in table are used in sense of monobasic and dibasic (1:2 and 1:1 divalent metal salts).

TABLE 14—(*Continued*)

Metal	Complex	Color (CCl_4)	Solubility in CCl_4 or $CHCl_3$	*p*H for extraction	Remarks
Platinum (II)		Violet or violet-red aqueous layer; green CCl_4		Weakly acid solution	Probably a colloidal solution; sometimes violet flocs are obtained (insoluble in $CHCl_3$). Pt (IV) does not react; neither do other Pt metals in quadrivalent or trivalent state.
Silver	*K*	Yellow	*S*	Dil. mineral acid soln.	
	E	Red-violet	*I*	Basic soln.	Slightly soluble in $CHCl_3$ (red solution).
Thallium (I)	*K*?	Red	*S*	9–12 (CCl_4)	Also formed in presence of cyanide.
(III)	*K*?	Yellowish red	*S*	3–4 (CCl_4)	Reaction not complete. Tl (III) also oxidises D_2.
Tin (II)	*K*	Red	*S*	>4 (optimum 6–9 in CCl_4)	Not stable.
Zinc	*K*	Purplish red	*S*	Neutral or weakly basic soln. (optimum 8.3 in citrate buffer with $CHCl_3$).	With an excess of D_2 extraction can be made complete in weakly acid medium. Thiosulfate does not prevent reaction.

with a chloroform solution of dithizone.[9] The ratio $[ZnDz'_2]_o/[Zn^{++}]_w$ was varied from 0.3 to 27 at *p*H 3.97 and K was found to remain sensibly constant and equal to 3.2. At *p*H 3.05 the value of K was found to be 4.5 (the activity coefficient of the zinc ion was not taken into account).[10] It is worth noting that a *p*H change of one unit alters the value of the ratio $[MeDz'_2]_o/[Me^{++}]_w$ one-hundred fold.

Equation (4) may be derived on the basis of the following considerations. In the aqueous phase there is an equilibrium between metal ions, dithizonate ions (monovalent), and the metal dithizonate:

$$MeDz'_2 \rightleftharpoons Me^{++} + 2\,Dz'^{-}.$$

The equilibrium constant for this reaction will be denoted by K_m (the subscript m referring to the metal dithizonate):

$$\frac{[Me^{++}]_w[Dz'^{-}]_w^2}{[MeDz'_2]_w} = K_m. \tag{6}$$

[9] I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.*, **63**, 1906 (1941).

[10] From data given by K. Buch, *Finska Kemistsamfundets Medd.*, **53**, 25 (1944), K, as defined above, for zinc dithizonate in carbon tetrachloride can be calculated to have the value 4. An acetate buffer was used. The approximate agreement in constants for carbon tetrachloride and chloroform is unexpected and further work will probably show that they are actually considerably different. So far as known, the optimum *p*H range for extraction of all metals with a chloroform solution of dithizone is higher than the range for a carbon tetrachloride solution.

The metal dithizonate partitions between the aqueous and organic solvent phases:

$$(MeDz_2')_w \rightleftharpoons (MeDz_2')_o$$

$$\frac{[MeDz_2']_o}{[MeDz_2']_w} = P_m. \tag{7}$$

Dividing (7) by (6):

$$\frac{[MeDz_2']_o}{[Me^{++}]_w} = \frac{P_m}{K_m}[Dz'^-]_w^2. \tag{8}$$

The value of $[Dz'^-]_w$ in terms of $[Dz]_o$ and $[H^+]$ is (equation 3):

$$[Dz'^-]_w = \frac{K_d[Dz]_o}{P_d[H^+]_w} = \frac{[Dz]_o}{F[H^+]_w}. \tag{9}$$

From (8) and (9) we obtain the final expression:

$$\frac{[MeDz_2']_o}{[Me^{++}]_w} = \frac{P_m}{K_m F^2}\frac{[Dz]_o^2}{[H^+]_w^2} = K\frac{[Dz]_o^2}{[H^+]_w^2}. \tag{10}$$

If the *p*H of the aqueous solution is such that the metal ion is more or less completely hydrolyzed, the expression for the extractability of the metal becomes

$$\frac{[MeDz_2']_o}{[Me]_w} = K\frac{[Dz]_o^2}{\{[H^+]_w^2 + K_{1_{hyd.}}[H^+]_w + K_{2_{hyd.}}\}} \tag{11}$$

where $[Me]_w = [Me^{++}] + [MeOH^+] + [Me(OH)_2]$

$$K_{1_{hyd.}} = \frac{[MeOH^+][H^+]}{[Me^{++}]}$$

$$K_{2_{hyd.}} = \frac{[Me(OH)_2][H^+]^2}{[Me^{++}]}$$

This equation has not been tested experimentally. If the metal hydroxide has amphoteric properties and reacts with hydroxyl ions to form metalate ions another expression must be derived.

The equilibrium constants of copper and silver dithizonates have been determined roughly. Preliminary work has given a value of approximately 10^{10} for the constant of cupric keto dithizonate in carbon tetrachloride. The determination was made in 1 *M* hydrochloric acid and the hydrogen-ion concentration in the equation was set equal to unity. This value may be compared with that of Buch (*loc. cit.*) who found approximately 5×10^8, as calculated from his data. For silver dithizonate a value of the order 10^7 has been obtained for

$$K = \frac{[AgDz']_{CCl_4}}{[Ag^+]_w}\frac{[H^+]_w}{[Dz]_{CCl}}$$

from a determination in 6 N sulfuric acid. The constants for the other metal dithizonates are mostly unknown.[11] When they become known it will be possible to state the fraction of a metal in a solution of given pH that can be extracted by a specified volume of dithizone solution of known concentration (see, for example, p. 297). If complex-forming substances are present in the solution, the complex constant for the metal compound must also be known of course.[12] At the present time our knowledge of the extractability of various metals is chiefly qualitative. Palladium, gold, mercury, silver, and copper can be extracted in fairly acid solutions.

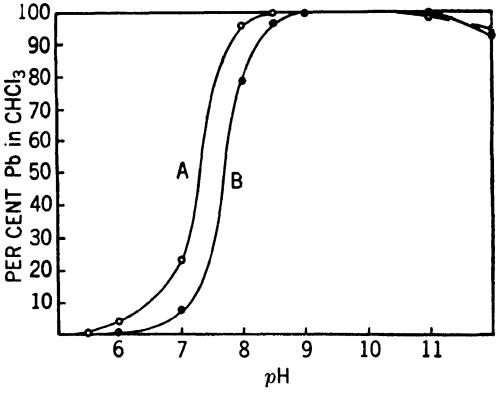


Fig. 17. Extraction of lead with dithizone. Curve A: with 50% excess dithizone, Curve B: with 25% excess dithizone. (From data of Clifford and Wichmann, *J. Assoc. Official Agr. Chem.*, **19**, 134 (1936).)

These metals react in the order given, *i.e.*, palladium can be extracted from a more acid solution than can copper, or if palladium and copper are both present in a solution of low acidity, more palladium than copper will react with a restricted amount of dithizone. Bismuth can be extracted in weakly acidic medium, while zinc, lead, and other metals require a neutral or slightly alkaline solution for easy extraction. A number of metals such as lead, zinc, and bismuth are less easily extracted as the pH is increased in the alkaline range. The behavior of lead[13] is illustrated in Fig. 17 which

[11] Apparently, the constants for zinc, cadmium, and lead dithizonates have been determined by A. K. Babko and A. T. Pilipenko, *J. Anal. Chem. Russ.*, **2**, 33 (1947).

[12] Any substance which combines with a metal to form a slightly dissociated complex makes it more difficult to extract the dithizonate of the metal. For this reason, the anions present in a solution may have a considerable effect on the ease of extraction. Thus cobalt is extracted more easily from an acetate solution than from a citrate solution. The effect becomes less pronounced in the most favorable pH region.

[13] P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **19**, 130 (1936). See also p. 388 of this book.

is based on figures given by Clifford and Wichmann. Some dithizonates are stable at high alkalinities (1 *N* or stronger sodium hydroxide). Among these may be mentioned the complexes of cadmium, cobalt, nickel, copper, mercury, and silver, some of which exist as the enol form under the conditions.

The greater tendency for the enol complexes to be formed in basic medium is understandable from the equilibria in aqueous solution:

$$Dz \rightleftharpoons Dz'^{-} + H^{+} \quad (1)$$

$$Dz'^{-} \rightleftharpoons Dz''^{--} + H^{+} \quad (2)$$

$$Me^{++} + 2\,Dz'^{-} \rightleftharpoons MeDz'_2 \quad (3)$$

$$Me^{++} + Dz''^{--} \rightleftharpoons MeDz'' \quad (4)$$

The lower the hydrogen-ion concentration, the greater will be the concentration of Dz''^{--} (enolate ion). Whether the enol complex will be formed in preference to the keto will depend on the value of the constants for reactions (3) and (4). If $MeDz''$ is much less dissociated than $MeDz'_2$, it may be formed in preference to the keto form, even if the concentration of Dz'^{-} in the solution is greater than that of Dz''^{--}. For metals such as lead and zinc, which are not known to form enol complexes, the tendency of reaction (4) to run from left to right must be comparatively small.

A factor which deserves mention is the rate at which equilibrium is attained in dithizone extractions. In basic or weakly acidic solutions reactions are usually very rapid. This is not always the case in more acidic solutions. At *p*H 1.4 the reaction between cupric ions and dithizone in chloroform is very slow; even after 25 minutes shaking the reaction is incomplete.[14] Under the same conditions a carbon tetrachloride solution reacts much more rapidly, provided inhibiting impurities are not present in the solvent. The reaction between zinc and dithizone in carbon tetrachloride at *p*H *ca* 5 is slowed down by the presence of thiosulfate, but the same equilibrium is said to be reached as in its absence if shaking is continued long enough (p. 619).

Various workers have reported that high electrolyte concentrations reduce the speed of reaction of metal ions with dithizone.

[14] H. Barnes, *J. Marine Biol. Assoc. United Kingdom*, **26**, 305 (1946). For some remarks on the kinetics of dithizone reactions see H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1949**, 1845. For observations on the difference in rate of extraction of cupric and mercuric dithizonates into carbon tetrachloride and chloroform, see H. Irving, G. Andrew, and E. J. Risdon, *J. Chem. Soc.*, **1949**, 541.

3. Specificity of Dithizone Reactions

Although dithizone reacts with nearly a score of metals, the reaction can be made almost or quite specific for certain metals by resorting to one or more of the following devices:

1. Adjusting the *p*H of the solution to be extracted.
2. Altering the valence of interfering metals (of minor importance).
3. Adding a complex-forming agent which will tie up other reacting metals.

Separation of metals by the adjustment of the *p*H of the sample solution can be successfully carried out only with certain combinations of metals, namely those whose dithizonates have equilibrium constants differing markedly from each other. Extraction in a fairly acid (0.1–0.5 *N*) solution serves to separate such metals as palladium, silver, mercury, and copper from other metals.[15] Lead and bismuth can be separated at *p*H 3.0 (p. 389). By making a solution strongly basic (1 *N* in sodium hydroxide) after adding citrate or tartrate to prevent precipitation of metal hydroxides, cadmium can be quantitatively extracted with a carbon tetrachloride solution of dithizone and separated from metals such as lead and zinc, but not from the noble metals, mercury, copper, cobalt, and nickel.

Instead of extracting a metal from a solution of adjusted *p*H it is sometimes preferable with a low total content of reacting metals to extract under such conditions (for example, from a faintly ammoniacal solution) that other metals also are extracted, and then to shake the separated organic solvent containing the dithizonates with dilute acid of such concentration that the desired metal either remains in the organic solvent alone, or goes into the aqueous phase while the other dithizonates remain undecomposed. Thus if a carbon tetrachloride solution containing the dithizonates of copper, zinc, and lead is shaken with one or two portions of dilute acid (0.05 *N* or even weaker), copper remains in the carbon tetrachloride, while zinc and lead go into the aqueous phase.

Since this procedure is frequently applied, it may be worth while to con-

[15] A metal such as zinc which in small quantities does not react perceptibly with dithizone in a fairly acid solution will react if present in high concentration according to the law of mass action expressed by equation 10, p. 94, so that difficulties may arise when, for example, a trace of copper is to be determined in zinc metal. In such a case a perceptible amount of zinc may be extracted with the copper. If the amount of co-extracted zinc is not too great, the carbon tetrachloride or chloroform phase containing the two dithizonates may be drawn off and shaken with dilute acid which will decompose the zinc complex, thus leaving the copper dithizonate alone in the organic solvent (see p. 98). Another difficulty in a case of this kind may be the practical impossibility of the initial extraction of the trace metal on account of the reaction of most of the dithizone with the other metal present in much higher concentration.

sider how sharply separations of metals can be made in this way. As an illustration, we may take the case of two divalent metals whose dithizonates have the equilibrium constants 10^{10} (metal L) and 100 (metal M).[16] Suppose that the metals are extracted with a 4×10^{-4} M (approximately 0.01 per cent weight by volume) solution of dithizone in an organic solvent, and the resulting solution of dithizonates is shaken with an equal volume of 0.01 N hydrochloric acid. First let us find the extent of dissociation of a pure 2×10^{-4} M solution of LDz_2', containing no excess dithizone, under these conditions. It will be assumed that the equilibrium may be expressed by

$$\frac{[LDz_2']_o}{[L^{++}]_w} = \frac{K[Dz]_o^2}{[H^+]_w^2}$$

o and w referring to the organic solvent and aqueous phases respectively. Since the volume of o is equal to the volume of w,

$$[Dz]_o = 2[L^{++}]_w$$

and

$$\frac{[LDz_2']_o}{[L^{++}]_w} = \frac{K \times 4[L^{++}]_w^2}{[H^+]_w^2}$$

$$[L^{++}]_w = \sqrt[3]{\frac{[LDz_2']_o[H^+]_w^2}{4K}}$$

Since the value of K is very large, the concentration of LDz_2' in the organic phase will change little on shaking with dilute acid, and it may be set equal to 2×10^{-4} M; the concentration of metal in the aqueous phase when equilibrium is established is given by

$$[L^{++}]_w = \sqrt[3]{\frac{2 \times 10^{-4} \times 10^{-4}}{4 \times 10^{10}}} = 7.9 \times 10^{-7}.$$

(Any change in $[H^+]$ is neglected.) The percentage of L going into the aqueous phase is therefore about 0.4. In any actual case, more or less free dithizone would be present and the amount of L^{++} going into the acid solution would be enormously reduced. Thus if the dithizone concentration of the organic solvent phase were 4×10^{-5} M, $[LDz_2']_o/[L^{++}]_w = 1.6 \times 10^5$. It is evident that the organic phase could be shaken successively with many fresh portions of 0.01 N acid without the loss of any significant amount of L^{++}, provided a little free dithizone is present.

To find the extent of decomposition of MDz_2' on shaking with acid, we

[16] The equilibrium constant of $CuDz_2'$ in carbon tetrachloride is of the order 10^{10} as already mentioned. The constant for $ZnDz_2'$ in chloroform is approximately 3; the value in carbon tetrachloride is probably greater.

may first assume that all of M goes into the aqueous phase, and we then find

$$\frac{[MDz'_2]_o}{[M^{++}]_w} = \frac{10^5 \times (4 \times 10^{-4})^2}{10^{-4}} = 0.16.$$

This value indicates that an appreciable amount of MDz'_2 remains in the organic solvent and that the method of successive approximations should be applied in the calculation to obtain a more exact value. The exact value of $[M^{++}]_w$ is found to be 1.78×10^{-4} *M*, which corresponds to 89 per cent decomposition of the dithizonate by acid. Evidently the organic solvent must be shaken with a fresh portion of 0.01 *N* acid in order to decompose most of MDz'_2. If again an equal volume of acid is used, $[MDz'_2]_o/[M^{++}]_w = ca.\ 0.16$, and $[M^{++}]_w = 0.19 \times 10^{-4}$. Accordingly two shakings with acid transfers (1.78 + 0.19) 100/2 or 98.5 per cent of M to the aqueous phase. In other words, L and M can be separated in this way without much difficulty. As a matter of fact, M can be separated from a metal whose dithizonate has an equilibrium constant of 10^5 provided the free dithizone concentration during the shaking with acid is fairly high. Thus if $[Dz] = 4 \times 10^{-4}$, less than 1 per cent of the metal whose dithizonate constant is 10^5 would be brought into the aqueous phase when shaken with an equal volume of 0.01 *N* acid, since the ratio of metal in organic solvent and acid will be $[10^5 \times (4 \times 10^{-4})^2]/10^{-4} = 160$. It appears then that divalent metals whose dithizonate constants differ by the factor 1000 can be separated fairly satisfactorily in the way described by the proper choice of acid and free dithizone concentration, but a bigger difference in constants is desirable. The rate of attainment of equilibrium on shaking with acid is rapid, only 1 or 2 minutes of vigorous shaking generally being required.

As we have already seen, iron, tin, and platinum do not form complexes with dithizone when present as Fe^{III}, Sn^{IV}, and Pt^{IV}.

Reagents forming stable complexes with interfering metals play an important role in dithizone procedures. It will be seen from Table 15 that the number of metals reacting with dithizone is greatly reduced in the presence of such complex forming agents as cyanide, thiocyanate, and thiosulfate. A striking example is provided by the determination of lead. The only metals reacting in slightly basic medium containing cyanide are lead, univalent thallium, divalent tin, and bismuth. Since stannic tin does not react and bismuth can be separated from lead by extraction with dithizone in slightly acid medium, the only other metal which will interfere in the lead determination is thallium; a special procedure has been worked out for the determination of lead in its presence (p. 401).

At a *p*H of approximately 5 in the presence of a sufficient quantity of

thiosulfate the only metals reacting appreciably with dithizone in carbon tetrachloride solution are zinc, stannous tin, and palladium.[17] Large amounts of nickel and cobalt will react slightly under these conditions, but can be made harmless by the addition of cyanide, which also prevents the reaction of palladium. Sodium diethyldithiocarbamate has also been used as a general complex former in the determination of zinc after removal of copper (p. 620).

Some of the complex forming agents used in dithizone procedures are listed in Table 15. Further information will be found in the chapters dealing with the individual metals.

TABLE 15

COMPLEX-FORMING AGENTS IN DITHIZONE REACTIONS

Conditions	Metals reacting
Basic solution containing cyanide	Pb, Sn^{II}, Tl^{I}, Bi
Slightly acid solution containing cyanide	Pd, Hg, Ag, Cu
Dilute acid solution containing thiocyanate	Hg, Au, Cu
Dilute acid solution containing thiocyanate + cyanide	Hg, Cu
Dilute acid solution containing bromide or iodide	Pd, Au, Cu
Slightly acid solution (*p*H 5) containing thiosulfate (CCl_4 solution of dithizone)	Pd, Sn^{II}, Zn (Cd, Co, Ni)
Slightly acid solution (*p*H 4–5) containing thiosulfate + cyanide	Sn^{II}, Zn
Citrate and tartrate in basic medium	Usually do not interfere with extraction of reacting metals (*cf.* p. 617 and p. 388)

4. Colorimetric Determination of Metals by Dithizone

Dithizone determinations can be carried out by mono- or dicolor (mixed color) methods. In the mono-color method, the aqueous solution after adjustment to the proper *p*H is shaken with successive portions of a carbon tetrachloride or chloroform solution of dithizone until it can be seen from the unchanged green color of the last portion that all of the metal has been extracted. The combined extracts are then shaken with a very dilute solution of a base, such as ammonium hydroxide, to remove excess dithizone. This step involves a source of error: if the alkalinity of the wash solution is too high some of the metal dithizonate may be decomposed, or if the alkalinity is not high enough, an appreciable amount of

[17] H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **107**, 241 (1936). In 2 per cent (*v/v*) sulfuric acid solution, thiosulfate prevents the reaction of mercury but not that of copper, so that the two metals can be separated under these conditions.

free dithizone may be left in the organic solvent. It is easier to remove dithizone from a carbon tetrachloride solution than from a chloroform solution. For 1:200 ammonium hydroxide, Clifford and Wichmann[18] found the distribution ratios to have the following values:

$$\frac{[Dz'^-]_{NH_4OH}}{[Dz]_{CCl_4}} = 41\ (31\,^\circ C.) \text{ and } \frac{[Dz'^-]_{NH_4OH}}{[Dz]_{CHCl_3}} = 1.6\ (30\,^\circ C.)$$

At *p*H 10 the respective ratios are 19.4 and 0.76. Dithizone can be extracted from a carbon tetrachloride solution, but hardly at all from a chloroform solution, by an aqueous solution of *p*H 8. Offsetting the ease of removal of dithizone from carbon tetrachloride is the greater ease of dissociation of dithizonates in carbon tetrachloride than in chloroform when the organic solvent is shaken with an aqueous basic solution. The magnitude of the error when carbon tetrachloride is the solvent is illustrated by some figures given by Clifford and Wichmann. Twenty-five ml. of carbon tetrachloride containing lead dithizonate equivalent to 35.8 γ of lead lost 6.4 γ when shaken for 1 minute with 25 ml. of 1:200 ammonia; and when shaken for 10 minutes it lost 10.8 γ (partial precipitation of lead in the aqueous phase). Another objection to the mono-color technique is the possibility of transformation of the keto complexes of certain metals into the enol complexes on washing with an alkaline aqueous solution. Thus it is hardly possible to wash all the dithizone out of a carbon tetrachloride solution of keto copper dithizonate without forming some of the enol compound, as is made evident by a slight change in the hue of the originally violet solution (the enol dithizonate is brown). Mono-color methods in which all of the excess dithizone must be removed from the organic solvent phase are not sound in principle. It is true that with some metals good results can be obtained, especially if the comparison solution is prepared under identical conditions, but the mixed color method is much to be preferred. If a photometer is available, the mono-color method need rarely be used.

In the so-called mixed-color method, the excess dithizone is allowed to remain in the organic solvent with the dithizonate. In visual work the hue of the solution is compared with a series of standards, all prepared with the same amount of dithizone as the sample solution. The standards exhibit a series of hues ranging from the unchanged green of the dithizone to the color of the metal dithizonate alone, if the *p*H is such that most of the dithizone remains in the organic solvent. The comparison is conveniently made in glass-stoppered tubes (p. 52), and the organic solvent layers are examined transversely against a white background. The dithizone solution should not be stronger than 0.001 per cent *w/v*, else

[18] P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, 19, 130 (1936).

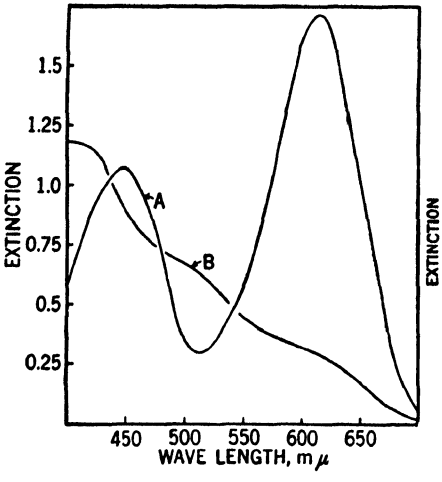


Fig. 18. Absorption curves of (*A*) dithizone, and (*B*) its oxidation product, both in carbon tetrachloride solution. (According to Fischer and Weyl, *Wiss. Veröffentl. Siemens-Konzern*, **14**, No. 2, 41 (1935).)

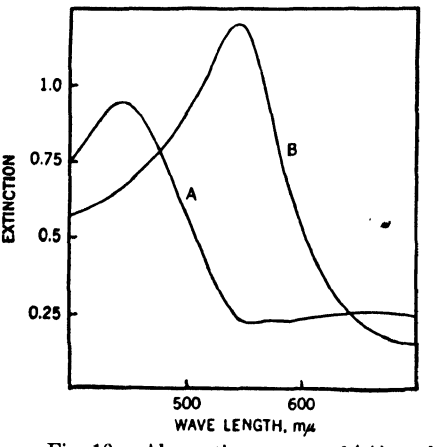


Fig. 19. Absorption curves of (*A*) enol, and (*B*) keto cupric dithizonate in carbon tetrachloride. (Fischer and Weyl.)

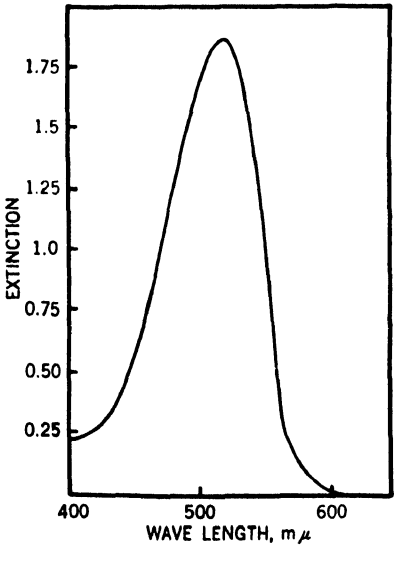


Fig. 20. Absorption curve of lead dithizonate in carbon tetrachloride. (Fischer and Weyl.)

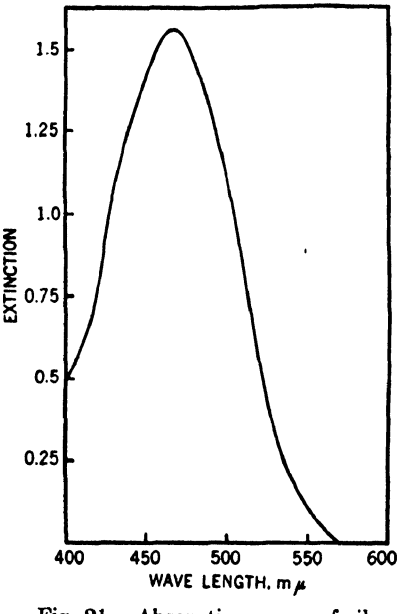


Fig. 21. Absorption curve of silver keto dithizonate in carbon tetrachloride. (Fischer and Weyl.)

the solutions will be too strongly colored for comparison at a depth of 1–2 cm. If the approximate amount of the metal is not known, the dithizone solution is added in small portions from a buret with shaking after each addition until a suitable mixed color is obtained.[19] A carbon tetrachloride or chloroform solution containing somewhere near equal amounts of dithizone and dithizonate gives the most satisfactory hue for precise comparison. A grayish mixed color is then obtained with red or violet-red dithizonates, and the eye can detect differences of about 3 per cent in the metal concentration.

When a spectrophotometer is used in determining a metal by the mixed color method there are usually two possibilities in the choice of a wave length. One may measure the absorption of light by the metal complex or by the excess of dithizone remaining after the reaction is completed. In carbon tetrachloride, the approximate wave lengths (mμ) of maximum absorption by dithizone and keto dithizonates of some metals (Figs. 18–21) are the following according to H. Fischer and others:

Dithizone	620, 450 (secondary)
Bismuth	500
Cadmium	520
Copper (II)	545
Indium	510
Lead	525
Mercury (II)	530
Silver	460
Zinc	535

It will be seen from Fig. 18 that there is a minimum in the absorption curve of dithizone at about 510 mμ, or close to the wave length of maximum absorption of the dithizonates of most of the metals listed above. On the other hand most of these dithizonates in carbon tetrachloride solution absorb very little light above 600 mμ, whereas the strongest absorption is shown by dithizone at approximately 620 mμ. Therefore by using light of a wave length in the neighborhood of 620 mμ, or a suitable red filter, high sensitivity can be obtained in mixed color methods. When the reaction must be carried out in a basic medium at a *p*H at which some of the dithizone goes into the aqueous phase, it is usually better to measure the absorption of the metal complex instead of that of the residual dithizone.

Since both dithizone and the dithizonates of copper, zinc, lead, etc. obey Beer's law in carbon tetrachloride or chloroform, a plot of the extinction

[19] If the reaction between metal and dithizone proceeds sufficiently rapidly the colorimetric titration technique can be applied, *i.e.*, a standard solution of the metal is added to a solution of the same *p*H as the unknown and containing the same volume of dithizone, until after thorough shaking the hues of the organic solvents match.

of a dithizone–dithizonate solution against the metal concentration in the organic solvent gives a straight line, provided the light is "monochromatic." When a filter is used, deviation from linearity may occur (see, for example, Fig. 51). If a sufficient excess of dithizone is present in the mixture, the extinction will be proportional to the amount of the metal originally present in the aqueous phase. When the excess of dithizone becomes very small, dissociation of the dithizonate may be sufficiently great to cause failure of this relation.

There is another possibility in the photometry of a mixed solution of metal dithizonate and free dithizone. The transmittancy of the solution may be measured at two suitable wave lengths, namely one at which dithizone absorbs strongly and the dithizonate as little as possible, and another at which the reverse is true. The advantage of this method lies in the possibility of using dithizone solutions whose exact strengths need not be known, *i.e.*, it is not necessary to prepare a new standard curve every time a new batch of reagent solution is made up. The metal concentration is calculated from the extinction values at the two wave lengths and the previously determined extinction coefficients of dithizone and the metal dithizonate at these two wave lengths. There must be a linear relation between metal concentration and extinction (which is not always the case when filters are used) if the usual formula (p. 70) is to be applied. Formation of the oxidation product of dithizone may lead to error so that decomposition of the dithizone solution on standing must be guarded against. This method has been applied in the determination of copper, lead, and mercury.

A newly proposed procedure for the determination of metals with dithizone (and other organic reagents giving colored complexes) is based on the principle of reversion, *i.e.*, on the change in optical density of a mixture of free dithizone and a metal dithizonate in an organic solvent produced by the addition of a substance which forms a stable complex compound with the metal and thus liberates an equivalent amount of dithizone.[20] A plot of the increase in extinction at *ca.* 600 mμ (where dithizone absorbs strongly and most dithizonates only slightly) against the concentration of metal will generally give a straight line. An advantage of this procedure is that the dithizone solution need not be of known or constant strength. Mineral acid can be used as reversion reagent for lead and bismuth dithizonates; iodide and acid can be used for silver and mercury. 2,3-Dimercaptopropanol is a general reversion agent for dithizonates over a wide *p*H range.

It may be pointed out that when one works in alkaline medium it may be possible to raise the *p*H to a point where the excess dithizone will be

[20] H. Irving, E. J. Risdon, and G. Andrew, *J. Chem. Soc.*, 1949, 537.

transferred virtually completely to the aqueous phase. The method then becomes similar to a mono-color method. Thus it is possible to extract lead practically completely from an aqueous medium of *p*H 11 without extracting an appreciable amount of dithizone when chloroform is used as solvent (p. 393). Such a procedure is advantageous whenever it can be applied.

A metal frequently cannot be determined directly with dithizone in the solution of the sample: oxidizing agents attacking dithizone to a greater or less extent may be present, it may be difficult to adjust the acidity of the solution to the exact value required, and there may be interference from other heavy metals or even neutral salts. When such conditions exist, a preliminary extraction with dithizone (0.01 per cent w/v) is made to separate completely the metal in question. The dithizonate in the organic solvent layer may next be decomposed and the metal converted into ionic form for final determination in a number of ways:

1. The dithizonates of lead, zinc, cadmium, and thallium are readily decomposed and the metal transferred to the aqueous phase when the organic solvent is shaken with dilute acid.[21] As we have already seen, this procedure provides a separation from such metals as copper whose dithizonates are not appreciably attacked by dilute acids.

2. The organic solvent phase may be evaporated to dryness and the dithizonate residue may be heated with a few drops of concentrated sulfuric acid and perchloric acid to destroy organic matter completely. This method may be used for copper and other metals forming dithizonates not decomposed by dilute acids.

3. The organic solvent may be shaken with an acid solution of a strong oxidizing agent such as potassium permanganate, ceric sulfate, or bromine to destroy the dithizonate radical or any free dithizone (conversion to the diazone and also other oxidation products). The metal enters the aqueous phase and the excess of the oxidizing agent can be destroyed by a suitable reducing agent such as hydroxylamine hydrochloride. This procedure has been used to decompose mercuric dithizonate, which cannot be treated by either of the two preceding methods.

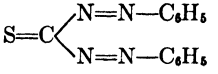
4. The organic solvent solution of the dithizonate may be shaken with an aqueous solution of a reagent forming a stable complex with the metal. This method has been applied in decomposing silver and mercuric dithizonates. Before the metal in the aqueous layer can be determined with dithizone, the complex must be destroyed or at least made much weaker

[21] Zinc and cadmium dithizonates in carbon tetrachloride or chloroform may be decomposed with 0.01–0.02 *N* hydrochloric acid (p. 617). Lead dithizonate is decomposed at even lower acidities.

compared to the dithizone complex by a change in conditions, *e.g.*, in the acidity (see p. 442 for an example).

5. Oxidation of Dithizone

Dithizone is oxidized to diphenylthiocarbodiazone



under weak oxidizing conditions.[22] This compound is insoluble in acid and basic aqueous solutions, but it dissolves in chloroform and carbon tetrachloride to give a yellow or brown solution. It does not react with metals. This oxidation product is sometimes present in commercial dithizone and the purification of the reagent is based on the insolubility of the thiocarbodiazone in ammonia (see below).

Ferric iron oxidizes dithizone, especially in basic solution (containing citrate or tartrate).[23] The oxidation by iron is very pronounced in alkaline cyanide solutions. Copper in basic cyanide solutions also oxidizes the reagent; the extent of oxidation appears to depend on the excess of cyanide, being less when the excess is small. Low concentrations of the halogens, nitrous acid, permanganate, etc. produce the yellow or brown oxidation product at least in part. Under strong oxidizing conditions dithizone is decomposed, the sulfur of the compound being attacked and a splitting of the molecule occurring. If dithizone has been oxidized only as far as to diphenylthiocarbodiazone, regeneration of the dithizone can be effected by the action of reducing agents such as hydroxylamine hydrochloride and sulfur dioxide.

Oxidation of dithizone by ferric iron and other oxidizing agents naturally leads to difficulties in quantitative work and even in qualitative (confusion

[22] H. Fischer, *Angew. Chem.*, **50**, 919 (1937); E. Fischer, *Ann.*, **212**, 316 (1882). Irving and coworkers (reference in footnote 7) have made some observations on the decomposition of dithizone in alkaline aqueous medium. They found that a solution in 1.5 *N* ammonium hydroxide decreased in concentration by 20 to 30 per cent per hour at room temperature. The rate was not much affected by light or oxygen. In 0.15 *N* ammonia the decomposition was found to be very slow. Hydrolysis or a base-catalyzed dismutation is suggested as a possible cause of the decomposition.

[23] E. C. Dawson, *Analyst*, **73**, 618 (1948), reports that ferrous and ferric iron react with dithizone in an organic solvent at a *p*H of about 9 to give a yellow compound which is believed not to be a dithizonate. The compound dissolves in acids with some loss in color. It is not affected by sulfur dioxide or hydrogen peroxide; its iron content is about 15 per cent. The iron is thought to be present in the ferrous state. Dawson believes that this previously undescribed compound (and not the diazone) is largely formed when ferric iron reacts with dithizone in basic medium.

of the yellow color produced with that given by mercury and silver dithizonates). The oxidation can in large measure be prevented by adding hydroxylamine hydrochloride to the aqueous solution to be extracted. A preliminary extraction of the metal will often be necessary in practical work in order that difficulties due to oxidizing agents may be avoided.

6. Purification of Dithizone. Stability of Dithizone Solutions

Purification of dithizone is not always necessary. Some of the products sold are fairly pure.[24] If a 0.01 per cent solution in carbon tetrachloride yields a carbon tetrachloride layer that is colored only a faint yellow after shaking with dilute (1:100) metal-free ammonia, the product may ordinarily be used as it is. The presence of a small amount of the yellow oxidation product in dithizone is usually of no importance. Only when minute traces of such metals as lead and cadmium are determined by extraction from a fairly basic solution is the yellow color of the carbodiazone likely to prove disturbing. When purification is deemed desirable one may proceed as follows. One-half gram of dithizone is dissolved in 50 ml. of chloroform and the solution is filtered through a coarse fritted glass crucible to remove any insoluble material. The solution is shaken in a separatory funnel with 4 successive portions of pure 1:100 ammonia, each 50 to 75 ml. in volume. The aqueous extracts are separated from the chloroform and filtered through a small plug of cotton to remove droplets of chloroform. The ammoniacal solution is made slightly acid with pure hydrochloric acid[25] to precipitate dithizone, which is extracted with 2 or 3 portions of chloroform each having a volume of 15–20 ml., and the combined chloroform extracts are shaken twice with an equal volume of pure water. The chloroform solution is delivered into a beaker and the chloroform evaporated off at 50° C. The product may be dried in a desiccator.

A simpler and more rapid purification procedure than that just described involves crystallization from chloroform. An almost saturated, filtered solution of dithizone in chloroform is evaporated at about 40 °C. in a stream of filtered air until $^1/_3$ to $^1/_2$ of the dithizone has crystallized out. The precipitate is collected in a sintered-glass filter crucible, washed with a few small portions of carbon tetrachloride, and air-dried. An Eastman product of 94 per cent purity (as determined by silver nitrate titration) yielded a 98 per cent material by this purification procedure. The deficit

[24] The dithizone content of a product can be found by preparing a solution of known concentration and extractively titrating a standard silver nitrate solution with it.

[25] A strong solution of sulfur dioxide in water can be used in place of hydrochloric acid and would seem to be preferable, since it should prevent the formation of any diazone in the operations. Its use is recommended by H. Barnes, *Analyst*, **72**, 469 (1947).

of 2 per cent is at least in part accounted for by the presence of water. None of the yellow oxidation product was present.

Both chloroform and carbon tetrachloride solutions of dithizone decompose rapidly with formation of the carbodiazone if exposed to strong light and subjected to relatively high temperatures. High temperatures, such as exist in many laboratories during the summer months, have a greater effect than diffuse light. Direct sunlight bleaches dithizone solutions rapidly. Clifford[26] states that sunlight acts on the solvent (chloroform), rather than on the reagent directly, to yield decomposition products such as phosgene which then oxidize the dithizone.

In order to prepare a stable dithizone solution it is necessary to use chloroform and carbon tetrachloride free from oxidizing substances. Clifford[26] recommends the procedure of Biddle[27] for the purification of chloroform. This procedure may be used both for the recovery of chloroform from used dithizone solutions, and for improving the quality of U.S.P. chloroform. It is carried out as follows. The chloroform, separated from any aqueous phase, is washed until colorless with commercial sulfuric acid equal to 5 or 10 per cent of its volume, and is then treated with lime to remove sulfuric acid. The chloroform is distilled slowly in the presence of a little lime, and alcohol is added to the distillate to the extent of 1.0–1.5 per cent of its volume.[28] The alcohol acts as a preservative, and Clifford has shown that it is more effective as such if it is freshly distilled from potassium hydroxide, instead of being added as the ordinary 95 per cent material. It is advisable to add the calculated amount of alcohol to the receiver before the distillation is begun, and to swirl the contents of the receiver during distillation so as to mix the alcohol and chloroform. The distillation should be carried out in an all-glass apparatus, and heating should be done with a water bath.

Dithizone solutions prepared from chloroform thus purified are quite stable if stored at 40° F. in the dark. A chloroform solution containing 4 mg. of dithizone per liter lost 5 per cent in strength after 6½ months storage under these conditions (Clifford). Overlaying a chloroform-dithizone solution with an aqueous solution of sulfur dioxide or hydroxylamine hydrochloride does not increase the stability of the solution.

Carbon tetrachloride is purified in the same manner as chloroform except that alcohol is not added as a preservative. Contrary to the behavior of chloroform solutions, carbon tetrachloride dithizone solutions are stabilized by covering with a 0.1 *M* solution of sulfur dioxide[28] in water

[26] P. A. Clifford, *J. Assoc. Official Agr. Chem.*, **21**, 695 (1938).

[27] D. A. Biddle, *Ind. Eng. Chem., Anal. Ed.*, **8**, 99 (1936).

[28] In reclaiming chloroform which has been treated with alcohol, additional alcohol should not be added.

having about one-tenth the volume of the organic solvent.[29] A carbon tetrachloride solution of dithizone so protected showed no appreciable change in strength after being kept for 9 months at 40° F. in the dark (Clifford). Two weeks should be allowed to elapse after preparation of the solution and before it is used. It may then be considered to have reached a constant strength (reduction of any diphenylthiocarbodiazone present). Carbon tetrachloride solutions protected by sulfurous acid may be used for the determination of lead and zinc but naturally not for metals that are easily reduced.

It may not always be worth while to go to all the trouble mentioned above in purifying carbon tetrachloride and chloroform and preparing the solutions. In much work with dithizone it suffices to make up a 0.01 per cent stock solution in *analytical reagent* carbon tetrachloride. This solution will show but little change for weeks if kept cool and in the dark. It may be used to prepare the 0.001 per cent *w/v* dithizone solution commonly used in the final determinations. The more dilute solution may be made up in sufficient quantity to last for a few days. It will usually show a progressive loss in strength, but this is immaterial if its strength is checked at the time the photometric determinations are made. The time required to check one or two points on the standard curve may be less than that required to redistil the organic solvents to obtain a more stable solution, which also will have to be checked at intervals for assurance.

The purity of the organic solvent is of greater importance when dithizone is used in an acid solution than when it is used in slightly basic medium.[30] It has been found that some carbon tetrachloride (not reagent quality) contains a substance, probably a sulfur compound, which markedly inhibits the reaction of dithizone with copper in 0.1 *N* mineral acid solution. Only analytical-grade carbon tetrachloride should be used for making up dithizone solutions to be employed in the determination of copper and other metals in acid medium. Methods for the purification of impure carbon tetrachloride have not been studied adequately as yet. Analytical-grade carbon tetrachloride of various manufacturers has been found to show appreciable differences in quality.

[29] H. Fischer and G. Leopoldi, *Z. anal. Chem.*, 119, 168 (1940), found a weakly acid solution of hydroxylamine hydrochloride to be slightly better than sulfurous acid for stabilizing a carbon tetrachloride solution of dithizone (*cf.* p. 401), whereas Clifford found the reverse to be true.

[30] Some brands of carbon tetrachloride, even though labeled reagent grade, are reported to give very unstable solutions of cadmium dithizonate when the extraction is made from 5 per cent sodium hydroxide solution (p. 229). Such products must be purified by the Biddle procedure, or by refluxing with 5 per cent sodium hydroxide (A. K. Klein).

7. *Errors in Dithizone Methods*

The following are some important possible sources of error in the determination of metals by dithizone which the trace analyst must always bear in mind:

1. Interference from other reacting metals.
2. Incomplete extraction of the dithizonate in a preliminary separation.
3. a. Decomposition of the dithizonate in an organic solvent on washing with an alkaline solution.
   b. Incomplete removal of free dithizone from the organic solvent in a mono-color method.
4. Separation of solid dithizonate because of low solubility in the organic solvent (may occur with carbon tetrachloride).
5. Oxidation of dithizone.
6. Adsorption (or coprecipitation) by precipitates in the solution to be extracted.
7. Instability of standard dithizone solutions and also of dithizonates.
8. Heavy metals in reagents and distilled water.

Some of these errors (3a and b) have already been considered in the previous discussion, and it has been shown that interference from other metals can be prevented in many cases by the proper adjustment of the acidity and the use of complex forming agents. Such measures do not always succeed, however, if large quantities of foreign metals are present and the analyst must always be on his guard against the possible interference of other metals. This source of error is considered further under the respective metals.

Error (2) is easily avoided by extracting the solution at the proper acidity with an excess of dithizone and shaking for a sufficient length of time; by using a sufficient number of portions of dithizone in the extraction, the quantity of metal in the aqueous phase can usually be reduced to insignificant proportions. It has been noticed that certain metals hinder the extraction of dithizonates. Thus it has been found that relatively small amounts of titanium (5 mg. and more in a volume not specified) prevent the complete extraction of lead from an ammoniacal citrate medium (*p*H varied from 7 to 11).[31] A comparatively high concentration of aluminum under the same conditions makes the extraction of lead difficult, and a larger number of portions of dithizone is then required for quantitative extraction. Preliminary isolation of lead as sulfide is to be recommended in these cases. H. Fischer noted that aluminum prevented the complete extraction of zinc in a faintly acid solution. The effect of titanium and

[31] J. Schultz and M. A. Goldberg, *Ind. Eng. Chem., Anal. Ed.*, **15**, 155 (1943).

aluminum may possibly be due to a hydrolysis which results in the formation of a colloidal dispersion having strong adsorptive properties (point 6 above).

The solubility of dithizonates in carbon tetrachloride is not great, and if the metal or dithizone concentration is high the dithizonate may be precipitated.[32] It then forms flocs in the organic solvent or gathers as a scum at the interface of the two liquids, and losses can then occur in the separation of the carbon tetrachloride and in washing. This error can be avoided by working with smaller amounts of metal. In general the accuracy of a dithizone procedure is not increased by working with large amounts of metal. For example, results with 10 γ of a metal are as accurate as with 100 γ, and can as a matter of fact be obtained more conveniently and more rapidly because of the smaller volumes involved. If for any reason it should be necessary to extract a large amount of a metal ($> 100\ \gamma$), a chloroform dithizone solution is preferable to a carbon tetrachloride solution because of the greater solubility of dithizonates in the former. The comparative advantages of carbon tetrachloride and chloroform solutions on other grounds were considered in the last section. Unless chloroform has special advantages, carbon tetrachloride is preferred as a solvent because of its lesser volatility, greater density, and lower solubility in water.

The formation of a precipitate or a turbidity in an aqueous solution to be extracted with dithizone must be regarded with suspicion. Thus solutions of samples high in phosphorus (biological material) may give a precipitate of calcium phosphate on addition of ammonia, even if citrate is present, and such a precipitate will carry down the greater part of the lead in the solution. Metastannic acid will also retain lead.

Since dithizone solutions are not very stable, standard curves for use in photometry with a particular solution should be checked at frequent intervals. Dithizonate solutions should not be allowed to stand for any length of time before their transmittancy is determined and they should be protected from strong light.[33] Dithizonates extracted from strongly basic medium are sometimes quite unstable and the color fades fairly rapidly. In the standard series method it is preferable to prepare the standards at the same time that the sample is treated.

[32] For example, the solubility of cadmium dithizonate in carbon tetrachloride corresponds to about 1.2 γ of cadmium per milliliter according to Klein and Wichmann.

[33] Mercuric dithizonate (keto) shows a peculiar behavior when exposed to strong light. The yellow-orange color of the organic solvent changes to green; the color change is reversed when the solution is placed in darkness or in subdued light. The light sources in some photometers are sufficiently intense to cause a fairly rapid change in the transmittancy of the solution, and readings must be made without delay. Recently it has been found that the color can be stabilized by adding acetic acid to the aqueous solution before extracting (p. 445).

The extinction coefficient of at least some metal dithizonate solutions is a function of the temperature. Thus it has been found that the extinction values of zinc dithizonate in carbon tetrachloride decrease approximately 0.5 per cent for a 1° C. rise in temperature in the range of 20° to 25°.[34]

Reagents for use in dithizone methods should be purified by appropriate methods (p. 16). Redistilled water and ammonia must be used. Redistilled acids are desirable but usually not necessary. Weakly basic and neutral solutions can frequently be freed from reacting heavy metals by extracting them with dithizone. The glassware employed should be of Pyrex (see p. 14). Vessels should be rinsed with dilute acid before use. Blanks must always be run.

II. Di-β-naphthylthiocarbazone

This reagent is similar in its properties to dithizone; it reacts with the same heavy metals to give strongly colored complexes soluble in chloroform and carbon tetrachloride. A marked difference between the two lies in the impossibility of transferring the naphthylthiocarbazone from chloroform to an ammoniacal aqueous solution by shaking the two together; it can be so transferred from a carbon tetrachloride solution, however, in which it is much less soluble than in chloroform. Certain metals, such as zinc, can be extracted readily as the naphthyl compound from aqueous solutions as alkaline as *p*H 10 or 11 (chloroform solution).

Suprunovich[35] was the first to use the naphthylthiocarbazone as an analytical reagent and claimed that the sensitivity for lead was greater than with dithizone. However, Hubbard[36] found no significant difference in the determination of lead and bismuth, and the same is likely true for other metals. Compared to dithizone and its metal complexes, the minima in the transmission curves of di-β-naphthylthiocarbazone and its compounds lie at longer wave lengths. The colors of the corresponding lead and bismuth complexes are fairly different and those of the mercury (II) salts markedly so, as shown by Hubbard.

Metal	Color with dinaphthylthiocarbazone ($CHCl_3$)	Color with dithizone ($CHCl_3$)
Hg	Red (blue shade)	Yellow-orange
Pb	Purple	Rose-red
Bi	Magenta	Orange

Procedures have been described for the determination of mercury, zinc, and cadmium in bio materials with naphthylthiocarbazone as reagent.

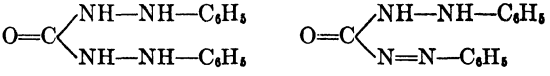
[34] G. Kortüm and B. Finckh, *Die Chemie*, **57**, 73 (1944).
[35] I. B. Suprunovich, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 839 (1938).
[36] D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, **12**, 768 (1940).

There appears to be no marked advantage in the use of this reagent in place of dithizone for the determination of mercury now that it has been discovered that the photodecomposition of mercuric dithizonate can be prevented by the addition of acetic acid. The new reagent possesses a real advantage in the determination of zinc.

Di-β-naphthylthiocarbazone in pure form is not readily obtained in good yield.[37] The commercial product available at present (1948) is of low purity. Even after one purification it contains little more than one-half its weight of the active reagent (p. 450).

Di-α-naphthylthiocarbazone, di-*p*-diphenylthiocarbazone,[38] and di-*p*-tolylthiocarbazone[39] have also been synthesized by Hubbard and Scott and transmission curves of the mercury complexes determined.

III. Diphenylcarbazide and Diphenylcarbazone



These compounds react with heavy metals such as mercury (I and II), copper, and cadmium in weakly acid solution to yield internal complex salts having blue, violet, or reddish colors.[40] The products can be extracted with benzene, chloroform, and other solvents. It appears that the reaction of diphenylcarbazide first involves its air-oxidation to diphenylcarbazone which is the active reagent in the reaction with the metals mentioned, but the exact course of the reaction is obscure. These reagents are not very suitable for the determination of any heavy metal (except chromium as chromate), although the carbazone has been used to some extent in the past for the determination of mercury; it is far inferior to dithizone for the purpose. Derivatives of diphenylcarbazide and carbazone, and also the dinaphthyl compounds, have been prepared and used qualitatively.[41]

Diphenylcarbazide is an excellent reagent for the determination of chro-

[37] The most feasible method of preparation is described by D. M. Hubbard and E. W. Scott, *J. Am. Chem. Soc.*, **65**, 2390 (1943). See also Hubbard, *loc. cit.*; M. Preund, *Ber.*, **24**, 4178 (1891). S. S. Cooper and V. K. Kofron, *Anal. Chem.*, **21**, 1135 (1949), describe the purification of naphthylthiocarbazone. The molar extinction coefficient is thought to be 67,000 in chloroform at 650 mμ.

[38] See also D. S. Tarbell and J. F. Bunnett, *J. Am. Chem. Soc.*, **69**, 263 (1947) for preparation.

[39] For the synthesis of *o*-ditolylthiocarbazone see I. B. Suprunovich and D. L. Shamshin, *Zhur. Anal. Khimii*, **1**, 198 (1946); *Chem. Abst.*, **41**, 4116. This compound is said to be more resistant to oxidation than is dithizone.

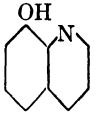
[40] F. Feigl and A. Lederer, *Monatsh.*, **45**, 63, 115 (1924).

[41] P. Krumholz and F. Hönel, *Mikrochim. Acta*, **2**, 177 (1937).

mium (VI), with which in dilute mineral acid solution it gives a soluble red-violet compound of unknown constitution.[42] Pure diphenylcarbazone does not react with chromium (VI). Molybdate also gives a red-violet color with diphenylcarbazide, but the reaction is much less sensitive than the one with chromate. Vanadate, permanganate, and ferric iron give brown colors with diphenylcarbazide and thus interfere in the determination of chromium. The chromium-diphenylcarbazide compound is not extractable by the usual organic solvents.

An indirect colorimetric method for the determination of lead is based on its precipitation as chromate or as the double chromate $K_2Pb(CrO_4)_2$ and the determination of chromate with diphenylcarbazide in the acid solution of the washed precipitate.[43]

IV. 8-Hydroxyquinoline (Oxine)



This reagent forms slightly soluble internal-complex salts with most metals. These complexes have the general formula $Me^{+n}(C_9H_6ON)_n$ (some exceptions are noted in Table 16). Determinations are usually made gravimetrically or volumetrically,[44] but colorimetric determination of metals is also possible, both directly and indirectly.

Indirect method. The indirect colorimetric determination of metals by oxine can be carried out in a number of ways after the hydroxyquinolate precipitate has been collected by filtration or centrifugation and washed free of excess oxine:

1. The oxine in the precipitate can be coupled with a diazo compound to yield a dye of strong color. Thus, Alten, Weiland, and Loofmann,[45] in the colorimetric determination of aluminum, dissolve the oxinate in a mixture of equal volumes of dilute hydrochloric acid and alcohol, add a mixture of sulfanilic acid and sodium nitrite in acetic acid, allow to stand for 10 minutes, and then make alkaline with sodium hydroxide. The yellow-red solution is compared with a standard similarly prepared.

2. Phosphotungstic, molybdotungstic, and phosphotungstomolybdic acid are reduced by oxine in basic medium and the resulting blue solution

[42] P. Cazeneuve, *Compt. rend.*, **131**, 346 (1900). See, further, p. 260.

[43] T. V. Letonoff and J. G. Reinhold, *Ind. Eng. Chem., Anal. Ed.*, **12**, 280 (1940).

[44] See the monograph of R. Berg, *Die analytische Verwendung von o-Oxychinolin (Oxin) and seiner Derivate.* 2nd ed., Enke, Stuttgart, 1938 (Vol. XXXIV in the series *Die Chemische Analyse*).

[45] F. Alten, H. Weiland, and H. Loofmann, *Angew. Chem.*, **46**, 668 (1933).

TABLE 16

SOME METAL HYDROXYQUINOLATES

Metal	*p*H range for complete precipitation[a]	Solubility in chloroform[b]
Aluminum	4.2–9.8	*S*
Antimony	>1.5	
Bismuth	4.8–10.5	*S*
Cadmium	5.4–14.6	*S*
Calcium	9.2–13	*I*
Cerium (III)	Faintly basic	
Chromium (III)	Slightly basic	
Cobalt	4.3–14.5	*S*
Copper	5.3–14.6	*S*
Gallium	—	*S*
Indium	Acetic acid-acetate	*S*
Iron (III)	2.8-*ca.* 12	*S*
Lead	8.4–12.3	*S*
Magnesium	9.4–12.7	*I* (dihydrate)
Manganese	5.9–10.0	*S*
Molybdenum[c]	3.6–7.3	*S*
Nickel	4.3–14.6	*S*
Palladium	Dilute HCl	*S*
Plutonium (VI)[d]	3.5–9	*S*
Scandium	—	*S*
Thallium (III)	Acetic acid-acetate	*S*
Thorium[e]	4.4–8.8	*S*
Titanium[f]	4.8–8.6	*S*
Tungsten[g]	5.0–5.7	*I*
Uranium[h]	5.7–9.8	*S*
Vanadium	Acetic acid-acetate	*S*
Zinc	4.6–13.4	*S*
Zirconium	Acetic acid-acetate	*S*

[a] Values for Co, Cu, Mg, Ni, W, U, and Zn from H. R. Fleck and A. M. Ward, *Analyst*, **58**, 3888 (1933); most of the others from H. Gotô, *J. Chem. Soc. Japan*, **54**, 725 (1933); **56**, 314 (1935).

[b] *S* = extracted, *I* = not extracted.

[c] Formula of hydroxyquinolate $MoO_2(C_9H_6ON)_2$.

[d] $PuO_2(C_9H_6ON)_2 \cdot C_9H_7ON$.

[e] $Th(C_9H_6ON)_4 \cdot C_9H_7ON$.

[f] $TiO(C_9H_6ON)_2$.

[g] $WO_2(C_9H_6ON)_2$.

[h] $UO_2(C_9H_6ON)_2 \cdot C_9H_7ON$.

containing tungsten or molybdenum in a lower valence can be compared with a standard obtained in the same way.[46]

3. Certain quinolate precipitates, *e.g.*, magnesium quinolate, may be dissolved in dilute acid and a ferric chloride solution added to give a green

[46] M. Teitelbaum, *Z. anal. Chem.*, **82**, 366 (1930). R. Berg, W. Wölker, and E. Skopp, *Mikrochemie* (*Emich Festschrift*), **1930**, p. 18.

solution (maximum absorption at about 650 mμ)[47]; or they may be converted into ferric quinolate which is filtered off and dissolved in alcohol (green-black color).[48]

4. The precipitate may be dissolved in dilute hydrochloric acid and the absorption of the solution measured at 365 mμ (more sensitively at 252 mμ), where 8-hydroxyquinolinium ion absorbs strongly. The usual photoelectric photometers with tungsten lamps may not have sufficient sensitivity in this region. Some photometers of this type can be used if a mercury H-4 lamp with a narrow band filter is employed, but a spectrophotometer may be preferable. Relatively small amounts of magnesium have been determined in this way.[49] The acidic solution of 8-hydroxyquinoline is stable for several days. Beer's law is followed. This is the best procedure for the indirect determination of metals by oxine when a suitable photometer is available.

By adjusting the *p*H of the solution, various separations can be made with oxine (*cf.* Table 16). Also by the addition of complex-forming agents certain separations become possible. For example, in sodium hydroxide-tartrate medium iron (III) is not precipitated whereas magnesium is precipitated. In acetic acid solution containing malonic acid, iron (III) is precipitated but not aluminum, etc. A consideration of the various separations possible lies outside the scope of this book, but these separations may be found useful in colorimetric as well as in gravimetric and volumetric oxine determinations and should be borne in mind.[50]

Oxine is generally dissolved in alcohol, acetone, or acetic acid for use as a precipitant. Certain hydroxyquinolates such as those of iron (III) and aluminum are readily soluble in organic solvents and such metals should be precipitated with an acetic acid solution of the reagent. Oxine is but slightly soluble in water and errors may arise from the precipitation of the reagent itself in certain cases, and possibility of error from this source must be taken into consideration. The use of an unregulated excess of oxine in precipitations must be avoided.

Direct method. Most of the metal hydroxyquinolates are soluble in chloroform and can be extracted by this solvent. Since the chloroform

[47] R. Wolff, *Compt. rend. soc. biol.*, **127**, 1445 (1938); L. Gerber, R. I. Claassen, and C. S. Boruff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 660 (1942); M. E. Weeks and J. R. Todd, *ibid.*, **15**, 297 (1943). The green color is due to the ion $FeOx'^{++}$.

[48] J. Lavollay, *Bull. soc. chim. biol.*, **17**, 432 (1935).

[49] H. C. Deterding and R. G. Taylor, *Ind. Eng. Chem., Anal. Ed.*, **18**, 127 (1946).

[50] For further information see W. Prodinger, *Organic Reagents Used in Quantitative Inorganic Analysis* (translated by S. Holmes), Elsevier, New York, 1940, pp. 103–112. J. F. Flagg, *Organic Reagents Used in Gravimetric and Volumetric Analysis*, Interscience, New York, 1948, pp. 157–188. G. E. F. Lundell and H. B. Knowles, *Bur. Standards J. Research*, **3**, 91 (1929).

solution is colored (ferric iron and vanadium green-black, most of the other hydroxyquinolates yellow), a direct photometric determination of metals can be based on this property; Beer's law is obeyed up to at least 10 p.p.m. of the metal complex. Moreover, some of the hydroxyquinolates, notably those of aluminum, gallium, and indium, show strong fluorescence in chloroform medium, and extremely small amounts of these metals can thus be determined. At least so far as traces are concerned, the direct determination is of much greater importance than the indirect.

A brief treatment of the theoretical basis for the isolation and separation of metals by chloroform extraction of their hydroxyquinolates seems called for.[51] Imagine a chloroform solution of 8-hydroxyquinoline to be shaken with an aqueous solution in which the metal is present in simple ionic form. There will be a distribution of hydroxyquinoline and the hydroxyquinolate between the two phases. In the aqueous solution the following relation exists (as an approximation, concentrations will be written in place of activities):

$$\frac{[Me^{+n}][Ox'^{-}]^n}{[MeOx'_n]_w} = K, \tag{1}$$

where Ox'^{-} represents the hydroxyquinolate (oxinate) ion and K is the ionization constant of the metal hydroxyquinolate. If the aqueous phase is in equilibrium with the chloroform phase, the following expression must hold:

$$\frac{[MeOx'_n]_{CHCl_3}}{[MeOx'_n]_w} = P, \tag{2}$$

where P is the partition coefficient of the metal complex between chloroform and water saturated with chloroform.[52]

Dividing (2) by (1):

$$\frac{[MeOx'_n]_{CHCl_3}}{[Me^{+n}][Ox'^{-}]^n} = \frac{P}{K} = \text{constant}. \tag{3}$$

The value of P/K is obtained by finding the respective concentrations when solid hydroxyquinolate is in equilibrium with the two phases. The numerator then represents the solubility of the complex in chloroform, the denominator the solubility product in water saturated with chloroform.

[51] See S. Lacroix, *Anal. Chim. Acta*, 1, 260 (1947), for a comprehensive treatment of the equilibria involved in the extraction of the hydroxyquinolates of aluminum, gallium, and indium.

[52] If the hydroxyquinolate forms a hydrate, complications may arise. The metal may first be extracted as the anhydrous quinolate, which gradually becomes hydrated on continued shaking and then precipitates out of the chloroform. This behavior is shown by cadmium and zinc (p. 152). Anhydrous magnesium hydroxyquinolate is believed to be soluble in chloroform, whereas the dihydrate is insoluble.

In making use of this expression to find the distribution of a metal between water and chloroform, we must first find the concentration of Ox'^- from the known amount of hydroxyquinoline added, and the known value for the partition coefficient of undissociated hydroxyquinoline between chloroform and water:

$$\frac{[Ox]_{CHCl_3}}{[Ox]_w} = 720^{53}$$

(at 18°, according to Lacroix[51]). Hydroxyquinoline is an amphoteric substance in aqueous medium:

$$Ox{\cdot}H^+ \rightleftharpoons Ox + H^+ \qquad K_1 = \frac{[Ox][H^+]}{[Ox{\cdot}H^+]} = 8 \times 10^{-6} \qquad (18°)$$

$$Ox \rightleftharpoons Ox'^- + H^+ \qquad K_2 = \frac{[Ox'^-][H^+]}{[Ox]} = 1.5 \times 10^{-10} \qquad (18°)$$

The total concentration (*i.e.*, sum of all forms) of 8-hydroxyquinoline in the aqueous phase is given by the general expression:

$$[\Sigma Ox]_w = [Ox]_w + [Ox{\cdot}H^+] + [Ox'^-]$$

$$= [Ox]_w + \frac{[H^+][Ox]_w}{K_1} + \frac{K_2[Ox]_w}{[H^+]}. \qquad (4)$$

Since $[Ox]_{CHCl_3} = 720\ [Ox]_w$, we find:

$$D_{\Sigma Ox} = \frac{720}{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}}, \qquad (5)$$

where $D_{\Sigma Ox}$ is the coefficient of distribution of hydroxyquinoline in all its forms between chloroform and water (see Table 17).

TABLE 17

DISTRIBUTION OF 8-HYDROXYQUINOLINE BETWEEN CHLOROFORM AND AQUEOUS PHASES AS A FUNCTION OF THE ACIDITY[a]

pH	0	1	2	3	4	5–9	10	11	12
$D_{\Sigma Ox} = \frac{[Ox]_{CHCl_3}}{[\Sigma Ox]_{H_2O}}$	0.006	0.06	0.6	5.9	59	720	500	50	5

[a] S. Lacroix, *loc. cit.* Calculated values, 18°C.

The preceding expression enables us to calculate the total concentration of hydroxyquinoline in the aqueous phase (if the original amount of reagent is known), from which the concentration of oxinate ion is found at any pH:

[53] D. C. Spindler, University of Minnesota, 1948, found the value 630 for this coefficient at 25°.

$$[Ox'^-]_w = \frac{[\Sigma Ox]_w}{1 + \frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2}} \quad (6)$$

Equation (3) gives the distribution of total metal between chloroform and aqueous phases only when the metal is present entirely in the form of simple ions in the aqueous phase. If the *p*H is such that the metal ions are hydrolyzed, or if complex or undissociated compounds (*e.g.*, $FeOx'^{++}$) are formed, the values of additional constants must be known for resolution of the system.

Lacroix (*loc. cit.*) determined P/K for aluminum, gallium, and indium hydroxyquinolates (Table 19) and tested equation (3) at various *p*H's for these complexes. Substantial conformity was found. Complete extraction of aluminum hydroxyquinolate in the *p*H range 4 to 9 is predicted when

TABLE 18

WAVE LENGTHS OF MAXIMUM ABSORPTION OF METAL HYDROXYQUINOLATES IN CHLOROFORM[54]

Metal	Fe (III)	Al	Bi	Co	Ni	Cu (II)
λ, mμ	470, 570	395	395	420	395	410

TABLE 19

CONSTANTS FOR SOME TRIVALENT METAL HYDROXYQUINOLATES (18°)[51]

	$[MOx_3]_{CHCl_3}$	$[M^{+++}][Ox'^-]^3$	P/K[a]
$AlOx_3'$	0.045	$10^{-32.3}$	9×10^{30}
$GaOx_3'$	0.092	$10^{-40.3}$	6×10^{39}
$InOx_3'$	0.24	$10^{-33.9}$	2×10^{33}

[a] This ratio is equal to the molar solubility of the hydroxyquinolate in chloroform divided by the solubility product in water saturated with chloroform.

a 0.1 *M* solution of hydroxyquinoline in chloroform is shaken with an equal volume of 0.01 *M* aluminum salt in water. It should be pointed out that if an aluminum solution is made almost neutral before hydroxyquinoline is added, aluminum hydroxide is precipitated and the quinolate is not formed. This undoubtedly explains the finding of some (p. 120) that aluminum is not extracted in the middle of the predicted range. If hydroxyquinoline is added before the *p*H is adjusted, and the chloroform extraction then made, all the aluminum should go into the chloroform.

Although the P/K values have so far been determined only for aluminum, gallium, and indium hydroxyquinolates, figures have been reported[54] for the *p*H ranges of virtually complete extraction of a number of metals

[54] T. Moeller, *Ind. Eng. Chem., Anal. Ed.*, **15**, 346 (1943).

when 25 ml. of aqueous solution are extracted with four 5 ml. portions of 0.01 *M* 8-hydroxyquinoline chloroform solution: ferric iron 1.9–3.0, aluminum 4.3–4.6, bismuth 4.0–5.2, cobalt >6.8, nickel >6.7, cupric copper 2.7–7.0. As already mentioned, the upper limits have no real significance; they only indicate the *p*H at which the hydroxide or a basic salt begins to form in the absence of hydroxyquinoline. Vanadium (V) and molybdenum (VI) can be extracted in fairly acidic medium, much like copper. For other observations on extractability see p. 152.

It is evident that by close control of *p*H, various separations of metals can be effected by chloroform extraction of the hydroxyquinolates. When the respective *P/K* values become known, predictions can be made concerning the sharpness of such separations. It seems likely that extensive use can also be made of complexing agents in keeping some metals in the aqueous phase while allowing others to be extracted. Cyanide has been used to prevent reaction of such metals as copper, nickel, zinc, and iron in the determination of aluminum (p. 153).

8-Hydroxyquinoline-5-sulfonic Acid

This compound and its halogen derivatives (in the 7-position) have been used for the colorimetric determination of ferric iron and vanadium.[55]

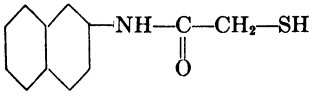
8-Hydroxyquinoline and Iodide

Oxine and iodide form a complex iodide with bismuth in dilute acid solution which can be extracted by amyl acetate or a mixture of amyl acetate and acetone (orange-colored solution).[56]

5,7-Dibrom-8-hydroxyquinoline

This reagent precipitates titanium, copper, and iron (III) from mineral acid solution.[57]

V. Thioglycolic β-aminonaphthalide (Thionalide)



Thionalide yields very slightly soluble white or pale-colored salts of the type Me^{II} $(C_{12}H_{10}ONS)_2$ with most of the metals of the hydrogen sulfide

[55] J. Molland, *Tids. Kjemi Bergvesen*, **19**, 119 (1939); *Arch. Math. Naturvidenskab.*, **43**, 67 (1940).

[56] R. Sazerac and J. Pourzergues, *Compt. rend. soc. biol.*, **109**, 79, 370 (1932).

[57] R. Berg and H. Küstenmacher, *Z. anorg. allgem. Chem.*, **204**, 215 (1932).

group.[58] The reagent is used chiefly for the gravimetric or volumetric determination of these metals, but it also finds application in their indirect colorimetric determination, which is based on the reduction of phosphotungstomolybdic acid by the thionalide in the metal complex (see the determination of thallium, p. 562). The nephelometric determination of copper, mercury, and arsenic by thionalide has been described.[59]

Thionalide, like hydrogen sulfide, precipitates copper, silver, gold, mercury, tin, arsenic, antimony, bismuth, platinum, palladium, rhodium,[60] and ruthenium[61] from dilute mineral acid solutions. The precipitates are extremely slightly soluble (Table 20). Unlike hydrogen sulfide, thionalide

TABLE 20

SENSITIVITY OF PRECIPITATION OF METALS BY THIONALIDE[a]

(In 0.2 *N* mineral acid solution)

Metal	Limiting concentration
Cu	$1:10^7$
Ag	$1:5 \times 10^6$
Au	$1:2.5 \times 10^6$
Hg	$1:1.5 \times 10^7$
Sn	$1:1.25 \times 10^7$
As	$1:10^6$
Sb	$1:4 \times 10^7$
Bi	$1:10^7$
Pt	$1:10^7$
Pd	$1:10^7$

[a] According to R. Berg.

does not precipitate lead and cadmium in dilute mineral acid medium. In a tartrate solution made basic with sodium carbonate, copper, gold, mercury, cadmium, and thallium are precipitated; in an alkaline cyanide-tartrate solution, gold, thallium, tin, lead, antimony, and bismuth are precipitated; in a sodium hydroxide-cyanide-tartrate solution only thallium is precipitated. Thionalide is superior to hydrogen sulfide as a precipitant because coprecipitation is less and the precipitates have the theoretical composition.

[58] R. Berg and W. Roebling, *Ber.*, **68**, 403 (1935); *Angew. Chem.*, **48**, 430, 597 (1935). R. Berg and E. S. Fahrenkamp, *Z. anal. Chem.*, **109**, 305 (1937); **112**, 162 (1938).

[59] R. Berg, E. S. Fahrenkamp, and W. Roebling, *Mikrochemie (Molisch Festschrift)*, 1936, p. 42.

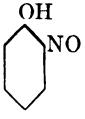
[60] H. Kienitz and L. Rombock, *Z. anal. Chem.*, **117**, 241 (1939).

[61] W. J. Rogers, F. E. Beamish, and D. S. Russell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 561 (1940).

Thionalide is readily soluble in the common organic solvents, but only slightly soluble in water or dilute mineral acid medium. In water the solubility in 100 ml. is 0.01 g. at 20° and 0.08 g. at 95°. Acetic acid increases the solubility. Usually a 1 per cent solution of the reagent in ethyl alcohol or glacial acetic acid is used. The solution decomposes in a few hours and should be prepared fresh before use.

The solvent effect of alcohol or acetic acid on the metal-thionalide complexes is not of importance as long as the volume of the organic solvent is not greater than 10 to 15 per cent. Oxidizing agents, including ferric iron, destroy the reagent, and hydroxylamine sulfate should be added before precipitation when these are present.

VI. Orthonitrosophenol



This reagent forms highly colored internal complexes with a number of heavy metals in faintly acid solution.[62] It is generally used in the form of a petroleum ether solution, yellowish green in color, which is stable for 2–3 weeks if kept in a refrigerator.

With the following metals *o*-nitrosophenol[63] gives salts soluble in water or in certain organic solvents such as ethyl ether, but insoluble in petroleum ether: divalent copper (red-violet), divalent mercury (red-violet), nickel (red), and divalent iron (green). The complexes with palladium (green), cobalt (gray-brown), and trivalent iron (brown) are distinguished from the other complexes by their extractability by petroleum ether. The solutions are stable for some hours.

Regulation of the *p*H is very important in work with *o*-nitrosophenol. If the acidity is too high the complexes are not quantitatively formed. On the other hand if the acidity is too low, a mixture of two compounds is said to be produced in the case of the water-soluble compounds:

$$\mathrm{Np - Me - R} \qquad (1)$$

and

$$\mathrm{Np - Me - Np} \qquad (2)$$

in which Np is the *o*-nitrosophenol radical and R may be Cl, NO_3, etc. Compound (1) is soluble only in water, compound (2) in certain organic

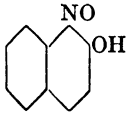
[62] G. Cronheim, *Ind. Eng. Chem., Anal. Ed.*, **14**, 445 (1942); *J. Org. Chem.*, **12**, 1 (1947). Regarding substituted *o*-nitrosophenols see Cronheim, *J. Org. Chem.*, **12**, 7, 20 (1947).

[63] For preparation see O. Baudisch, *J. Am. Chem. Soc.*, **63**, 622 (1941).

solvents such as ethyl ether. Methods have been worked out for the determination of cobalt[62] and ferrous iron,[64] but they appear to find but little application.

o-Nitrosocresol (1-methyl-3-hydroxy-4-nitrosobenzene) exhibits the same general behavior as *o*-nitrosophenol. It has been used as a reagent for cobalt, with which it gives a more intense color than does nitrosophenol. Seemingly, nitrosocresol has no advantages as a reagent for palladium or iron.

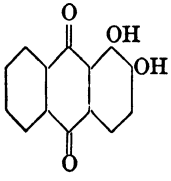
VII. α-Nitroso-β-naphthol



This reagent forms slightly soluble internal complexes with a number of metals, but these have been investigated only slightly from the standpoint of colorimetric analysis. Cobalt may be determined colorimetrically by dissolving the washed precipitate of cobalt nitroso-naphtholate in chloroform.[65] The ferrous complex can be extracted with chloroform (strong green color). The use of α-nitroso-β-naphthol is rendered somewhat unattractive by its intense color, which moreover is quite similar (brownish) to that of most of the complexes it forms.

Nitroso-R-salt (1-nitroso-2-hydroxy-3,6-naphthalene disodium sulfonate) is a most important colorimetric reagent for the determination of cobalt (p. 274), but it has also been used for determining ferrous iron, with which it yields a green color in basic medium.[66] Copper and nickel give strong yellow-brown colors with the reagent at a *p*H less than 7.

VIII. Alizarin

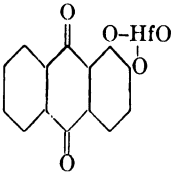


Alizarin (1,2-dihydroxyanthraquinone), or alizarin S (sodium alizarin sulfonate), forms slightly soluble, strongly colored lakes with most cations at proper acidities. The zirconium and hafnium lakes are formed in solutions of fairly high acidity and are made the basis of a sensitive method

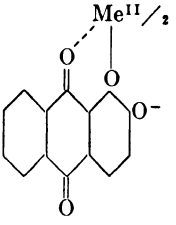
[64] G. Cronheim and W. Wink, *Ind. Eng. Chem., Anal. Ed.*, **14**, 447 (1942).
[65] L. Waldbauer and N. M. Ward, *Ind. Eng. Chem., Anal. Ed.*, **14**, 727 (1942).
[66] C. P. Sideris, *Ind. Eng. Chem., Anal. Ed.*, **14**, 756 (1942).

for the determination of these elements (p. 639). The most common colorimetric method for the determination of fluorine depends upon the bleaching of the red color of the zirconium-alizarin S lake by traces of fluoride as a consequence of the formation of slightly dissociated complex zirconium fluoride. Alizarin S is also used for the determination of aluminum (p. 162).

According to Liebhafsky and Winslow,[67] alizarin and hafnium combine in a 1:1 molar ratio to form a definite chemical compound, to which the following formula is assigned:



The zirconium lake will then have an analogous composition.[68] On the other hand, the structure of the other metal-alizarin lakes, which are unstable toward acid, is thought to be:



Quinizarin (1,4-dihydroxyanthraquinone)

In basic medium this reagent reacts with beryllium to give a red fluorescent compound. The sulfonic acid has been used as a colorimetric reagent for the same element.

1-Amino-4-hydroxyanthraquinone

An alcoholic solution (0.1 per cent) of this compound produces a purple colloidal precipitate with thorium in weakly acid solution (*p*H 2) which

[67] H. A. Liebhafsky and E. H. Winslow, *J. Am. Chem. Soc.*, **69**, 1130 (1947).

[68] It has been shown by Brita Hök, University of Minnesota, 1948, that the combining ratio ZrO^{++}/alizarin sulfonic acid is almost unity in dilute mineral acid medium. In the presence of excess alizarin sulfonic acid the ratio is a little greater than 1, presumably because of adsorption of the dye.

shows a reddish fluorescence in ultraviolet light.[69] The sensitivity is low, approximately 1:125000.

Gallium and praseodymium also fluoresce under these conditions but not as strongly as thorium (0.1 mg. Th ≡ 1.5 mg. Ga ≡ 10 mg. Pr). Zirconium and iron (III) decrease the thorium fluorescence, and cerium (IV), silver, gold, and mercury (I) as well as metals of the platinum group are stated to destroy the reagent. Phosphate, fluoride, and sulfate in small amounts destroy the thorium fluorescence. In basic medium the reagent produces a fluorescence with beryllium.

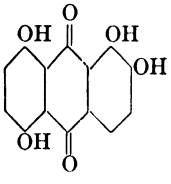
Purpurin (1,2,4-trihydroxyanthraquinone)

A reagent for zirconium (p. 639). It gives a sensitive fluorescence reaction with stannic tin at *p*H 4.5; gallium also reacts sensitively at this *p*H.

1,2,7-Trihydroxyanthraquinone

Hydroxyanthraquinones with a hydroxy group in the ortho position are stated to give sensitive color reactions with stannic tin.[70] One of the most suitable of these is the 1,2,7 compound.

Quinalizarin (1,2,5,8-tetrahydroxyanthraquinone)



This dye dissolves in alkalies to give a red-violet solution which is turned yellow by acids. It is also soluble in alcohol and acetone. Quinalizarin has been used for the colorimetric determination of beryllium, gallium, magnesium, aluminum, and boron, and for the detection of germanium[71] and the rare earths.[72]

The addition of quinalizarin to a sodium hydroxide solution containing beryllium gives a blue color which is quite different from the violet color obtained in the absence of beryllium.[73] Aluminum does not react in the

[69] C. E. White and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.*, **13**, 809 (1941).

[70] E. Eegriwe, *Z. anal. Chem.*, **120**, 81 (1940).

[71] A. S. Komarovsky and N. S. Poluektov, *Mikrochemie*, **18**, 66 (1935).

[72] A. S. Komarovsky and I. M. Korenman, *Z. anal. Chem.*, **94**, 247 (1933).

[73] H. Fischer, *Wiss. Veröffent. Siemens-Konzern*, **5**, 99 (1926); *Z. anal. Chem.*, **73**, 54 (1928).

strongly basic solution. A method for the determination of beryllium has been based on this behavior. Other metals giving a sensitive reaction (blue color) in sodium hydroxide solution are magnesium, scandium, rare earths, nickel, and cobalt.[74] Various other metals react less sensitively (p. 202). Attempts to determine scandium in this way did not lead to reproducible results.[74]

Gallium at *p*H 4.5 to 6 yields a pink to amethyst color with quinalizarin, and Willard and Fogg[75] have worked out a quantitative method for the element with this reagent (p. 329).

Magnesium hydroxide adsorbs quinalizarin and gives a blue lake.[76]

In faintly acid solution aluminum produces a violet color due to lake formation.[77]

In strong sulfuric acid, boric acid gives a blue color with quinalizarin which is due to the formation of an internal complex boronhydroxyanthraquinone compound.[78] Columbium and tantalum also react in sulfuric acid medium (p. 293).

Many metals will react with quinalizarin in slightly acid medium, giving color changes. Thus at *p*H 5, iron (III) and lead produce a blue color, tin (II), antimony (III), copper (II), indium (III), germanium, vanadium (IV and V), and molybdenum (VI) a pink color. These reactions are not prevented by the addition of fluoride. The following metals also react at *p*H 5 but fluoride prevents the reaction: zirconium, thorium, rare earths (all blue colors); tin (IV), beryllium, aluminum, thallium (III), titanium (IV), arsenic (III), antimony (V) (all pink colors). The alkalies, alkaline earths, magnesium, manganese, iron (II), mercury (II), thallium (I), cadmium, uranium (V), and tungsten (VI) give rise to no color at *p*H 5, while other metals such as silver, mercury (II), bismuth, tantalum, etc. are precipitated as chlorides or hydrolyzed out.[79]

[74] W. Fischer and J. Wernet, *Angew. Chem.*, **A60**, 729 (1948).

[75] H. H. Willard and H. C. Fogg, *J. Am. Chem. Soc.*, **59**, 40 (1937).

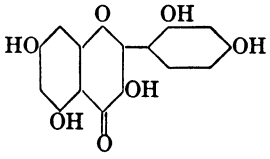
[76] F. L. Hahn, H. Wolf, and G. Jäger, *Ber.*, **57**, 1394 (1924). F. L. Hahn, *Mikrochemie (Pregl-Festschrift)*, **1929**, p. 127.

[77] I. M. Kolthoff, *Chem. Weekblad*, **24**, 447 (1927); *J. Am. Pharm. Assoc.*, **17**, 260 (1928).

[78] F. Feigl, *Specific and Special Reactions*, Elsevier, New York, 1940, pp. 41, 126. G. S. Smith, *Analyst*, **60**, 735 (1935); K. C. Berger and E. Truog, *Ind. Eng. Chem., Anal. Ed.*, **11**, 540 (1939).

[79] The material in this paragraph is taken from H. H. Willard and H. C. Fogg, *J. Am. Chem. Soc.*, **59**, 40 (1937).

IX. Morin



In acidic medium morin (3,5,7,2′,4′-flavone) reacts with a considerable number of metals to give compounds of lake-like character that show strong fluorescence, especially in ultraviolet light (Table 21). A few metals, particularly zirconium, and scandium[80] and thorium to a lesser extent, react in mineral acid medium. Most metals react most sensitively in weakly acidic (acetic acid-acetate) medium. The rare earth metals show weak fluorescence. The morin complexes of the metals can be extracted by butyl and amyl alcohols and cyclohexanol. Aluminum has been determined by its fluorescence in acidic medium and doubtless other metals could be determined in the same way.

TABLE 21

SENSITIVITY (MOLE/L.) OF FLUORESCENCE REACTIONS OF MORIN WITH VARIOUS METALS[a]

	1 *N* HCl	*p*H 3	*p*H 4.5
Zr[b]	10^{-4}	10^{-4}	10^{-4}
Ti		No fluorescence	
Th	10^{-3}	10^{-3}	10^{-4}
Ga	10^{-2}	10^{-3}	10^{-5}
Al	10^{-1}	10^{-3}	10^{-4}
In	—	10^{-4}	10^{-4}
Sc[c]	10^{-3}	$10^{-4.3}$	$10^{-4.3}$
Y	—	10^{-2}	10^{-3}
Ce (III)	—	10^{-2}	10^{-4}
Be	—	1	10^{-1}
Sb (III)	10^{-3}	—	—
Sn (IV)	—	10^{-4}	10^{-5}

[a] G. Charlot, *Anal. Chim. Acta*, 1, 233 (1947). Values pertain to qualitative conditions: about 10 drops of solution.

[b] Sensitivity in 6 and 10 *N* HCl is also 10^{-4} mole/l.

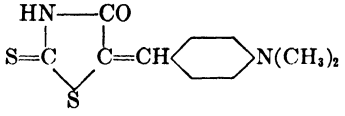
[c] Sensitivity in 2 *N* NaOH is 10^{-4}.

In strongly basic medium (0.1–1 *M* in sodium hydroxide) morin becomes almost a specific reagent for beryllium. Aluminum, gallium, indium, and most other metals whose hydroxides are soluble in excess sodium hydroxide

[80] G. Beck, *Mikrochim. Acta*, 2, 9 (1937). Scandium also fluoresces in basic medium but the intensity is greatly weakened by pyrophosphate.

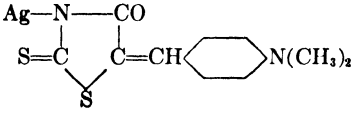
then do not react. Zinc fluoresces under these conditions but cyanide prevents its interference. Lithium fluoresces very weakly. Calcium can be prevented from interfering by addition of pyrophosphate. Further details are given in the chapter on beryllium.

X. *p*-Dimethylaminobenzylidenerhodanine



This reagent (or the ethyl analogue) gives slightly soluble red or violet precipitates in acid solution with silver, mercury (I and II), cuprous copper, gold, and palladium. Platinum (IV) also reacts, but not very sensitively, possibly by reduction to the platinous state. Many other metals react in alkaline solution. The reagent has been recommended by Feigl for the detection of the metals mentioned.

The compound formed with silver has the formula:



and it seems likely that the cuprous and mercurous compounds have similar formulas. According to Feigl the palladium compound is probably a chloro addition product with the rhodanine. Gold appears to be reduced to the aurous state in its reaction and probably gives a product analogous to the silver compound. Strong oxidizing agents such as chlorine (sometimes found in distilled water) convert the reagent into a reddish product in acidic medium.

Dimethylaminobenzylidenerhodanine has been used for the colorimetric determination of silver (p. 540),[81] mercury,[82] and gold (p. 346).[83] Since the colored reaction products are very slightly soluble, the reagent is not an ideal one for colorimetry. However, in very dilute solutions the colloidal suspensions are fairly stable, and in less dilute solutions they can be made so by the addition of a suitable protective colloid.

Minute amounts of palladium—as little as 0.1 γ—can be determined in 0.02 *N* hydrochloric acid solution. Small amounts of silver give no color in the hydrochloric acid medium. Gold, however, reacts with a sensitivity approaching that of palladium and this is a serious objection to the practical use of the rhodanine for the determination of palladium. The re-

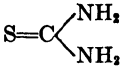
[81] I. C. Schoonover, *J. Research Natl. Bur. Standards*, **15**, 377 (1935).
[82] N. Strafford and P. F. Wyatt, *Analyst*, **61**, 528 (1936).
[83] B. K. Merejkovsky, *Bull. soc. chim. biol.*, **15**, 1336 (1933); see, further, p. 349.

action of gold cannot be prevented by the addition of complex-forming reagents without destruction of the color given by palladium. For this reason nitrosodiphenylamine is generally a better reagent for palladium (p. 488).

XI. Tannic Acid

This reagent is better known as a metal precipitant than as a colorimetric reagent, but as the latter it may at times find some application, since in faintly acid solutions it gives fairly sensitive reactions with titanium (red-orange), vanadium (blue), molybdenum (reddish), and iron (bluish, turning red with ammonia). All of these metals yield precipitates above a minimum concentration. Uranium (VI) gives a brown color, and a colorimetric method based upon this reaction has been described.[84]

XII. Thiourea

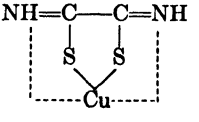


In acid solutions thiourea[85] produces a yellow color with bismuth and palladium, and is occasionally used for the determination of the former. Antimony gives a slight color with the reagent, and silver, platinum, and mercury give precipitates. Selenite is reduced to red selenium.

A hydrochloric acid solution of osmium (as OsO_4 or $OsCl_6^{=}$) heated with thiourea becomes red owing to the formation of $Os(NH_2 \cdot CS \cdot NH_2)_6 Cl_3 \cdot H_2O$.[86] The reaction is applicable to the determination of traces of osmium. Ruthenium gives a blue color under the same conditions.

XIII. Rubeanic Acid

This compound, the diamide of dithiooxalic acid (dithiooxamide), is better known as a qualitative reagent than as a reagent for the colorimetric determination of metals, but it has been used as such for copper (p. 311). In weakly acidic solution the internal complex salt is formed. Because it is strongly colored (greenish) it can be used as a determination form, but



[84] P. N. Das Gupta, *J. Indian Chem. Soc.*, **6**, 763 (1929).

[85] J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.*, **14**, 435 (1942), found that some substituted thioureas gave slightly more sensitive reactions than thiourea with bismuth. Benzidinedithiourea gives a sensitivity about four times as great as that given by thiourea.

[86] L. Chugaev, *Compt. rend.*, **167**, 235 (1918).

since it is insoluble it is open to the usual objections that can be raised against such substances for a colorimetric method. Rubeanic acid yields a strong blue color with ruthenium (p. 529); in this case the reaction product is soluble.

XIV. Toluene-3,4-dithiol

This compound (4-methyl-1,2-dimercaptobenzene), usually called dithiol, gives slightly soluble colored products with a number of heavy metals. The reactions with tin, tungsten, and molybdenum are distinctive enough to have been made the basis of colorimetric methods for these elements. Stannous salts yield a red precipitate in acidic medium. This is one of the most characteristic reactions for tin. Molybdenum and tungsten give yellow-green and blue-green precipitates respectively in acid medium, which can be extracted by certain organic solvents such as butyl and amyl acetates. The composition of these colored products has not been established, nor have the reactions been studied in a critical way. Further details may be found in the corresponding chapters.

XV. Thiocyanate

An alkali metal thiocyanate alone or in conjunction with other reagents is a colorimetric reagent for ferric iron, molybdenum, rhenium, tungsten, uranium, cobalt, and bismuth. The red compound given by thiocyanate ion in acid solution with ferric ion has been assigned various formulas. Actually more than one colored species is formed. At low thiocyanate concentrations the ion $Fe(CNS)^{++}$ predominates[87]; as the thiocyanate concentration is increased to 0.1 *M* and above, ions with a greater proportion of thiocyanate are formed (p. 364). The reaction is a sensitive one and provides a good method for the determination of ferric iron in spite of the pronounced effect of such factors as thiocyanate concentration and the time of standing on the color intensity.

Molybdate with thiocyanate yields an amber to red solution when treated with a reducing agent such as stannous chloride. The colored compound contains molybdenum in the quinquevalent state and may have the formula $Mo(CNS)_5$. Other colored species may also be formed according to

[87] H. E. Bent and C. L. French, *J. Am. Chem. Soc.*, **63**, 568 (1941); S. M. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941); R. K. Gould and W. C. Vosburgh, *ibid.*, **64**, 1631 (1942).

present evidence. Rhenium (VII) gives a similar color under the same conditions, perhaps due to $ReO(CNS)_4$. The colored compounds can be extracted with ether, and the interference of various colored foreign ions thus eliminated.

In strong hydrochloric acid medium, tungsten (VI) will give a strongly colored soluble yellow compound when treated with thiocyanate and a strong reducing agent such as stannous chloride or titanous chloride.[88] The colored compound is soluble in ethers and esters.

In neutral or slightly acidic solution containing 50 per cent of acetone, thiocyanate produces a blue color with cobalt which is possibly due to some such ion as $Co(CNS)_4^{=}$. The reaction is fairly sensitive and specific (a reducing agent such as stannous chloride prevents interference of iron and copper in small amounts).

The yellow compound given by uranyl ion with thiocyanate in acid medium is not very strongly colored. It can be extracted by such organic solvents as ethyl acetate and butyl alcohol.

A comparatively high concentration of an alkali thiocyanate will give a yellow color with bismuth. The reaction is not very sensitive and usually of little value in trace analysis.

Thiocyanate and Pyridine

These reagents in combination give precipitates with cupric, cadmium, zinc, nickel, cobalt, and other metal ions. These precipitates are soluble in chloroform; the copper compound, $Cu(CNS)_2 \cdot 2\,Py$, gives a green solution, the nickel compound, $Ni(CNS)_2 \cdot 4\,Py$, a blue, and the cobalt compound, $Co(CNS)_2 \cdot 4\,Py$, a pink solution. The Biazzo[89] method for copper involves extraction of the copper compound with chloroform and comparison or measurement of the color of the latter. This method has now been supplanted by others (p. 300). Occasionally traces of the metals mentioned are isolated by extraction of their pyridine-thiocyanate complexes preparatory to determination by other methods.

XVI. Halogen Acids

Hydrochloric Acid

Strong hydrochloric acid forms chloro acids with a number of metals and some of these are strongly colored, especially those with ferric iron (yellow), copper (yellow), cobalt (blue), quadrivalent iridium (brown), and trivalent rhodium (rose-red). Hydrochloric acid has been employed

[88] When tungsten is reduced with tin amalgam, the colored product contains tungsten and thiocyanate in equimolar amounts and is thought to have the composition WOCNS (p. 585).

[89] R. Biazzo, *Ann. chim. applicata*, **16**, 96 (1926).

as a colorimetric reagent for these metals, but the sensitivity is inferior to that of other methods (except for iridium) and such metals as platinum, palladium, gold, ruthenium, nickel, and others interfere by giving more or less strong colors.

Copper (II) gives the maximum color intensity with hydrochloric acid when the acid concentration is 28 per cent or higher.[90] Iron interferes seriously since, weight for weight, it produces twice as strong a color as copper. The coloration given by cobalt is much less intense than that of copper.

Chloroplatinous acid, obtained by reduction of chloroplatinic acid with stannous chloride, is an important determination form of platinum (p. 494).

Hydrobromic Acid

Bromide ion in acid solution gives strongly colored (yellow, brown, etc.) complexes with iron (III), copper (II),[91] platinum (IV), iridium (IV) and gold (III). Chromium, nickel, cobalt, molybdenum, and vanadium interfere to a greater or less extent. Bromoauric acid is easily extracted from aqueous solution by ethyl acetate.

Hydriodic Acid

Iodide ion in excess yields strongly colored soluble complexes in acid solution with bismuth (iodobismuthous acid, yellow), quadrivalent platinum ($PtI_6^=$, brownish red), and palladium ($PdI_4^=$, brown). The reaction with bismuth is the basis of one of the most sensitive methods for the colorimetric determination of this element. The formation of iodoplatinic acid is applied not only in the determination of platinum but also in the indirect determination of potassium after precipitation as chloroplatinate.

It may be mentioned that the iodide reaction with antimony (III) is very sensitive if a high concentration of iodide is used. Indirectly iodide may be used for the determination of thallium by liberation of iodine by reaction with thallic salts, the free iodine being determined colorimetrically after extraction with an organic solvent (p. 559). Calcium may also be determined indirectly after oxidation of the oxalate with ceric salt (p. 243).

XVII. Ammonium Hydroxide

Ammonium in excess gives fairly strong colors with copper (II), nickel, and trivalent cobalt (rose-pink)[92] and has been used for the determination of these metals. The sensitivity, however, is inferior to that of other methods so that ammonia is not an important colorimetric trace reagent,

[90] C. Hüttner, *Z. anorg. Chem.*, **86**, 351 (1914).
[91] G. Denigès and E. Simonot, *Bull. soc. pharm. Bordeaux*, **54**, 337 (1914).
[92] B. S. Evans, *Analyst*, **50**, 389 (1925).

although it may render good service when larger amounts of these metals are to be determined.

XVIII. Hydrogen Peroxide

In acid solution hydrogen peroxide produces a yellow color with titanium (IV), a reddish brown with vanadium (V), and a yellow with molybdenum (VI). Hydrogen peroxide reacts mole for mole with titanium and vanadium over a range of acidities; the equimolecular peroxy compound of molybdenum is formed only at high acidities (18 *M* sulfuric acid) and low molybdenum concentrations.[93]

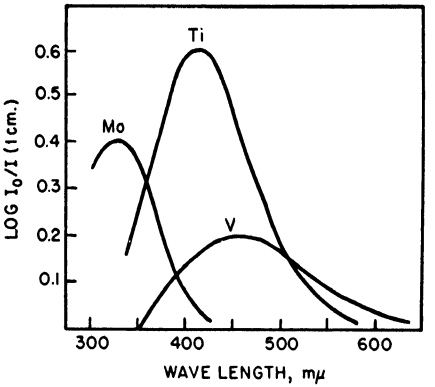


Fig. 22. Extinction curves of the peroxy complexes of molybdenum, titanium, and vanadium. (According to A. Weissler, *Ind. Eng. Chem., Anal. Ed.*, **17**, 698 (1945).)

The reaction with titanium is very sensitive and is the basis of the most generally useful colorimetric method for this element (p. 572). Vanadium also can be determined by the hydrogen peroxide method. The color given by titanium can be destroyed by adding hydrofluoric acid but the vanadium color is not affected.

At high sulfuric acid concentrations, columbium gives a moderately strong yellow color with hydrogen peroxide. The color intensity increases as the sulfuric acid concentration is increased from 5 to 16 *M*. In 5 *M* sulfuric acid, columbium and hydrogen peroxide have been shown to react in the molar ratio 2:1.

In a mixture of strong sulfuric and phosphoric acid, containing 40 per cent of the latter, hydrogen peroxide may be used to determine columbium (yellow coloration) in the presence of small amounts of titanium, the color

[93] Y. Schaeppi and W. D. Treadwell, *Helv. Chim. Acta*, **31**, 577 (1948).

of the latter being repressed by the phosphoric acid.[94] Tantalum gives no color.

A colorimetric method has been described for the determination of molybdenum by the formation of permolybdate (reddish brown) in alkaline solution with hydrogen peroxide.[95] Uranium and cerium give fairly intense yellow colors in basic medium (p. 601 and p. 235). The reaction with molybdenum is of slight importance, but those with uranium and cerium are of practical value.

XIX. Molybdate and Reducing Agents

The heteropoly molybdic acids formed when molybdate reacts in acid solution with phosphate, arsenate, silicate, and germanate may be made the basis of sensitive methods for the determination of the corresponding elements.[96] In the case of phosphorus,[97] germanium and silicon the heteropoly acids may be used directly in the method; they yield moderately strongly colored yellow solutions. As is well known, the heteropoly molybdic acids are more easily reduced then molybdic acid itself, so that it is possible to determine phosphate, silicate, arsenate, and germanate by treating the acid solution of these ions with ammonium molybdate and a suitable reducing agent. Under the proper conditions only the molybdenum combined with the ions mentioned will be reduced to a lower valence to give the intensely colored "heteropoly blue." The blue reduction product has a variable composition and its constitution is uncertain.[98] The transmission curves of the heteropoly blues of the four elements mentioned are similar, and show a minimum in the region 820–830 mμ. The transmission curve of molybdenum blue (formed from molybdate alone under stronger reducing conditions) does not show this characteristic band, although otherwise similar to the curves of the heteropoly blues.

Various reducing agents are used in ceruleomolybdenum methods. Stannous chloride and certain organic reducing agents such as 1-amino-2-naphthol-4-sulfonic acid and hydroquinone are widely used for the determination of phosphorus. Hydrazine sulfate is very suitable for the reduction of arsenomolybdate in boiling solution and may also be used for phosphomolybdate. Ferrous sulfate has been employed for the reduction of germanomolybdate.

[94] G. Thanheiser, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, **22**, 255 (1940).

[95] A. D. Funck, *Z. anal. Chem.*, **68**, 283 (1926).

[96] In addition, phosphorus can be determined as phosphovanadomolybdic (molybdivanadophosphoric) acid. See R. E. Kitson and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **16**, 379 (1944), who give references to earlier work.

[97] D. F. Boltz and M. G. Mellon, *Anal. Chem.*, **20**, 749 (1948).

[98] For a recent study of the constitution of the heteropoly molybdenum blue, consult W. D. Treadwell and Y. Schaeppi, *Helv. Chim. Acta*, **29**, 771 (1946).

Systematic studies on the heteropoly blue methods have been made,[99] and reference should be made to these papers for the effect of a number of factors and for transmission curves.

XX. Hydrogen Sulfide

Under proper conditions hydrogen sulfide (or a soluble sulfide) can be used to produce a colloidal suspension of various heavy metal sulfides suitable for photometric measurement of comparison. In most cases dithizone can be substituted for sulfide with advantage because of higher sensitivity and greater selectivity.

XXI. Oxidizing and Reducing Agents

Many organic compounds can be oxidized to strongly colored products in inorganic systems of high oxidation potential, and sometimes colorimetric methods of practical value can be based on these reactions. Such methods are likely to be lacking in specificity and must be applied with caution.

Another drawback of these methods is the frequent poor stability of the colored organic product. A few methods of this type may be mentioned. Benzidine gives a fugitive blue-green color with permanganate in acid solution and a blue color with quadrivalent iridium. *o*-Tolidine in acid solution is oxidized by auric gold to a yellow product; many other strong oxidizing agents produce the same color. Lead has been determined by anodic deposition of the dioxide, followed by solution of the latter in an acetic acid solution of tetramethyldiaminodiphenylmethane to give a blue diphenylmethane dye. The leuco base of malachite green may be used for determining gold and iridium; tetramethyl-*p*-phenylenediamine has been recommended as a reagent for osmium. Diphenylamine has been used for the colorimetric determination of vanadium (V).[100] Phenolphthalin (obtained by reduction of phenolphthalein with zinc in sodium hydroxide solution) together with hydrogen peroxide gives a pink color with the most minute amounts of copper.

The reduction of an organic compound to a strongly colored product by an inorganic substance is rarely applied in colorimetry. Cacotheline, the nitro compound of brucine, is reduced by stannous tin and other strong

[99] J. T. Woods and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 760 (1941); D. F. Boltz and M. G. Mellon, *Anal. Chem.*, **19**, 873 (1947); R. E. Kitson and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **16**, 466 (1944).

[100] For the mechanism of the color change in the oxidation of diphenylamine and some of the other compounds mentioned above, consult the section on redox indicators, pp. 105–141, in I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. I, Interscience, New York, 1942.

reducing agents[101] to a soluble violet-colored substance. This reaction is used for the detection of tin, but has not been successfully applied quantitatively.

Inorganic reagents which are oxidized or reduced to strongly colored substances find considerable use in the indirect determination of metals. Thus iodide may be employed for the determination of ceric cerium and thallium, as well as calcium. Either the brown tri-iodide ion or the blue iodine-starch product may be made the basis of these methods. Reference has already been made to the use of ammonium molybdate in molybdenum blue methods and the use of phosphotungstomolybdic acid for the determination of many metals precipitated as oxinates or thionolates. The latter reagent is also reduced by certain metals in their lower valence states, as for example antimony (III) and tin (II).

In a different class are oxidizing and reducing agents which convert metals into colored products. For example persulfate at 100° in the presence of a little silver as catalyst oxidizes manganese, chromium, and cerium to their strongly colored highest valence states. On the other hand, stannous chloride is a valuable reagent for the determination of gold, tellurium, platinum, and rhodium by reduction to the colloidal metal or lower valence state, as well as for the determination of other metals in conjunction with other reagents as we have already seen.

[101] L. Rosenthaler, *Mikrochim. Acta*, **3**, 190 (1938).

SPECIAL PART

PROCEDURES FOR THE DETERMINATION OF TRACES OF METALS

EXPLANATORY NOTES

The plan of treatment is the following. First the separation of the metal in question from other elements is considered, chief attention being given so far as possible to those likely to interfere in the colorimetric determination and to those frequently associated with the metal in question. For many metals, methods worked out specifically for the separation of traces are lacking and a brief general outline of separations is all that can be given, with the hope that some of these separations can be extended with suitable modifications to work involving small quantities. Next the important methods of determination are described. The procedures are given in general form so far as possible, independent of the nature of the original sample. The effect of foreign elements, so far as known, is mentioned. Finally, for many of the more important trace elements, directions are given for the determination of the metal in important classes of material. To a large extent these procedures pertain to the preparation of the sample and the isolation of the metal; the final determination is usually made according to the preceding general procedure but in some instances the nature of the sample makes it advisable to give special directions for the final determination. The materials considered include silicate rocks, which are of great scientific interest and which in great measure serve as models for other samples, and biological materials in general.

Directions in most of the procedures assume the use of some form of a photoelectric photometer, but often very little change need be made when other photometers or a color comparator of the Duboscq type is to be employed. The photometer should permit the use of as little as 5 ml. of solution in transmittancy measurements. The possibility of using cells having a depth greater than 1 cm. is often of great advantage. Trace analyses can frequently be expedited by reducing the size of sample and retaining the desired sensitivity and photometric precision by using final smaller volumes and greater cell thicknesses.

Standard curves are given for some of the procedures with the purpose of indicating the sensitivity of the method, the reproducibility, and, sometimes, adherence to Beer's law. These curves were for the most part obtained with a filter photometer and do not necessarily reflect the best optical methods of measurement; in some cases a more selective filter or the use of a spectrophotometer will give much greater sensitivity as well as closer conformity to Beer's law. Since the concentration-extinction curves

are intended primarily for trace analysis, they have been restricted to low concentrations.

It will be understood that the color development in the standard solutions is to be made under the same conditions, as far as this is possible, as in the sample solution itself, even if no specific directions are given in this respect. A blank should be run through the whole procedure.

When extremely small amounts of a substance are being determined colorimetrically (using this term in its general sense), it is important to make certain that the sample solution does not absorb light (at the wave length used) before the color-producing reagent is added.

CHAPTER V

ALUMINUM

I. Separations

A. Precipitation Methods

Aluminum can be separated from magnesium and the alkaline earth metals by precipitation with ammonium hydroxide in the presence of an ammonium salt. A few milligrams of zirconium or ferric iron should be added to gather the aluminum. Although iron is a good collector it has the disadvantage that it must later be separated, since it interferes in all the colorimetric methods for aluminum. Zirconium will interfere in some procedures. Only a slight excess of ammonia should be added (*p*H 7–7.5). If chromium is first oxidized to the sexivalent state it largely remains in solution in the ammonia precipitation.

A possible method for the separation of aluminum from relatively much iron (say 50 mg.) is by ammonia precipitation in the presence of mercaptoacetic acid (*cf.* p. 207).

Phosphate precipitation. Aluminum may be precipitated as phosphate in weakly acid medium, with ferric phosphate as collector, and thus separated from such metals as calcium and magnesium whose phosphates are not precipitated under these conditions. This method is frequently applied in isolation of aluminum from the ash of bio materials (p. 161). A small amount of phosphate does not interfere in some colorimetric methods for aluminum (p. 147).

Sodium hydroxide precipitation. Separation of traces of aluminum from other metals by the precipitation of the latter with an excess of sodium hydroxide is a dubious method at best because of the coprecipitation of aluminum with the metal hydroxides, which is especially marked with magnesium and nickel hydroxides. The method may be of some use when the amount of the precipitated hydroxides is small; a double precipitation should be made. Sodium hydroxide precipitation has been used to separate iron, but the precipitation of the latter is not entirely complete.[1]

[1] N. Strafford and P. F. Wyatt, *Analyst*, **68**, 319 (1943), obtained very poor results by the sodium hydroxide separation. When the method was applied to a mixture containing 52 γ of Al and 64 γ of Fe, 15 γ of Al and 37 γ of Fe were found in the precipitate and 38 γ of Al and 30 γ of Fe in the filtrate.

Better results can be obtained in separating aluminum from a number of metals if a mixture of sodium hydroxide and sodium sulfide (a solution containing 10 per cent of each) is used instead of sodium hydroxide alone. Aluminum is less strongly adsorbed on the metal sulfides than on the corresponding hydroxides (as of iron and manganese). A small amount of copper may be added to aid in obtaining a better filterable precipitate of iron sulfide (low concentrations of iron tend to give a green colloidal solution).

TABLE 22

ISOLATION OF ALUMINUM BY PRECIPITATION WITH PHOSPHATE IN THE PRESENCE OF IRON[a]

Al added γ	Al found γ	Al recovered γ
0	5.0	
0	5.2	
1	6.3	1.3
1	5.9	0.9
5	10	5
5	12	7
30	35	30
30	37	32
50	57	52
50	54	49

[a] Conditions as in the procedure on p. 161.
Figures from J. Cholak, D. M. Hubbard, and R. V. Story, *Ind. Eng. Chem., Anal. Ed.*, **15**, 57 (1943).

Precipitation should be made in hot solution followed by digestion. Account must be taken of the introduction of aluminum from the glassware (platinum should preferably be used) or from the reagents. Usually other methods of separation will be preferred.[2]

B. EXTRACTION METHODS

Cupferron extraction. In 1:10 sulfuric acid, cupferron precipitates ferric iron, titanium, zirconium, vanadium, stannic tin, and some other elements less frequently encountered. Usually the separation from aluminum is made by extracting these cupferrates with an organic solvent, rather than by filtration. Strafford and Wyatt[3] have described the chloroform extrac-

[2] Some use has been made of sodium hydroxide or sodium carbonate fusion for separating aluminum from small amounts of such metals as iron and titanium. The carbonate fusion has been studied by T. D. Parks and L. Lykken, *Anal. Chem.*, **20**, 1102 (1948).

[3] N. Strafford and P. F. Wyatt, *Analyst*, **72**, 54 (1947).

tion of ferric cupferrate. The sample solution, containing not more than 10 mg. of iron, should be 5 to 6 *N* in sulfuric acid and may have a volume of 20–25 ml. It is treated with 2.5 ml. of freshly prepared 6 per cent aqueous cupferron solution (from reagent-grade material) and shaken vigorously for 40 seconds with 10 ml. of chloroform. The chloroform layer is drawn off and the aqueous phase is washed, without mixing, with a few ml. of chloroform to displace the drop of cupferrate solution on the surface of the aqueous layer. The aqueous solution is next shaken for 30 seconds with 5 ml. of chloroform, which is drawn off. Then 0.5 ml. of cupferron solution is added (the turbidity produced should be white and should show no color due to iron) and extraction made successively with a 10 ml. and two 5 ml. portions of chloroform. This treatment should remove all but a trace of cupferron from the aqueous layer. After each extraction, the stopper of the funnel may be rinsed with a little water, but the acidity of the final solution should not be less than 4 *N*, or traces of aluminum may tend to be extracted. Copper is also extracted according to these authors.

For extraction of ferric cupferrate with a mixture of ether and benzene see p. 161.

8-Hydroxyquinoline extraction. Minute amounts of aluminum can be separated from the alkaline earth metals, magnesium, beryllium, manganese, chromium (III), and the rare earths by extraction of the 8-hydroxyquinoline complex with chloroform from a solution having a *p*H of 4.5–5.0 (*cf.* p. 119). Many other metals (see p. 115), including ferric iron, are simultaneously extracted so that the method has limited applicability. Aluminum can also be extracted at *p*H *ca.* 9. In basic medium, such metals as copper, zinc, nickel, and iron can be complexed with cyanide; beryllium and magnesium, as well as some other metals, react under these conditions. Tungstate and molybdate are not extracted in basic medium. For further particulars see p. 152.

Other extraction methods. Small amounts of iron have been separated from aluminum by extraction of ferric thiocyanate with amyl alcohol[4] or a mixture of amyl alcohol and ether.[5] Cupric copper is extracted at the same time. This method is much less generally applicable than the cupferron extraction. The partition coefficient in the thiocyanate extraction is not very favorable and much iron is not easily removed. Moreover, many anions (even sulfate) forming complexes with ferric iron, hinder or prevent the extraction.

[4] A. P. Musakin, *Z. anal. Chem.*, **105**, 351 (1936); *Zavodskaya Lab.*, **9**, 507 (1940).

[5] Strafford[1] extracts a solution about 0.5 *N* in hydrochloric acid and about 0.1 *N* in ammonium thiocyanate with an equal volume of amyl alcohol-ethyl ether (5:2 by volume). It should be noted that at high thiocyanate concentrations aluminum is extracted by ether (p. 535).

Large amounts of ferric iron can in great measure be removed by extracting a 1:1 hydrochloric acid solution with ethyl ether or better with isopropyl ether (p. 157).[6]

C. Electrolysis

A very useful method for eliminating many metals at one stroke involves electrolysis with a mercury cathode in dilute sulfuric acid solution. Large quantities of the following elements can thus be separated from aluminum: iron,[7] copper, nickel, cobalt, zinc, gallium, germanium, silver, cadmium, indium, tin, antimony, chromium, molybdenum, lead, bismuth, arsenic, selenium, tellurium, mercury, thallium, rhenium, gold, and the platinum metals (except ruthenium). Manganese is only partially removed, but the amount remaining usually does not interfere in the aurintricarboxylate method.[8] Elements remaining in solution with aluminum include beryllium, vanadium, phosphorus, magnesium, the alkaline earth metals, and the rare earth metals. The procedure is described on p. 159.

II. Methods of Determination

The usual method for the colorimetric determination of aluminum is based on the formation of a strongly colored lake with a suitable organic reagent. The exact nature of the lakes produced is uncertain. They have been regarded as internal complexes of aluminum which exist in colloidal solution or as colloidal aluminum hydroxide on which the organic compound is adsorbed in one fashion or another with a pronounced change in color. At least some of the dyes used as reagents form internal complexes with the aluminum, judging from the stoichiometric ratio existing between the reactants in the product under certain conditions.[9] The resulting compounds

[6] Various ketones are more effective than the ethers, as shown by V. I. Kuznetsov, *J. Gen. Chem.* (*U. S. S. R.*), **17**, 175 (1947). He recommends a mixture consisting of 3 volumes of methyl amyl ketone with 1 volume of bromoform, which is heavier than water and separates readily. In 8 *N* hydrochloric medium the partition coefficient $[Fe]_{Ketone}/[Fe]_{H_2O}$ is stated to have the value 3300. Amyl acetate has been used to extract ferric iron from concentrated hydrochloric acid solutions by J. E. Wells and D. P. Hunter, *Analyst*, **73**, 671 (1948); sulfate and phosphate may be present.

[7] Strafford and Wyatt[1] as well as others state that the separation of iron may not be quite complete. Two micrograms were found to remain in solution after electrolysis in a Melaven cell.

[8] According to A. C. Holler and J. P. Yeager, *Ind. Eng. Chem., Anal. Ed.*, **14**, 719 (1942), quantitative removal of manganese is obtained when an acetic acid-acetate solution is electrolyzed.

[9] Thus Babko[14] found that alizarin S at *p*H 8.8 gives a complex containing 3 moles of alizarin S to 1 of aluminum, and that at *p*H 4.7 this ratio is 2 to 1. Likewise eriochromcyanin R, morin, and Pontachrome Blue Black R appear to form definite compounds.

are but slightly soluble and form colloidal suspensions of greater or less stability. The *p*H range in which the lakes can exist is approximately that in which aluminum hydroxide is capable of existence.

These lake reactions for the determination of aluminum can hardly be said to be of ideal type. Close control of the *p*H is necessary for reproducible results. The acidity affects not only the lake formation but also the color of the excess reagent. The colloidal nature of the reaction product introduces further complicating factors. The color may be slow to develop at room temperature. At higher temperatures a protective colloid must be used to stabilize the suspension. Neutral salts may affect the color intensity. Various metals, especially ferric iron and cupric copper, also form strongly colored lakes. Besides, many anions tend to reduce the color intensity by forming rather stable complexes with aluminum in the weakly acidic medium in which the reaction is usually carried out. Counterbalancing these disadvantages is the great sensitivity of the lake reactions and the rapidity of the procedures.

Some of the more common lake-forming reagents used for the determination of aluminum are ammonium aurintricarboxylate, eriochromcyanin, sodium alizarin sulfonate (alizarin S), and hematoxylin.[10] No one of these is so markedly superior (in the present state of our knowledge) that it eliminates the others from consideration. Aurintricarboxylate is much used in the U. S. A., whereas eriochromcyanin and alizarin sulfonic acid find greater favor in Europe. Because of the greater fund of information available on the aurin method, it has been given first place below. This should not be interpreted to mean that aurin is necessarily the best reagent available. In some respects it appears to be inferior to eriochromcyanin. The latter is said to give less color with ferric iron. Further study of the various lake-forming reagents for aluminum is greatly to be desired.

Some of the aluminum lakes are strongly fluorescent and a few fluorimetric methods have been proposed. In such methods the general difficulties associated with the use of lake formation are encountered together with others resident in fluorescence measurements. In special cases such fluorescence methods may have certain advantages.

What appears to be a promising method for aluminum is based on the extraction of aluminum hydroxyquinolate with chloroform. This method has the advantages of requiring less close control of *p*H, the use of a true solution, and a more stable product. However, many metals interfere. A chloroform solution of aluminum hydroxyquinolate fluoresces in ultra-

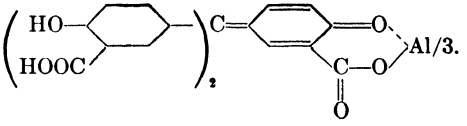
[10] For a comprehensive account of lake methods for the determination of aluminum see H. Fischer, A. von Unruh, and F. Kurz in Fresenius-Jander, *Handbuch der analytischen Chemie*, Part III, Vol. III, pp. 305–341, Springer, Berlin, 1942.

violet radiation, and use has been made of this behavior for the determination of traces of aluminum.

For a comparative study of various colorimetric methods for the determination of aluminum see a paper by Schams.[11]

A. The Aurintricarboxylate Method[12]

A dilute neutral or weakly acidic solution of ammonium aurintricarboxylate (aluminon) has a yellow-brown color (maximum intensity at *p*H 4), which becomes pale yellow when the solution is made basic; addition of mineral acid precipitates aurintricarboxylic acid.[13] In weakly acidic (acetate-acetic acid buffer) or neutral medium the reagent gives a deep red color with minute amounts of aluminum. The red color has been ascribed by Feigl to an internal complex salt having the formula:



In some procedures the solution is made basic with ammonia or an alkaline buffer before comparison. The writer concurs in the recommendation of Roller (*loc. cit.*) and others[14] that the determination be carried out in weakly acid solution. The advantages in making the solution basic after developing the color in acid medium are stated to be the weaker color of the excess reagent in basic medium and the possibility of reducing the interference of certain metals such as chromium. On the other hand the sensitivity of

[11] O. Schams, *Mikrochemie*, **25**, 16 (1938).

[12] For work on the aurin method before 1940 see: J. A. Scherrer and W. D. Mogerman, *J. Research Natl. Bur. Standards*, **21**, 105 (1938); O. B. Winter, W. E. Thrun, and O. D. Bird, *J. Am. Chem. Soc.*, **51**, 2721 (1929); P. S. Roller, *ibid.*, **55**, 2437 (1933); G. E. F. Lundell and H. B. Knowles, *J. Ind. Eng. Chem.*, **18**, 60 (1926); J. H. Yoe and W. L. Hill, *J. Am. Chem. Soc.*, **49**, 2395 (1927); V. C. Myers, J. W. Mull, and D. B. Morrison, *J. Biol. Chem.*, **78**, 595 (1928); D. F. Eveleth and V. C. Myers, *ibid.*, **113**, 449 (1936); K. B. Lehmann, *Arch. Hyg.*, **106**, 309 (1931); L. H. Lampitt, N. D. Sylvester, and P. Belham, *Analyst*, **57**, 418 (1932).

[13] The quality of the ammonium aurintricarboxylate is a factor of importance in the success of the colorimetric method. According to J. A. Scherrer and W. H. Smith, *J. Research Natl. Bur. Standards*, **21**, 113 (1938), some products on the market are not satisfactory because they are too strongly colored, yield unstable solutions, or produce "muddy" precipitates. A satisfactory product can be prepared according to directions given by these authors, and is, moreover, commercially available. Further studies on the preparation of aurintricarboxylic acid have been made by W. H. Smith, E. E. Sager, and I. J. Siewers, *Anal. Chem.*, **21**, 1334 (1949).

[14] A. P. Musakin, *Zavodskaya Lab.*, **9**, 507 (1940); L. M. Kul'berg and E. I. Rovinskaya, *ibid.*, **9**, 145 (1940); A. K. Babko, *J. Applied Chem. U. S. S. R.*, **12**, 560 (1939).

the reaction is diminished in basic medium, the lake then becomes less stable, and the precipitation of various metals takes place. Furthermore, the addition of ammonia must be made under controlled conditions to obtain reproducible results in the basic medium procedure. When a spectrophotometer or a filter photometer is used to measure the color intensity, the color of the excess aurin is of little moment.

A number of more or less different "acid medium" procedures for aluminum have been described. Satisfactory systematic studies are lacking. The first procedure given below has been selected on the basis of the statements of the authors that Beer's law is obeyed, the color of the lake is stable and reproducible, and no interference is produced by as much as 10 mg. of calcium, magnesium, and phosphorus pentoxide, or 1 mg. of the common heavy metals (not including iron).[15] More information on the effect of foreign substances would be desirable. The lake is formed in an acetate-buffered solution at 100° and the color of the excess reagent is diminished by the addition of an ammonium borate solution to give a *p*H of about 6. This last step may not actually be necessary.

The second procedure below provides a simple means of preventing the interference of ferric iron, namely by reducing it to the ferrous state by the use of mercaptoacetic (thioglycolic) acid. Ferric iron gives a transient blue color (ferric mercaptoacetate) which quickly fades, leaving a colorless solution in which iron is present wholly in the divalent form. Up to 10 γ of aluminum in 5 ml. of solution can be accurately determined in the presence of as much as 0.2 mg. of iron, more than 2 mg. of magnesium, and 0.2 mg. of phosphate ion. Chromium and the rare earths must be removed if their weight exceeds $^1/_8$ that of aluminum.

Special Solutions for Procedure A

Ammonium aurintricarboxylate, 0.2 per cent aqueous solution prepared from a tested product. Allow the solution to stand a few days before use.

Gum arabic, 5 per cent aqueous solution.

Buffer, 156 g. of ammonium acetate and 108 g. of ammonium chloride in 1 liter.

Ammonium borate. Dissolve 93 g. of boric acid in 1 liter of 1 *N* ammonia, filter, and dilute to 0.8 *N* alkalinity (as determined by titration with hydrochloric acid).

Standard aluminum solution, 10 γ of Al per ml. in 1 *N* hydrochloric acid. Prepare from the pure metal or uneffloresced potassium alum ($KAl(SO_4)_2 \cdot 12H_2O/Al = 17.6$).

Special Solutions for Procedure B

Aluminum reagent, 0.75 g. of ammonium tricarboxylate, 15 g. of gum acacia, 200 g.

[15] N. Strafford and P. F. Wyatt, *Analyst*, **72**, 54 (1947). For other recent aurin procedures, see pp. 156–158. These have been developed particularly with applications to special materials in mind. The method of Makepeace and Craft (p. 156) is similar to the above procedure, but simpler. Beer's law is not followed however. See also A. L. Olson, E. A. Gee, and V. McLendon, *Ind. Eng. Chem., Anal. Ed.*, **16**, 169 (1941).

of ammonium acetate, and 190 ml. of hydrochloric acid dissolved separately in water, mixed, filtered, and made up to 1500 ml.

Mercaptoacetic acid, 1 ml. in 100 ml. of water.

§ Procedure A

If iron and copper have been removed by cupferron-chloroform extraction as described on p. 143, transfer the solution to a 100 ml. Erlenmeyer flask and boil to expel chloroform. Cool to room temperature, add 1 drop of methyl red, and then 10 *N* ammonia to make the solution just alkaline. Add 5 *N* hydrochloric acid dropwise until the solution is acid and then 5.0 ml. in excess, followed by 2 drops of saturated bromine water to destroy the indicator. (If the indicator color does not disappear, the excess of cupferron has not been properly extracted.) Finally add 0.5 ml. of 10 per cent hydroxylamine hydrochloride solution to reduce the excess of bromine and dilute to 100 ml. in a volumetric flask. It is advisable to test this solution for iron by adding 2 ml. of 1 *M* sodium citrate, 1 ml. 10 per cent mercaptoacetic acid and 5 ml. of 10 *N* ammonia, to 50 ml. No pink color should appear.

Transfer 20 ml. of the mixed solution to a 100 ml. Erlenmeyer flask, add 30 ml. of water, 1.0 ml. of gum arabic solution, 5.0 ml. of ammonium acetate buffer, and 2.0 ml. of ammonium aurintricarboxylate. Mix, heat to boiling, and boil gently for 5 minutes. Cool to room temperature, add 4.0 ml. of ammonium borate solution, mix, and dilute to 50 ml. Allow to stand for not less than 5 minutes and determine the transmittancy at 525 mμ or with a green filter. Use a 1 cm. cell for the range 10–70 γ of aluminum, and a 4 cm. cell for 0–10 γ. If the amount of aluminum is greater than 70 γ take a smaller aliquot, and add enough hydrochloric acid to make the total amount present 1.0 ml. of 5 *N*. Establish the standard curve by taking 0, 10, 20, ... 70 γ of aluminum, adding 1.0 ml. of 5 *N* hydrochloric acid, diluting to 30 ml. and proceeding as described.

TABLE 23

RELATION BETWEEN ALUMINUM CONCENTRATION AND EXTINCTION IN AURIN METHOD FOR ALUMINUM[15]

Concentration of Al, p.p.m.....	0.2	0.4	0.6	0.8	1 0	1.2	1.4
Extinction (Ilford green No. 604 filter), 1 cm.....	0.14	0.285	0.43	0.57	0.72	0.86	1.00

§ Procedure B[16]

Transfer the sample solution, containing not more than 10 γ of aluminum in 3 ml., to a 15 × 130 mm. Pyrex test tube graduated at 5 ml. The sample

[16] E. M. Chenery, *Analyst*, **73**, 501 (1948).

solution should be only slightly acidic so that the final solution will have a *p*H not less than 4. Add 0.2 ml. of mercaptoacetic acid solution, mix, and follow with 1 ml. of aluminon reagent. Make up to 5 ml., mix, and heat for exactly 4 minutes in a boiling water bath. Allow to cool slowly. After 1.5–2 hours or longer make up to the mark again and obtain the transmittancy of the solution with the aid of a green filter. The lake is stable for 24 hours.

TABLE 24

DETERMINATION OF ALUMINUM WITH AURINTRICARBOXYLIC ACID IN THE PRESENCE OF MERCAPTOACETIC ACID TO REDUCE FERRIC IRON

(4.75 γ of Al taken in each case)

Fe present, γ	0	50	100	200	500
Al found, γ	4.75	4.75	4.8	5.0	5.5

TABLE 25

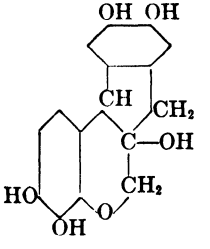
SENSITIVITY OF REACTION OF AURINTRICARBOXYLIC ACID WITH VARIOUS METALS[a]

Metal	Limiting concentration, mole/l.	
	*p*H 3.0	*p*H 4.5
Zn	10^{-4}	10^{-3}
Ti	$10^{-3.3}$	10^{-2}
Th	$10^{-4.3}$	10^{-4}
Ga	$10^{-2.3}$	10^{-4}
Sc	10^{-5}	10^{-4}
In	Negligible color at 10^{-2}	
Al	10^{-1}	10^{-4}–10^{-5}
Be	—	$10^{-3.5}$

[a] G. Charlot, *Anal. Chim. Acta*, 1, 223 (1947). Sensitivity values pertain to qualitative conditions: a few drops of solution in a micro test tube.

B. HEMATOXYLIN METHOD[17]

Hematoxylin



[17] H. W. Knudson, V. W. Meloche, and C. Juday, *Ind. Eng. Chem., Anal. Ed.*, 12, 715 (1940); W. D. Hatfield, *Ind. Eng. Chem.*, 16, 233 (1924); J. L. Steenkamp, *J. S. African Chem. Inst.*, 13, 64 (1930); G. U. Houghton, *Analyst*, 68, 208 (1943); N. Strafford, *Analyst*, 68, 319 (1943). G. Ginsberg, *Angew. Chem.*, 51, 663 (1938), had no success with the hematoxylin method and regards it as unsuitable for quantitative purposes.

gives a violet-purple lake with aluminum in slightly basic solution, the optimum *p*H range being 7–8.5. On acidification (*p*H *ca.* 4.5) the lake is stabilized and the color of the excess dye changes from red to yellow. Ferric iron under the same conditions yields a bluish lake and interferes seriously. The absorption curves of the aluminum and iron lakes overlap but the absorption maxima are sufficiently far apart to enable aluminum to be determined in the presence of a comparable amount of iron by measurement of the optical densities of the solution at wave lengths corresponding to the two absorption maxima (see p. 70).

The suspensions of both the aluminum and iron lakes follow Beer's law, so that the following expression holds:

$$C_{Al} = \frac{K^A_{Fe}E^B - K^B_{Fe}E^A}{K^A_{Fe}K^B_{Al} - K^B_{Fe}K^A_{Al}}$$

where C_{Al} is the aluminum concentration, E extinctions, K constants, and A and B refer to the wave lengths at which the extinction measurements are made. The values of K^A_{Al}, K^A_{Fe}, K^B_{Al}, and K^B_{Fe} are found by making calibration curves for the aluminum and iron for each filter (if such are used) and determining the slopes of the respective lines.

Filters with maximum transmission at 540 mμ (corresponding to the maximum in the aluminum absorption curve) and 660 mμ (corresponding to the iron maximum) are suitable for differential spectral separation of the two metal lakes. Transmission of light below 500 mμ must be avoided because absorption by the excess hematoxylin becomes appreciable at wave lengths shorter than this.

The effect of other metals on the determination of aluminum by this method has not been systematically investigated. It is known that calcium and magnesium are without appreciable effect, at least in low concentrations.

The color of the aluminum-hematoxylin solutions changes quite rapidly on standing and comparisons or measurements should be made immediately after developing the color. Aside from the possibility it offers of determining comparable amounts of aluminum and iron at the same time it may be doubted that hematoxylin is as good a reagent as some of the other lake formers that have been proposed.

Reagents

Acetic acid, 35 per cent. Prepare by dilution of glacial acetic acid (99 per cent).

Ammonium carbonate. Dissolve 50 g. of ammonium carbonate monohydrate in 200 ml. of water. Prepare fresh each 3 days, and keep cool.

Hematoxylin solution. Dissolve 0.1 g. of C. P. hematoxylin in 100 ml. of hot water and dilute to 200 ml. The solution is stable for 2–3 weeks.

Starch solution. Dissolve 2 g. of soluble starch in 100 ml. of boiling water.

§ Procedure

The combined content of aluminum and ferric iron should not exceed about 0.3 p.p.m., and the aluminum content should be at least 0.05 p.p.m.

To 50 ml. of neutral sample add 1 ml. of starch solution and 1.0 ml. of hematoxylin solution, mix, and then add 1.0 ml. of ammonium carbonate solution. Mix, allow the solution to stand for 10 minutes, and add 1 ml. of acetic acid so as to obtain a mixture having a *p*H of 4.5–4.6. Remove excess carbon dioxide by shaking. Transfer the solution to an absorption cell and immediately obtain the optical density of the solution using filters giving maximum transmission at 540 and 660 mμ. Substitute the values obtained in the equation above, and solve for the aluminum concentration.

C. The Pontachrome Method (Fluorescence)[18]

Pontachrome Blue Black R (the sodium or zinc salt of 4-sulfo-2-hydroxy-α-naphthalene-azo-β-naphthol)[19] at an optimum *p*H of 4.8–4.9 gives a red fluorescent compound with aluminum in which the ratio of dye to aluminum is 2:1. The complex can be extracted with *n*-amyl alcohol, in which it also shows strong fluorescence. The fluorescence intensity increases to a maximum and then decreases as the concentration of reagent is increased. Almost an hour is required for the full development of fluorescence at room temperature. The relation between aluminum concentration and fluorescence intensity is very nearly linear up to 0.5 p.p.m. of aluminum; above 1 p.p.m. the fluorescence becomes constant under the conditions given below. The sensitivity of the reaction is approximately 0.01 p.p.m. of aluminum (about 0.5 γ Al in 50 ml.). The fluorescence strength of weak solutions decreases on irradiation.

Even a trace of iron destroys the aluminum fluorescence. Iron can conveniently be removed by electrolysis with a mercury cathode. Copper, cobalt, and various other interfering elements can be removed in the same way. Titanium, which is not removed by electrolysis, causes low results (40 γ of titanium produces an error of about 20 per cent in the determination of 10 γ of aluminum). Vanadium (V) in amounts four times as great as aluminum interferes more seriously than titanium, but zirconium is without effect. The possible effect of phosphate is not mentioned.

[18] A. Weissler and C. E. White, *Ind. Eng. Chem., Anal. Ed.*, **18**, 530 (1946). These authors also investigated Pontachrome Violet SW as a fluorescence reagent for aluminum and found that it could be used to determine even a few tenths of a microgram of the element, but on the whole it was not as suitable as Pontachrome Blue Black R. For other fluorescence reagents for aluminum that have been used qualitatively, see J. A. Radley, *Analyst*, **68**, 369 (1943), and M. Bourstyn, *Bull. soc. chim.*, **8**, 540 (1941).

[19] Color Index 202. Also known as Superchrome Blue Black.

The use of Pontachrome has been worked out specifically for the determination of aluminum in steels, bronzes, and minerals and the directions will be found under "Applications," p. 155.

D. The 8-Hydroxyquinoline Method

A promising method for the direct[20] determination of aluminum is based on the extraction of aluminum hydroxyquinolate by chloroform and photometry of the resulting yellow extract. Aluminum hydroxyquinolate in chloroform absorbs most strongly at approximately 395 mμ; 8-hydroxyquinoline alone in chloroform absorbs strongly below 370 mμ. The method has been investigated by Gentry and Sherrington,[21] who give the following particulars. Complete extraction of aluminum is obtained by shaking 50 ml. of the buffered solution (*p*H 8.9) with one 10 ml. portion of a 1 per cent solution of 8-hydroxyquinoline in chloroform; reagent solutions weaker than 0.5 per cent do not provide complete separation in one extraction. So far as *p*H is concerned, extraction of aluminum is complete with 1 per cent reagent solution in the range 4.5–*ca.* 6.5 (acetate buffer) and *ca.* 8–11.5 (ammonia buffer). In the *p*H interval 6.5–8 extraction is incomplete, which perhaps is to be explained by the formation of aluminum hydroxide before aluminum ion can react with the hydroxyquinoline in the chloroform. Hydroxyquinoline alone is extracted to the maximum extent near a *p*H of 7. At *p*H 9, the standard deviation in the determination of 10 to 50 γ of aluminum was found to be 0.5 γ.

Qualitative experiments with about 20 mg. of various metal salts in 25 ml. of aqueous solution shaken with 5 ml. of chloroform reagent solution showed no extraction of tungsten, calcium, or chromium (III) at either *p*H 5 or 9. Zirconium, molybdenum (VI), and vanadium (V) react only in the acidic medium. Beryllium, magnesium, manganese, cerium (III), neodymium, and praseodymium do not react at *p*H 5 but do react at *p*H 9. The color of the magnesium extract fades and a precipitate is formed on continued shaking.[22] The metals reacting at both *p*H 5 and 9 are anti-

[20] Aluminum can be determined indirectly with 8-hydroxyquinoline by converting the hydroxyquinoline in the washed precipitate into an azo dye (see Alten *et al.*, footnote 45, p. 114 and Schams[11]) or reducing phosphomolybdotungstic acid with it (Teitelbaum, p. 115). More simply the transmittancy of the mineral acid solution of the precipitate can be measured at 252 or 365 mμ (absorption by oxinium ion).

[21] C. H. R. Gentry and L. G. Sherrington, *Analyst*, **71**, 432 (1946). For a general discussion of extraction of hydroxyquinolates by chloroform, see p. 117 of this book. Fluorimetric determination of aluminum following chloroform extraction of its hydroxyquinolate has been described by J. W. Tullo, W. J. Stringer, and G. A. F. Harrison, *Analyst*, **74**, 296 (1949).

[22] The authors explain this behavior of magnesium (and also of zinc and cadmium) by assuming that the anhydrous hydroxyquinolate is first extracted by chloroform and that it then reacts with water to give the insoluble dihydrate.

mony, bismuth, cadmium, cerium (IV), cobalt, copper, iron (II and III), lead, mercury (I and II), nickel, tin (II), titanium, uranium, and zinc. Chloroform solutions of the hydroxyquinolates of cadmium and zinc give precipitates on continued shaking. Chloride prevents the reaction of mercury (I and II).

It was found possible to determine 50 γ of aluminum in the presence of 0.1 g. of chromium, magnesium, beryllium, and manganese at *p*H 5, and in the presence of much tungstate and molybdate at *p*H 9. Acetate, chloride, nitrate, and sulfate do not have any effect on the extraction of aluminum, but fluoride interferes badly in both acidic and basic medium; tartrate in relatively large amounts also interferes, whereas phosphate interferes to a moderate extent (0.15 g. of disodium phosphate gave an apparent aluminum content of 46.5 γ, when 50.6 γ was present). By the use of cyanide in basic solution (see below), 50 γ of aluminum can be successfully determined in the presence of 0.1 g. of copper, nickel, cobalt, zinc, or cadmium. Interference by iron is prevented by converting it into ferrocyanide (thioglycolic acid was found to be ineffective as complex former). Preliminary experiments appear to show that moderate amounts of iron can be separated by first extracting the sample solution with the chloroform reagent at *p*H 2.

The following directions are based on statements of the authors.

§ Procedure

In the absence of interfering metals, buffer the sample solution (10–50 γ of aluminum) to a *p*H of 5 or 9 as the case requires (see above), dilute to 50 ml. and shake for 3 minutes in a separatory funnel with 10 ml. of a 1 per cent solution of 8-hydroxyquinoline in pure chloroform (purify the latter by shaking with an aqueous solution 2 *M* in ammonia and in ammonium chloride). Run the chloroform extract into a small stoppered flask containing a gram of anhydrous sodium sulfate and shake to remove droplets of water. Transfer the chloroform solution to an absorption cell and obtain the transmittancy at 395 mμ or in the range 385–410 mμ. Prepare the standard curve by taking appropriate amounts of aluminum and carrying through the procedure exactly as with the unknown. A close approximation to a linear relationship between aluminum concentration in the chloroform and the extinction should be obtained up to 5 p.p.m. or more with sufficiently monochromatic radiation. (The authors used a mercury vapor lamp in conjunction with a Chance No. 8 (OVI) and Wratten No. 2 filter.)

In the presence of as much as 0.1 g. of copper, nickel, cobalt, zinc, or cadmium, prepare a solution containing 2 g. of ammonium nitrate, 1 g. of

potassium cyanide, and 1 ml. of 1:1 ammonium hydroxide in a final volume of 50 ml. and extract with 10 ml. of the chloroform reagent.

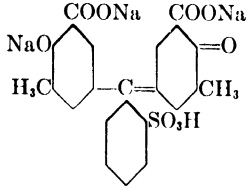
In the presence of iron (up to 25 mg. as metal), add 2 g. of potassium cyanide to the solution, warm at 50° for 3 minutes, and add 10 ml. of 10 per cent sodium sulfide solution. Transfer the cooled solution to a separatory funnel, dilute to 50 ml., add 2 g. of ammonium nitrate, and extract with the chloroform reagent.

Determination of aluminum in tungstic oxide. Fuse 6.3 g. of tungstic oxide (equivalent to 5 g. of tungsten metal) with 10 g. of sodium carbonate. Leach the melt with water and dilute to 500 ml. in a volumetric flask. Transfer a 50 ml. aliquot to a 100 ml. beaker, add 1 g. of potassium cyanide and 0.5 g. of sodium sulfide. Warm at 70° for 3 minutes, cool, and transfer to a separatory funnel with a minimum of water. Add 3 g. of ammonium nitrate, shake to dissolve, and extract with chloroform reagent solution as described above.

E. Other Methods

1. Eriochromecyanin-R[23]

This reagent



yields a red-violet lake with aluminum in acetate-buffered medium (*p*H *ca.* 3.8–6). It appears to be at least as good a reagent as the other lake formers. A recent procedure[24] calls for the development of the color at *p*H 5.4 and 70° in the presence of gum arabic. Phosphate ion does not cause low results if its amount is less than about 30 times that of aluminum. Ferric iron leads to positive errors if its concentration is greater than 2.5 p.p.m. in the solution. The concentration of magnesium should not exceed 2.5 p.p.m., else high results are obtained. Relatively much manganese, zinc, nickel, and copper may be present (the latter up to 25 p.p.m.). Chromic ion gives high results.

[23] F. Alten, W. Weiland, and E. Knippenberg, *Z. anal. Chem.*, **96**, 91 (1934); F. Alten, B. Wandrowski, and E. Hille, *Angew. Chem.*, **48**, 273 (1935); T. Millner, *Z. anal. Chem.*, **113**, 83 (1938); T. Millner and F. Kunos, *ibid.*, **113**, 102 (1938); F. Richter, *Z. anal. Chem.*, **126**, 438 (1944); **127**, 113 (1944).

[24] W. E. Thrun, *Anal. Chem.*, **20**, 1117 (1948).

2. Alizarin S (Sodium Alizarinsulfonate)[25]

This is a fairly popular reagent for aluminum. A procedure will be found on p. 162. Alizarin has also been used for the determination of aluminum.[26]

3. Quinalizarin (1,2,5,8-Tetrahydroxyanthraquinone)[27]

This is another lake-forming reagent; it has not been investigated in any detail.

4. Morin[28] *and Quercetin*[29]

Fluorescence methods have been based on the use of these compounds.

5. Cupferron[30]

A nephelometric and turbidimetric reagent of slight importance.

III. Applications

A. Steels

The first procedure below is fluorimetric, the second colorimetric.

1. Pontachrome Blue Black R as Reagent[18]

This method has specifically been shown to permit the determination of as little as 0.001 per cent of aluminum; the upper limit is about 1 per cent. Titanium and vanadium do not interfere (p. 151), apparently because their carbides do not dissolve in dilute sulfuric acid. Bureau of Standards steels containing 0.001 and 0.022 per cent aluminum gave the respective average values 0.001 and 0.022 per cent, the individual values in the latter case varying from 0.021 to 0.024 per cent.

[25] F. W. Atack, *J. Soc. Chem. Ind.*, **34**, 641, 936 (1915); D. S. Savchenko, *Zavodskaya Lab.*, **1933**, No. 2, p. 23; J. H. Yoe and W. L. Hill, *J. Am. Chem. Soc.*, **50**, **748** (1928); F. P. Underhill and F. I. Peterman, *Am. J. Physiol.*, **90**, 1 (1929); A. Stock, D. Praetorius, and O. Preiss, *Ber.*, **58**, 1571 (1925); J. Joshii and T. Jimbo, *Science Repts. Tôhoku Imp. Univ.*, **21**, 65 (1932); A. P. Musakin, *Z. anal. Chem.*, **105**, **351** (**1936**). Consult especially the paper of Musakin. A more recent procedure is described by C. J. Barton, *Anal. Chem.*, **20**, 1068 (1948), who determines the transmittancy of the lake at 370 mμ to minimize the effect of ferric iron.

[26] G. Gad, *Kl. Mitt. Wasser, Boden, Lufthyg.*, **15**, 126 (1936); G. Gad and K. Naumann, *Gas- und Wasserfach*, **80**, 58 (1937). The reagent is used for aluminum in water; iron up to 1 mg. per liter is made harmless with sodium thiosulfate.

[27] I. M. Kolthoff, *Chem. Weekblad*, **24**, 447 (1927); *J. Am. Pharm. Assoc.*, **17**, **300** (1928).

[28] C. E. White and C. S. Lowe, *Ind. Eng. Chem. Anal. Ed.*, **12**, 229 (1940).

[29] A. L. Davydov and U. S. Devekki, *Zavodskaya Lab.*, **10**, 134 (1941).

[30] L. de Brouckère and E. Belcke, *Bull. soc. chim. Belg.*, **36**, **288** (1927).

§ Procedure (Acid-soluble Aluminum)

Dissolve a 1 g. sample of steel (Al < 0.1 per cent) in 25 ml. of 1:9 sulfuric acid and dilute to 500 ml. without filtration. Electrolyze a 10 ml. aliquot of the solution for 1 hour in a small motor-stirred Melaven cell (p. 159) with a current of 0.5 ampere or slightly less. Run the solution and rinsings into a 50 ml. volumetric flask containing 5.0 ml. of 10 per cent ammonium acetate and 1.50 ml. of 0.1 per cent Pontachrome Blue Black R (95 per cent alcohol solution, allowed to stand a few days before use). Dilute to the mark and allow to stand for at least one hour. Compare the fluorescence against aluminum standards treated similarly (including electrolysis), using a fluorimeter. A Corning filter No. 5874 may be used to isolate the energizing radiation, and sheets of red plastic, transmitting above 600 mμ, to isolate the fluorescent radiation.

For the determination of acid-insoluble aluminum in steels, see the original.

2. *Aurintricarboxylate as Reagent*

Iron can be removed by electrolysis with a mercury cathode according to the directions given above under A1. The possible interference of

TABLE 26

INTERFERENCE OF ELEMENTS FOUND IN STEEL ON ALUMINUM DETERMINATION BY AURINTRICARBOXYLATE METHOD[31]

	Concentration of element, mg./ml.	Error, γ Al/ml.
Mn (II)	0.1	+0.04
P (orthophosphate)	0.0025	−0.08
Ni	0.25	+0.12
Cr (VI)	0.1	+0.4
Mo (VI)	0.15	+0.08
V (V)	0.01	+0.02
Cu (II)	0.0125	+0.12

phosphorus should be borne in mind. Iron can also be removed by extraction of ferric chloride with isopropyl ether; phosphorus is partly removed with the iron. The procedure following makes use of this separation.[31] This procedure is intended for aluminum steels (0.04–1.5 per cent Al) but is included here since the lower limit of the method falls in the trace range;

[31] Makepeace and Craft, *Ind. Eng. Chem., Anal. Ed.*, **17**, 207 (1945). Ether extraction has also been applied by P. Klinger, *Arch. Eisenhüttenw.*, **13**, 21 (1939–40), who tested various separation methods. For the use of eriochromecyanin as reagent for aluminum in steel see W. Koch, *ibid.*, **12**, 69 (1939).

with modification it can no doubt be applied to much smaller amounts. According to the authors the amount (0.02 mg.) of iron left after three extractions with isopropyl ether produces a color equivalent to 0.0016 per cent aluminum in the sample (0.5 g.). The ether separation therefore is not satisfactory when very small amounts of aluminum are involved. The effect of other elements found in steel is shown in Table 26.

Special Solutions

Ammonium aurintricarboxylate, 0.10 per cent. Dissolve 0.10 g. of the salt in water, add 10 ml. of 10 per cent benzoic acid in methyl alcohol and dilute to 100 ml.

Gelatin, 1 per cent. Dissolve 1 g. of Knox gelatin in hot water, cool, add 10 ml. of 10 per cent benzoic acid in methyl alcohol and dilute to 100 ml.

Buffer solution. Mix 470 ml. of 15 *M* ammonium hydroxide and 430 ml. of glacial acetic acid, cool to room temperature, and add more acid or base as required to give a *p*H of 5.25–5.35 when diluted 1 to 20. Dilute to 1 liter.

Composite reagent solution. Mix equal volumes of each of the above solutions. (The composite may be prepared from freshly dissolved aurin, but then the mixture should not be used until after 3 days.)

§ Procedure

Dissolve 0.5 g. of steel in 5 ml. of 60 per cent perchloric acid and 5 ml. of 1:1 nitric acid and evaporate the solution almost to dryness. Add 25 ml. of water and 10 ml. of concentrated hydrochloric acid, heat to boiling, and filter through a rapid paper. Wash with hot dilute hydrochloric acid. Evaporate the filtrate and washings to 20 ml. or less, cool to room temperature, and transfer to a separatory funnel. Dilute to 20 ml. with 1:1 hydrochloric acid if necessary. Add 10 ml. of concentrated hydrochloric acid and 30 ml. of isopropyl ether, shake cautiously, cooling if necessary to keep the temperature below 30°, and release the pressure. Finally shake vigorously for 15 seconds. Allow the layers to separate completely and draw off the aqueous layer into a second separatory funnel. Wash the ether layer with 2 ml. of 2:1 (8 *N*) hydrochloric acid and add the latter to the aqueous solution. Repeat the extraction twice, using 10 ml. of ether and washing with 1 ml. of the diluted hydrochloric acid. The third portion of ether should be colorless.

Carefully boil the aqueous solution to expel ether and then add 5 ml. of 60 per cent perchloric acid and 5 ml. of 6 *N* nitric acid. Evaporate to fumes of perchloric acid and continue the fuming until any chromium is oxidized. Cool and add 25 ml. of water. If any silica separates, filter it off. Neutralize the solution with pure ammonium hydroxide, using litmus paper as indicator. If a precipitate forms add just enough 1:1 hydrochloric acid to dissolve it. Dilute to a suitable volume and take for analysis a 5 ml. aliquot containing 10 to 40 γ of aluminum. Add 15 ml. of the com-

posite reagent and immerse the vessel (tube)[32] in a water bath (90–100°) for 10 minutes; then remove and allow to stand at room temperature for approximately 10 minutes. Dilute the solution to 100 ml. with water and determine the transmittancy at 525 mμ.

B. Non-Ferrous Alloys

1. Pontachrome Blue Black R as Reagent (Fluorescence)[18]

The following directions are for the determination of aluminum in bronze but no doubt the procedure can be extended to other non-ferrous alloys. Reliable results (*ca.* ±10 per cent) have been obtained in the thousandths and hundredths range of aluminum percentage, but the method can be used for much larger amounts also.

§ Procedure

Dissolve a 1 g. sample (Al < 0.1 per cent) in 10 ml. of 1:1 nitric acid in a beaker, add 20 ml. of 1:1 sulfuric acid, and evaporate down to copious fumes of sulfuric acid. Cool, wash down the sides of the beaker with 10–15 ml. of water, and again evaporate to strong fumes. Dilute the cooled solution with 100 ml. of water, add 10 per cent sodium hydroxide until just neutral to methyl red, and add 25 ml. of 1:9 sulfuric acid. Dilute to 500 ml. in a volumetric flask. Take a 10 ml. aliquot and electrolyze for one hour in a small motor-stirred Melaven cell (p. 159). Draw off the electrolyzed solution into a 50 ml. volumetric flask containing 5.0 ml. of 10 per cent ammonium acetate solution and 1.50 ml. of 0.1 per cent Pontachrome Blue Black R (95 per cent alcohol solution, allowed to stand a few days before use). Dilute to the mark and allow to stand for at least 1 hour. Then measure the fluorescence and compare with that of standards prepared similarly and simultaneously (*cf.* IIIA1).

2. Aurintricarboxylate as Reagent

The following procedure[33] was worked out for the determination of aluminum in bearing metals, solders, etc., but it should have more general applicability. Most of the interfering metals are removed by electrolysis with a mercury cathode.

§ Procedure

Dissolve a suitable weight of sample (0.01 to 0.10 mg. of Al) in an appropriate acid; sulfuric acid may often be used, but if another acid is re-

[32] It should not be etched or scratched, else erratic results may be obtained. Clean with chromic acid solution.

[33] J. A. Scherrer and W. D. Mogerman, *J. Research Natl. Bur. Standards*, 21, 107 (1938).

TABLE 27

DETERMINATION OF ALUMINUM IN NON-FERROUS ALLOYS WITH ALUMINON AFTER REMOVAL OF INTERFERING ELEMENTS BY ELECTROLYSIS WITH A MERCURY CATHODE[a]

Material	Al added mg.	Al found mg.
Antifriction metal (63.7% Pb, 20.5% Sn, 14.0% Sb, 1.6% Cu), 1 g. sample	None	None
	0.03	0.03
	0.05	0.05
	0.08	0.08
Bearing metal (79% Pb, 11% Sn, 10% Sb), 1.0 and 0.5 g. samples	None	<0.001
	0.10	0.10
Solder (50% Sb, 50% Sn), 1.0 g. sample	None	None
	0.05	0.05[b]

[a] Figures from Scherrer and Mogerman.[33]

[b] Lead sulfate filtered off before electrolysis.

quired, convert the metals to sulfates by gentle fuming with sulfuric acid, taking care that no nitric or hydrochloric acid remains. Dilute the solution, containing a minimum of sulfuric acid (not more than 5 ml.), to approximately 25 ml. Filter off any lead sulfate and wash the filtrate into a modified Melaven cell[34] provided with a motor stirrer and containing about 50 ml. of mercury.[35] Electrolyze with the highest current that will not cause boiling of the solution or excessive spraying (ordinarily 3 to 5 amperes). Stir the mercury and the solution vigorously during the electrolysis. One gram of copper or iron can usually be deposited in 35 to 45 minutes, and a like amount of tin, antimony, lead, or zinc in 2 to 3 hours. Care should be taken to wash down any spray that collects on the walls of the cell.

When the electrolysis is complete, separate the mercury and the aqueous solution while keeping the current at least partially on. If loose particles of amalgam float in the solution remove them by filtration. The volume of the solution should now be 40 to 75 ml.

[34] *Ind. Eng. Chem., Anal. Ed.*, 2, 180 (1930).

[35] The apparatus consists of a cylindrical electrolysis vessel (20 cm. in height and 3.5 cm. in diameter) provided at the bottom with a double-bored stopcock, one bore of which connects by means of rubber tubing with a similar slightly smaller vessel containing mercury; the other bore connects with a glass tube through which the solution is led off at the end of the electrolysis. The stirrer for the electrolysis vessel has two propellers, one dipping into the mercury and the other into the aqueous solution. A platinum wire 0.1 cm. in diameter serves as anode; it is dipped about 12 cm. into the solution. For a description of a larger electrolysis cell see M. H. Steinmetz, *Ind. Eng. Chem., Anal. Ed.*, 14, 109 (1942).

Add 5 ml. of concentrated hydrochloric acid, 5 ml. of glacial acetic acid, and 5 ml. of 0.2 per cent ammonium aurintricarboxylate solution. Next add ammonium hydroxide (or ammonium hydroxide saturated with ammonium carbonate if alkaline earths or rare earths are present) while stirring, until the cloudy appearance of the dye disappears and the solution becomes clear, but is still acid to litmus and strongly colored. Place a piece of litmus paper against the wall of the beaker, and while constantly stirring add ammonium hydroxide (or ammonium hydroxide-ammonium carbonate) at the rate of approximately 1 drop every 2 seconds until 2 ml. have been added; then add 1 drop every 3–4 seconds until the litmus paper becomes blue. Next add 5 ml. of glacial acetic acid, allow to stand for 10 minutes, and neutralize the solution as previously described. Finally add 5 ml. of ammonium hydroxide (or ammonium hydroxide-ammonium carbonate). Allow the solution to cool to room temperature and compare against standard solutions similarly prepared.

Notes. 1. A number of metals interfere, especially iron and beryllium which give red lakes also. The interference of these metals cannot be prevented and they must be removed. Certain elements will not interfere if ammonium carbonate is used with, or in place of, ammonium hydroxide in the procedure. These include the alkaline earth metals in moderate concentrations (10 mg. per 100 ml.), scandium, rare earths, zirconium (10 mg. per 100 ml.), thorium, and chromium. Magnesium in a concentration of 10 mg. per 100 ml. gives a pink color not discharged by ammonium carbonate, but in lower concentrations its effect can be prevented by the use of ammonium carbonate. Gallium in low concentrations (0.1 mg. per 100 ml.) gives no color, but at higher concentrations (2 mg. per 100 ml.) yields a red color even in the presence of ammonium carbonate. Indium and thallium in amounts up to 2 mg. or slightly more give no reaction. Quadrivalent vanadium alone (up to 2 mg. per 100 ml.) gives no color, but when as little as 0.1 γ of aluminum is present a deep color develops followed by the formation of a precipitate, which however dissolves in the course of 15 minutes, leaving the solution the same color as a blank. Quinquevalent vanadium in small amounts (1 mg.) does not interfere, but larger quantities give a color.

Metals such as titanium, molybdenum, tungsten, uranium, zinc, cadmium, lead, germanium, arsenic, etc. are without effect, at least in small amounts (*ca.* 1 mg.).

Ruthenium yields a colored solution, platinum gives a yellow chloroplatinate, and gold is reduced to the metal.[36]

2. Nitric acid, sulfur dioxide, hydrogen sulfide, and fluoride bleach the color, but all these can be removed by evaporating to fumes with sulfuric acid. Phosphoric acid in large amounts reduces the color intensity but below 25 mg. in 100 ml. of solution has little effect.

3. The method has not been studied photometrically.

C. Bio Materials

The following directions for the isolation of aluminum are those of

[36] G. E. F. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis.* Wiley, New York, 1938, p. 175.

Cholak, Hubbard, and Story.[37] These authors use alizarin S for the determination of aluminum.

§ Procedure

Take a suitable weight of sample (5 g. or less of blood, 5 to 50 g. of tissue, 100 ml. or less of urine) and destroy organic matter by acid oxidation (*cf.* p. 384) or by ashing. In the latter procedure use a platinum dish and ignite in a muffle furnace at about 500°C. until all or nearly all of the carbonaceous material has been destroyed. Treat the ash with 5 ml. (or more if judged necessary) of concentrated hydrochloric acid and 10 ml. of water, and evaporate just to dryness. Add 10 to 20 ml. of 1:5 hydrochloric acid, keep near the boiling point for 10 minutes, centrifuge or filter through a very small quantitative paper which has been washed with dilute hydrochloric acid, and wash the residue with a little dilute hydrochloric acid. Transfer the residue or the paper to a platinum crucible, ignite if necessary, and add a little sulfuric and hydrofluoric acid. Evaporate to dryness, add a few drops of dilute sulfuric acid, and evaporate to fumes to expel all hydrofluoric acid. Add a milliliter or two of dilute hydrochloric acid and warm. A clear solution should be obtained; combine it with the main solution.

Add 1 mg. of iron as any ferric salt[38] to the solution of the decomposed sample (volume of about 25 ml.) together with 1 ml. of saturated ammonium acetate and 200 mg. of diammonium phosphate. Then add 5 drops of 0.1 per cent aqueous bromcresol green indicator solution. Next add ammonium hydroxide until the *p*H of the solution is 4.2 (compare against a buffer). Heat on the steam bath for one-half hour and collect the precipitate by filtration (use a porous porcelain or sintered glass filter crucible) or by centrifuging. Wash the ferric-aluminum phosphate precipitate with small portions of warm water.

Dissolve the phosphate precipitate in 5 ml. of warm 1:10 sulfuric acid and dilute to 10 ml. with water. If the liquid contains any separated silica remove the latter by centrifuging or filtering. Transfer the clear solution to a separatory funnel and dilute to 20–25 ml. Add 2 ml. of freshly prepared 6 per cent aqueous cupferron solution. Mix and allow to stand for a few minutes. Add 10 ml. of a 1:1 volume mixture of benzene-ethyl ether (saturated with water), shake for a minute, and allow the phases to separate. Draw off the aqueous layer and extract again with a 10 ml. portion of benzene-ether. Transfer the aqueous solution to a 30 ml. Kjeldahl flask

[37] J. Cholak, D. M. Hubbard, and R. V. Story, *Ind. Eng. Chem., Anal. Ed.*, **15**, 57 (1943).

[38] If the sample contains sufficient iron, as is the case with blood, omit this addition; likewise, if the sample contains much phosphate an additional amount of this need not be added.

or a small Erlenmeyer flask, add 1 ml. of concentrated nitric acid, and heat until fumes of sulfuric acid appear. Cool, add a milliliter of water and again heat to fumes of sulfuric acid. Dilute the residual acid with water, transfer to a 25 ml. volumetric flask and dilute to the mark. Take a 10 ml. aliquot (1 to 25 γ of aluminum), neutralize with ammonia, and determine aluminum by the aurintricarboxylate method (p. 147).

Alternatively, aluminum can be determined with alizarin S as follows. For the 0–5 γ aluminum range dilute the residue from the destruction of excess cupferron to 14 ml. in a glass-stoppered cylinder, add 1 ml. of a 0.075 per cent aqueous solution of alizarin red S and 10 ml. of 3:7 ammonium hydroxide, mix, and determine the transmittancy immediately at 580 mμ. For the range 0–50 γ aluminum, dilute to 85 ml., and add 5 ml. of alizarin red S and 10 ml. of dilute ammonia. Beer's law is obeyed.

It is important to run a blank determination through the whole procedure.

CHAPTER VI

ANTIMONY

I. Separations

A. Sulfide Precipitation

The precipitability of antimony (III or V) sulfide in dilute mineral acid solutions (1 *N* or less in hydrochloric acid) will at times be of value in separating minute quantities of antimony. Possibly precipitation in the presence of oxalate (separation from quadrivalent tin) or fluoride (separation from tin and germanium) may find application in trace analysis as well as in macro analysis. The solubility of antimony sulfide in basic solution finds application in separations, as from copper (p. 171).

Very small amounts of antimony in bio material have been successfully isolated as the sulfide after destruction of organic matter.[1] The sulfuric-nitric-perchloric acid digest is neutralized with ammonia and treated with enough sulfuric acid to make the acidity 0.5 *N* after dilution to 500 ml. Hydrogen sulfide is passed into the solution, to which 1 mg. of copper has been added, for one-half to one hour. The mixture is allowed to stand overnight, the precipitate is collected on a retentive filter paper, and washed with 0.5 *N* sulfuric acid saturated with hydrogen sulfide. The standing overnight seems to be essential. If the solution is filtered immediately after treatment with hydrogen sulfide, antimony is lost by passage of the colloidal precipitate through the paper. Microgram quantities of antimony could be recovered satisfactorily in this way from the large volumes used, as shown by spectrographic determination.

B. Evolution as Stibine

Evolution of antimony as stibine has been employed for the isolation of traces of the element, but the method has not been fully exploited as yet. Conversion of antimony to stibine may be effected by the action of zinc in hydrochloric acid solution[2] or by electrolysis of a hydrochloric acid solution with a lead cathode, over which a stream of hydrogen is passed.[3] The evolved stibine is readily absorbed in a hydrochloric acid solution of

[1] J. Cholak and D. M. Hubbard, *J. Ind. Hygiene Toxicol.*, **28**, 121 (1946).

[2] C. R. Sanger and J. A. Gibson, *J. Soc. Chem. Ind.*, **26**, 58 (1907).

[3] J. Grant, *Analyst*, **53**, 626 (1928); H. J. S. Sand, *Electrochemistry and Electrochemical Analysis*, Vol. II, Chemical Publ. Co., Brooklyn, 1940, p. 141.

mercuric chloride.[4] Webster and Fairhall converted known amounts of antimony into stibine in an apparatus similar to the ordinary Gutzeit apparatus, passed the gas through mercuric chloride solution, and determined antimony by the rhodamine B method. An average recovery of 98 per cent was obtained with 25 to 50 γ of antimony.

It has been stated that the stibine evolution method is not satisfactory for samples of organic origin because "of inability to evolve stibine directly in the presence of other ions that occur commonly in biological material."[1]

C. Miscellaneous Separations

Antimony can be plated out on copper in hydrochloric acid medium (the Reinsch reaction). This is a useful method of isolating antimony in copper, copper alloys, and tin. As little as 0.001 per cent antimony in copper has been recovered satisfactorily in this way.

Prior reduction of cupric copper to cuprous and precipitation of arsenic can be effected with hypophosphite. Details are given on p. 171. Antimony can also be deposited by internal electrolysis from a hot dilute hydrochloric acid solution containing hydrazine hydrochloride; a spiral of copper wire is used as cathode, and iron or lead as the anode.[5] The electrolysis proceeds slowly unless about 1 mg. of arsenic is added.

Antimony is carried down by metastannic acid when non-ferrous alloys containing tin are treated with nitric acid. The ratio of tin to antimony must be at least 10:1 for quantitative separation of the latter. Small amounts of such metals as copper, lead, nickel, and iron will accompany antimony.

In weakly acid solution, antimony can be coprecipitated with manganese dioxide (obtained by adding permanganate to a solution containing manganous salt).[6] Much copper does not interfere. Ferric hydroxide is also a good collector for antimony (separation from copper and molybdenum).

Volatilization of antimony (III or V) as the bromide (see p. 42) may possibly be of use in the isolation of traces but there are no data available to show its value.[7]

Small amounts of many heavy metals (silver, mercury, copper, bismuth, nickel, cadmium, zinc, etc.) can be separated from antimony by extraction

[4] S. H. Webster and L. T. Fairhall, *J. Ind. Hygiene Toxicol.*, **27**, 184 (1945).

[5] Y. Y. Lur'e, E. M. Tal, and L. B. Fligel'man, *Zavodskaya Lab.*, **8**, 1222 (1939).

[6] B. Park and E. J. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **5**, 182 (1933); C. L. Luke, *ibid.*, **15**, 526 (1943). *Cf.* the references given under bismuth on p. 212.

[7] Cholak and Hubbard[1] had no success when they applied the antimony trichloride distillation of J. A. Scherrer, *J. Research Natl. Bur. Standards*, **16**, 253 (1936) and **21**, 95 (1938), to bio material. Recoveries of only 50 per cent were obtained with 10 to 20 γ of antimony.

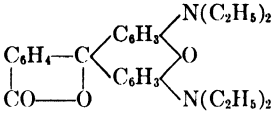
with dithizone from a weakly ammoniacal solution containing tartrate or citrate. Arsenic remains with the antimony.

Antimony (V) chloride can be extracted by ethyl or isopropyl ether from hydrochloric acid solution (*cf.* p. 174). The extraction has not yet been studied in a systematic way.

II. Methods of Determination

A. The Rhodamine B Method

In hydrochloric acid medium or in sulfuric acid solution containing chloride, quinquevalent antimony reacts with rhodamine B (tetraethylrhodamine), a red dyestuff, to give an insoluble red-violet compound of



unknown composition.[8] Two colorimetric methods for the determination of traces of antimony by means of this reaction have been described. In the earlier method[9] the excess of the strongly colored reagent is destroyed with bromine and the antimony complex is dissolved in alcohol. In the later procedure[10] the antimony compound is extracted with benzene, the excess of the reagent remaining in the aqueous phase. This method is to be preferred and will be described here in detail. The procedure as described below was worked out for the determination of stibine in air by absorption in a hydrochloric acid solution of mercuric chloride, but it is or more general applicability, if need be with some modification. The antimony in the solution of the absorbent is oxidized to the quinquevalent form with ceric sulfate and the excess of the latter is destroyed with hydroxylamine hydrochloride. After the addition of rhodamine B, the complex is extracted with benzene. The color intensity depends upon the amount and order of adding the reagents and on the timing of the various reactions, so that a regular schedule must be followed for reproducible results.

According to Webster and Fairhall, gold, thallium, and tungsten interfere by giving colors (and the last a precipitate) with the reagent. It is also known that ferric iron gives a red product with rhodamine B. In the

[8] The reaction was discovered by E. Eegriwe, *Z. anal. Chem.*, **70**, 400 (1927). Since a high chloride concentration is required for color production, it may be surmised that chloroantimonate ion is involved in the reaction. *Cf.* V. I. Kuznetsov, *Chem. Abst.*, **41**, 1947 (1947).

[9] W. G. Fredrick, *Ind. Eng. Chem., Anal. Ed.*, **13**, 922 (1941).

[10] Webster and Fairhall, *loc. cit.*

presence of mercuric ion, iodide and bromide give precipitates. Hydrides of carbon (acetylene), silicon, nitrogen, phosphorus, arsenic, sulfur, selenium, and tellurium were found not to interfere when absorbed in mercuric chloride solution. The following ions in amounts of a few milligrams do not give a color with rhodamine B according to the authors mentioned: bismuth, cadmium, cobalt, copper, fluoride, ferrous iron, magnesium, manganese, mercury, molybdenum, nickel, nitrate, sulfate, stannous tin, and zinc. See also the data in Table 29 (p. 173), from which it appears that there may be slight interference from relatively much arsenic and copper, and more serious interference from stannic tin and tungsten. Sexivalent chromium decolorizes rhodamine B.

Special Solutions

Mercuric chloride, 60 g. in 1 liter of 6 *N* hydrochloric acid.

Hydrochloric acid, 6 *N*.

Ceric sulfate, 0.1 *N*. Dissolve 33 g. of the anhydrous salt in 3 per cent sulfuric acid and dilute to 1 liter.

Hydroxylamine hydrochloride, 1 per cent aqueous solution.

Rhodamine B, 0.2 per cent aqueous solution. The Eastman Kodak Co. practical-grade product is suitable. If necessary filter the solution before use.

Benzene. The commercial grade, filtered if necessary, will serve.

Standard antimony solution, 20 γ Sb per ml. in 6 *N* hydrochloric acid. Prepare weekly by dilution of a solution containing 1 mg. Sb per ml. (0.274 g. of potassium antimonyl tartrate hemihydrate in 100 ml. of 6 *N* hydrochloric acid).

§ Procedure

Absorb the stibine in 20 ml. of mercuric chloride solution, using a Folin-type bubbler. Pour the solution into a dry 50 ml. glass-stoppered cylinder, rinse the absorption apparatus with 9 ml. of 6 *N* hydrochloric acid, and add to the cylinder. Make up the volume to 30 ml. with more acid, mix, and transfer 15.0 ml. of the solution to a 25 ml. graduate and thence to a 125 ml. conical beaker.

Add 0.5 ml. of ceric sulfate to the 25 ml. graduate, pour into the beaker, and set a timer for 1 minute. Rinse the graduate with the contents of the beaker and pour back into the latter. At the end of 1 minute blow clean air into the beaker for 5 or 10 seconds to remove free chlorine. Add 3 drops of hydroxylamine hydrochloride solution to the beaker and swirl. Next add 5.0 ml. of 6 *N* hydrochloric acid to the graduate for rinsing and transfer to the beaker. Blow out the air in the beaker with fresh clean air.

Without allowing to stand, add 1 ml. of rhodamine B solution and mix. Pour the resulting solution into a 60 ml. separatory funnel and add 25 ml. of benzene. Do this by rinsing the beaker with 2 ml. of benzene and adding the mixture to the funnel. Repeat once more and thoroughly drain the benzene into the funnel. Then add the remaining benzene from

a buret. Shake well for 1 minute. Allow to settle for one-half minute and drain off the orange-colored aqueous phase and a small amount of the benzene layer. Allow to stand until turbidity disappears. Time may be saved if a centrifuge is available by centrifuging 10 ml. of the benzene solution for 2 minutes in a stoppered tube to prevent evaporation. Obtain the transmittancy of the benzene extract at 565 mμ after adjusting its temperature to that existing when the standard curve was constructed.

Prepare standards as follows. Add to a beaker n ml. of standard solution of antimony, $5 - n$ ml. of 6 N hydrochloric acid, 10 ml. of mercuric chloride solution, and 0.5 ml. of ceric sulfate, and proceed according to the directions above. Use 0, 10, 20, and 40 γ portions of antimony.

Notes. 1. The color intensity depends upon the hydrochloric acid concentration of the solution in the oxidation step as well as at the time of extraction, as shown by the following figures (20 γ of antimony taken):

Acid concentration, initial, N....	8	6	4	2	6	6
Acid concentration, final, N.....	6	6	6	6	7.5	4.5
Antimony found, γ.....	21.5	20.0	17.2	8.9	15.0	22.9

2. Variation in the excess of rhodamine B does not affect the color intensity appreciably.

3. The excess of hydroxylamine hydrochloride is not critical. There is little tendency for hydroxylamine to reduce quinquevalent antimony. Chlorine remaining in the air above the solution may bleach rhodamine B and should be removed by blowing air through the vessel.

4. Benzene, toluene, ethyl benzene, and xylene readily extract the antimony complex without extracting rhodamine B. Carbon tetrachloride and ether do not extract the complex. Chloroform gives a fluorescent solution of the complex. Isoamyl alcohol extracts the reagent.

5. The color intensity of the antimony complex increases slightly as the temperature falls.

6. Mercuric chloride does not materially affect the color strength.

7. Beer's law is said to be obeyed up to about 1 p.p.m. of antimony in the benzene solution.

8. Duplicate samples of 10–30 γ of antimony show an average deviation of 0.3 γ.

B. Iodide Method[11]

In acid solution, iodide in excess yields iodoantimonite ion with antimony (III or V), which has a strong yellow color. With a sufficiently high concentration of iodide the sensitivity approaches that of the bismuth-iodide reaction. A suitable reducing agent must be present to destroy free iodine produced by air oxidation or by oxidizing foreign substances. Ascorbic acid has been recommended for the purpose by McChesney (*loc. cit.*); hypophosphite has also been used. The color in-

[11] M. L. Fauchon, *J. pharm. chim.*, **25**, 537 (1937); E. W. McChesney, *Ind. Eng. Chem., Anal. Ed.*, **18**, 146 (1946).

tensity of the antimony-iodide solution depends upon the sulfuric acid concentration (chloride ion should be avoided because of its bleaching effect), increasing with the acidity up to 2.2 *N*, then remaining constant to about 3.6 *N*, after which it increases again, slowly at first, then rapidly. Maximum color intensity is reached at about 6 per cent potassium iodide; at 8 per cent the intensity is virtually the same. The color diminishes rapidly as the iodide concentration is decreased, being nil with 1.6 per cent potassium iodide (difference from bismuth). According to McChesney, Beer's law is obeyed in the range 5 to 50 p.p.m. antimony, but below 5 p.p.m. there is a positive deviation. No interference is produced by 10 to 20 p.p.m. of arsenic, mercury, iron, copper, lead, and tungsten; thallium yields a precipitate of the iodide and causes low results by removing antimony. Nitrate and phosphate do not interfere. Oxidizing agents such as nitrite and hypochlorite will of course interfere if present in sufficient amounts to destroy the ascorbic acid in the reagent. Sulfites give a yellow color. Bismuth, if present, can be determined and its effect corrected for by developing the bismuth-iodide color alone at a low iodide concentration. For details see the paper of McChesney.

Reagent

Potassium iodide, 112 g. of the reagent-quality salt and 20 g. of crystalline ascorbic acid in 1 liter of solution. Make up only as needed and keep in a brown bottle. Discard the solution when molds form. It is stable for about 1 month.

§ Procedure

To a few milliliters of sample solution (50 to 500 γ of antimony) in a 10 ml. volumetric flask add enough sulfuric acid to make its concentration 3.0 *N* after dilution to volume. Add 5 ml. of potassium iodide reagent, dilute to the mark with water, and obtain the transmittancy of the mixed solution at 425 mμ after 5 minutes. The color is stable for as long as 2 days.

C. The Pyridine-Iodide Method

Various organic bases form slightly soluble colored double iodides with trivalent antimony (quinquevalent antimony gives the same reactions since it is reduced to the trivalent form by iodide) of the general formula $B \cdot HI \cdot SbI_3$. Clarke[12] has worked out a method based on the formation of yellow pyridine antimony iodide, kept in suspension by gum arabic. The solution is acidified with sulfuric acid. Chloride ion decreases the color intensity or destroys the color entirely. The maximum color intensity is attained in a solution which is 6 to 8 *N* in sulfuric acid. The iodide concentration should correspond to 1 per cent potassium iodide in the final

[12] S. G. Clarke, *Analyst*, **53**, 373 (1928).

solution. Too much pyridine bleaches the color. Alkali sulfates have no appreciable effect. The liberation of iodine by atmospheric oxidation is prevented by the addition of a small amount of sulfurous acid. The concentration of the latter must be kept low, else a yellow color is produced (see p. 214).

Tin and arsenic in low concentrations (several centigrams in 100 ml.) give no color and do not interfere with the determination. A number of heavy metals give slightly soluble iodides or double iodides, or liberate iodine. Bismuth gives an orange precipitate, nickel a green, cobalt a pink, zinc a white precipitate, etc.

It is doubtful whether this method has any advantages over the iodide method described in the preceding section; indeed, it is likely to be inferior because of lower sensitivity, poorer reproducibility because of the formation of a colloidal suspension, and more interferences. Nevertheless it is included here because it has found a number of applications, such as the determination of antimony in copper (p. 170) and in mercury ores.

Special Solutions

Pyridine, 10 per cent aqueous solution.

Potassium iodide, 20 per cent aqueous solution, freshly prepared.

Gum arabic, 1 per cent in water.

Sulfur dioxide. Saturate cold water with sulfur dioxide and dilute with 9 times its volume of water. Prepare fresh.

Standard antimony solution, 0.100 mg. Sb per ml. Dissolve 0.0274 g. of potassium antimonyl tartrate hemihydrate in 60 ml. of 6 *N* sulfuric acid and dilute to 100 ml. with water.

§ Procedure

Into a flat-bottomed tube of 25–30 ml. capacity measure 1 ml. of gum arabic solution, 0.5 ml. of potassium iodide, 0.10 ml. of pyridine solution, 0.10 ml. of sulfur dioxide solution, and 6 ml. of 1:3 sulfuric acid. To this mixture add a 1:3 sulfuric acid solution of the sample[13] having a volume of 3–4 ml. and containing not more than 0.1 mg. of antimony. The comparison mixture should contain the same amounts of iodide, pyridine, etc. as the unknown solution, but 9 to 10 ml. of 1:3 sulfuric acid instead of the 6 ml. in the sample tube. From a microburet add the standard antimony solution with shaking or stirring until the colors match when the tubes are viewed axially. Adjust the volumes near the end point by the addition of water so that they are approximately the same.

If the color intensity is very low, the double iodide may be extracted with a small volume of amyl alcohol.[14]

[13] The solution should contain no chloride. Chloride may be removed by evaporating to fumes of sulfuric acid after adding nitric acid to prevent loss of antimony.

[14] A. A. Vasil'ev and M. E. Shub, *J. Applied Chem. U. S. S. R.*, 6, 560 (1933).

D. Phosphomolybdic Acid Method

Trivalent antimony reduces phosphomolybdotungstic acid[15] or phosphomolybdic acid[16] to soluble blue compounds, and methods of determination based on this property have been proposed.

§ Procedure

Add enough sulfuric acid to the sample solution (50 to 500 γ of antimony) to make the acidity 0.4 *N* when diluted to 30 ml. Treat the solution with 2 or 3 ml. of saturated sulfur dioxide solution, boil to remove the excess, and again dilute to 30 ml. Add 2 ml. of freshly prepared 5 per cent phosphomolybdic acid and heat for 10 minutes on a water bath at 100°. Cool to room temperature, add 8 ml. of 1:4 sulfuric acid, shake at intervals for 5 minutes, dilute to 50 ml., and find the transmittancy with a yellow filter.

E. Other Methods

Microgram quantities of antimony have been determined as the sulfide after evolving as stibine, decomposing the latter in a heated tube, and dissolving the antimony coating in strong hydrochloric acid.[17]

A method for the determination of antimony in spray residues has been described in which stibine is evolved by the action of zinc in hydrochloric acid solution and led over a strip of paper impregnated with mercuric chloride as in the Gutzeit method for arsenic.[18] The length of the stain is measured after immersion of the paper in 5 per cent ammonia solution. The method is suitable for 25 to 150 γ of antimony. Arsenic interferes. Organic material may be ashed at 550° C. without loss of antimony originally present as potassium antimonyl tartrate.

III. Special Applications

A. Determination of Traces of Antimony in Copper and Copper Alloys[19]

The procedure given below involves reduction of cupric copper in acid solution by sodium hypophosphite, deposition of antimony on metallic

[15] S. Makishima, *J. Soc. Chem. Ind. Japan*, **34**, Suppl. binding, 322 (1931). The method is applied to the determination of antimony in copper after isolation by coprecipitation with manganese dioxide. Silver, ferrous iron, nickel, cobalt, arsenic, and bismuth are said not to interfere.

[16] A. I. Kokorin, *Zavodskaya Lab.*, **12**, 64 (1946).

[17] J. Grant, *loc. cit.*

[18] J. Davidson, G. N. Pulley, and C. C. Cassil, *J. Assoc. Official Agr. Chem.*, **21**, 314 (1938); T. C. Boyd and A. C. Roy, *Indian J. Med. Research*, **17**, 94 (1929); C. R Sanger and E. R. Riegel, *Proc. Am. Acad. Arts Sci.*, **45**, 21 (1909).

[19] S. G. Clarke and B. S. Evans, *Analyst*, **54**, 23 (1929). For a method for the determination of antimony in greater than trace amounts in copper-base alloys see A. C.

(*continued next page*)

copper, stripping the antimony film with sodium peroxide, and determination of antimony by the pyridine-iodide method. Doubtless the iodide method (B above) can be substituted for the latter in the final determination.

§ Procedure

Dissolve 5 g. of sample (copper, bronze, cupro-nickel, brass, etc.) in 30 ml. of 1:3 sulfuric acid and 15 ml. of concentrated nitric acid; evaporate until the sulfuric acid fumes strongly. Cool, dissolve the residue in 150 ml. of water, and add 150 ml. of concentrated hydrochloric acid and 10 g. of sodium hypophosphite. Boil for 10 minutes. If appreciable amounts of arsenic are absent proceed immediately as directed in the next paragraph. If a brown-black precipitate of arsenic separates, however, boil further for 20 minutes, cool, and shake the liquid with 20 ml. of benzene to coagulate the precipitate. Filter through a moist filter paper and wash with a minimum amount of hot water; reject the precipitate. In the case of tin bronze, dissolve 10 g. of oxalic acid in the hydrochloric acid solution before the addition of hypophosphite; ignore any white turbidity produced.

Roll a piece of pure electrolytic copper foil, 2.5 × 20 cm., into a flat spiral, clean by warming gently with dilute nitric acid (sp. gr. 1.2), wash with water, and drop it into the solution contained in a flask. Boil the solution gently for 2 hours, preferably with the coil upright, not on its side, in the liquid. Then lift the coil out of the solution with a hooked glass rod, rinse quickly by plunging into a beaker of water, and place without delay in a small beaker having a diameter only slightly greater than that of the coil. Cover with distilled water and add 1 g. of sodium peroxide at once. After allowing the solution to stand for 5–10 minutes, warm gently so that the copper becomes darkened with a layer of oxide. Pour off the liquid into a small flask, and rinse the coil twice with water. Test for completeness of stripping of antimony by immersing the coil in dilute sulfuric acid, which will dissolve the copper oxide and allow any remaining antimony to be seen.

Treat the antimony solution with a rapid stream of hydrogen sulfide for 15 seconds and allow the mixture to stand on the water bath for one-half hour. Filter off the copper and bismuth sulfides on a small filter and wash lightly with 1 per cent ammonium nitrate solution. Add 5 ml. of concentrated sulfuric acid to the filtrate and evaporate to fumes, adding a few

Holler, *Anal. Chem.*, 19, 353 (1947); antimony is coprecipitated with metastannic acid and finally determined by the iodide method. Still another method for antimony in copper or tin is described by Kokorin,[16] who uses phosphomolybdic acid as the colorimetric reagent after a Reinsch separation. See P. J. C. Kent, *Metallurgia*, 35, 91 (1946), for the determination of antimony in aluminum by the iodide method; copper is kept in solution by addition of urea.

drops of nitric acid near the end. Take up the sulfuric acid solution with 15 ml. of water, heat just to the boiling point and cool. Filter the solution, if necessary, and determine antimony by the pyridine-iodide method described above, increasing the volume of the reagents proportionately. Preferably the amount of antimony should not exceed 0.5 mg. when 100 ml. Nessler tubes are used.

TABLE 28

DETERMINATION OF ANTIMONY IN COPPER[a]

Sb present, %	0.001	0.002	0.006	0.010
Sb found, %	0.001	0.0019	0.0058	0.010

[a] Representative figures from Clarke and Evans, *loc. cit.*

B. BIO MATERIAL

Because of its specificity and great sensitivity, the rhodamine B method is usually preferred for the determination of traces of antimony in samples of organic origin. If the amount of antimony in an aliquot is greater than 10 γ the iodide method (p. 167) can be used. The determination of antimony in bio material with rhodamine B has been studied by Maren.[20] Destruction of organic matter and conversion of antimony to the quinquevalent state is best effected with sulfuric-nitric-perchloric acid.[21] If iron is present in excess of 1 mg. difficulties arise from the production of a red color with rhodamine B, even when phosphoric acid is added.[22] According to Maren, the interference of reasonable quantities of ferric iron (the upper permissible limit is not reported) can be avoided by extracting antimonic chloride with isopropyl ether from 1.5 *N* hydrochloric acid solution. All of the antimony is said to be removed from the aqueous phase, whereas more than 90 per cent of the iron remains in the latter. When the separated isopropyl ether phase is shaken with a small volume of aqueous rhodamine B solution, the antimony complex is formed in the ether layer, whose transmittancy is then determined. The complex does not form a true solution in the ether and Beer's law is not closely followed.

[20] T. H. Maren, *Anal. Chem.*, 19, 487 (1947).

[21] If sulfuric and nitric acids alone are used, part of the antimony is converted into a form (thought to be Sb_2O_4) which cannot be oxidized by ceric sulfate to the quinquevalent state, as required in the rhodamine B method. It is then necessary to treat the solution with sulfite to reduce all the antimony to the trivalent state, which can be completely oxidized to the quinquevalent stage with ceric sulfate.

[22] According to L. D. Freedman, *Anal. Chem.*, 19, 502 (1947), the interference of iron can be prevented by adding solid sodium pyrophosphate to the hydrochloric acid solution until the yellow color disappears. The amount of iron that can be made harmless in this way is not stated.

Aside from iron there are no elements in bio material that are likely to interfere (Table 29). The benzene extraction method is a little more precise than the isopropyl ether method, and the former is preferably used when the amount of iron present is not large enough to interfere. Results are reproducible to within 20 per cent for 2 γ of antimony and to

TABLE 29

EFFECT OF OTHER METALS ON THE DETERMINATION OF ANTIMONY WITH RHODAMINE B (BENZENE EXTRACTION)[a]

Metal, mg.	Sb taken, γ	Sb found, γ
As, 1	0.0	1.0
As, 1	2.0	2.8
Bi, 10	0.0	0.0
Bi, 10	2.0	2.0
Cu, 10	0.0	0.6
Cu, 10	2.0	2.5
Zn, 10	2.0	2.0
Sn (IV), 1	2.0	1.3
Sn (IV), 10	2 0	0[b]
Pb, 10	2.0	2.2
Hg, 10	2.0	2.2
Fe (III), 10	0.0	2.0
Fe (III), 1	2.0	2.6
Fe (III), 10	2.0	6.2
Mo, 10	2.0	2.0
W, 1	2.0	2.0
W, 10	2.0	0[b]
Co, 10	2.0	2.4

[a] Selected figures, Maren, *loc. cit.*

[b] Emulsion formation, benzene layer colorless.

10 per cent for larger amounts. Recoveries of antimony from blood and urine were within the same limits.

§ Procedure

To a suitable weight of sample (up to 15 g. of blood or tissue, containing not more than 50 γ antimony) in a 100 ml. Erlenmeyer flask add 5 ml. each of concentrated sulfuric[23] and nitric acids, a few glass beads, and a drop of capryl alcohol. Allow the digestion to begin spontaneously and shake to aid solution. Begin heating at a low temperature and increase the heat

[23] The sulfuric acid should be measured accurately and care should be taken to avoid appreciable volatilization losses later in the procedure, because the color intensity of the complex depends upon the sulfuric acid concentration in the final solution as shown by Freedman, *loc. cit.*

after one or two hours when the digestion is proceeding rapidly. If charring occurs, add 1–2 ml. of nitric acid, and repeat as often as may be necessary. When no further charring occurs and the solution remains colorless or only slightly yellow, add 2 drops of 60 per cent perchloric acid and heat strongly (maximum hot plate temperature) to fumes of sulfuric acid. If the liquid darkens add more nitric and perchloric acids and again evaporate to fumes of sulfuric acid. Cool the solution, add 3 ml. of water, and heat until fumes of sulfuric acid appear.

Carry out the succeeding steps in a water bath to keep the temperature below 23–25°C. Add 5 ml. of 6 *N* hydrochloric acid. If a deep yellow color develops, more than 1 mg. of iron is present and the ether extraction method should be used, otherwise the benzene extraction procedure.

Benzene extraction. Add 8 ml. of 1 *M* phosphoric acid (70 ml. of the 85 per cent acid diluted to 1 liter) and 5.0 ml. of 0.02 per cent aqueous rhodamine B solution to the flask and mix. Without delay transfer the solution to a separatory funnel and add 10.0 ml. of C.P. benzene. Shake for 1 minute, allow the phases to separate, draw off the benzene layer into a test tube, and allow to stand for a few minutes to let water droplets settle (centrifugation is usually not necessary). Obtain the transmittancy of the benzene solution at 565 mμ (or use a green filter). The color is stable for at least 4 hours.

Ether extraction. After the addition of the 5 ml. of 6 *N* hydrochloric acid, transfer the solution to a separatory funnel and add 13 ml. of water, first rinsing the flask with the latter. Add 15.0 ml. of isopropyl ether (analytical-reagent or C.P. quality). Shake for 1 minute. Discard the lower aqueous phase. Add 5.0 ml. of rhodamine B solution to the ether remaining in the funnel and shake for 1 minute. Discard the lower aqueous layer. Without delay find the transmittancy of the ether phase at 545 mμ (or use a green filter).

CHAPTER VII

ARSENIC

Thanks to the ease of separation of arsenic from other elements, and the precision and great sensitivity of the molybdenum blue method, minute amounts of arsenic can be determined colorimetrically without difficulty, provided there is no loss of the element in the decomposition of the sample. Until recent years small quantities of arsenic were determined nearly exclusively by the Gutzeit method, but now the position of the latter is seriously threatened by the rival molybdenum blue method, which, it seems likely, will displace the Gutzeit procedure.

I. Separations

A. Distillation Procedures

The commonly used distillation method for isolating both macro and micro quantities of arsenic involves distillation of arsenious chloride from hydrochloric acid solution. A reducing agent such as hydrazine sulfate is used to reduce quinquevalent arsenic to the trivalent form. The presence of bromide aids the reduction. Nitric acid and other strong oxidizing agents must be absent. The presence of sulfuric acid does no harm. Germanium accompanies arsenic in the distillation, and antimony may partially distil if the temperature rises above 107°. Neither of these elements interferes in the subsequent colorimetric determination. If phosphate is present in large amounts, the distillate should be redistilled under the same conditions as in the first distillation to avoid error due to any phosphorus carried over mechanically in the first distillation. Passage of carbon dioxide or nitrogen through the solution during the distillation facilitates the volatilization of arsenic. The distillate may be collected in cold water. Directions for carrying out the distillation with hydrazine sulfate as the reducing agent are given on p. 182.

Distillation of arsenic from a bromide-containing medium has been applied as a separation procedure by a number of workers. Robinson and coworkers distil from concentrated hydrobromic acid containing bromine.[1] Selenium and germanium accompany arsenic.

[1] W. O. Robinson, H. C. Dudley, K. T. Williams, and H. G. Byers, *Ind. Eng. Chem., Anal. Ed.*, **6**, 274 (1934); K. T. Williams and R. R. Whetstone, *U. S. Dept. Agric. Dept. Tech. Bull.* No. **732**, p. 4 (1940).

According to Magnuson and Watson,[2] quinquevalent arsenic can be distilled as such from a sulfuric acid solution containing bromide.[3] Arsenic pentabromide is thought to be the volatile substance. These authors apply the separation in the determination of arsenic in bio material after decomposition with sulfuric-nitric acid; doubtless it has further uses. The distillation can be made in five minutes if a special micro still is used. Simpler forms of distillation apparatus do not give satisfactory recovery. Since the volume of the distillate is kept small, and arsenic is present in the quinquevalent state, the molybdenum blue method can be applied directly to the solution. With 1 and 3 γ of arsenic, recoveries of at least 90 per cent are obtained, and at least 95 per cent above this level. The mechanical carry-over of phosphorus amounts to about 1 γ for 0.1 g. present. See p. 191 for details.

A comparative study of the arsenic trichloride and the arsenic bromide distillation methods would be desirable.

B. Volatilization as AsH_3

The second important method of isolation involves volatilization of arsenic as arsine by the action of zinc in hydrochloric or sulfuric acid solution.[4] This method may be applied to solutions not containing large amounts of certain reducible heavy metals which would be likely to interfere with the evolution of arsine; moderate amounts of iron may be present. The evolution method is conveniently used for solutions of decomposed organic material, silicates and other inorganic materials in which such heavy metals are not present in appreciable amounts. As much as 10 mg. of silver or 50 mg. of lead may be present. These metals, as well as others that are precipitated by zinc, slow down the evolution of hydrogen, and therefore the solution should be heated when they are present. Copper in more than small amounts prevents complete evolution of arsine; the error amounts to 20 per cent (for 5–10 γ of arsenic) with 50 mg. of copper. Iron, chromium, and molybdenum may be present in reasonably large amounts (the first two metals at least up to 50 mg.); they increase the rate of evolution of hydrogen. Low results are obtained in the presence of nickel and cobalt (Table 32, p. 181). Selenium is not evolved.

[2] H. J. Magnuson and E. Watson, *Ind. Eng. Chem., Anal. Ed.*, **16**, 339 (1944).

[3] In this connection it may be noted that data of Hoffman and Lundell (Table 8) show that macro quantities of quinquevalent arsenic can be quantitatively distilled from hydrobromic-perchloric acid, hydrobromic-phosphoric-perchloric acid, and hydrobromic-sulfuric acid.

[4] Various electrolytic methods for the generation of arsine have been described. See, for example, D. Rogers and A. E. Heron, *Analyst*, **71**, 414 (1946), who absorb the arsine in a sodium bicarbonate-iodine solution and determine arsenic by the molybdenum blue method.

The evolved arsine may be decomposed into elemental arsenic by passage through a silica tube heated to 800° C., or more conveniently it may be absorbed in an acid solution of mercuric chloride containing potassium permanganate,[5] in sodium hypobromite solution[6] or in a sodium bicarbonate solution of iodine. The chief source of error in the procedure is likely to be incomplete absorption of arsine. This method of separation can be carried out more rapidly and more conveniently than the arsenious chloride distillation method.

C. Extraction Procedures

Trivalent arsenic can be extracted as the xanthate by carbon tetrachloride from acid solution.[7] Antimony and other metal xanthates which are also extracted may be removed from the carbon tetrachloride by washing with concentrated hydrochloric acid containing stannous chloride; this treatment does not affect arsenic (III) xanthate. The carbon tetrachloride may then be evaporated, the arsenic oxidized to the quinquevalent state with bromine, and determined by the molybdenum blue method. It is stated that aluminum, manganese, zinc, lead, mercury, cadmium, and bismuth do not interfere. A detailed procedure is not given here because there are no data to show how well microgram quantities of arsenic can be isolated in this way. Amounts of arsenic equal to, or greater than, 0.1 mg. show excellent recoveries.

More complete extraction of arsenic is said to be obtained by the use of diethylammonium diethyldithiocarbamate as reagent.[8] Arsenic is first reduced to the trivalent state by adding 2 ml. of 20 per cent potassium iodide solution to the warm (40°) sample solution having a volume of about 20 ml. and which is 5–6 *N* in hydrochloric acid. Following the addition of 0.5 ml. of 5 per cent sodium bisulfite solution, the mixture is transferred to a separatory funnel and diluted with water to a volume of 35 ml. Five ml. of 1 per cent diethylammonium diethyldithiocarbamate in chloroform (prepared fresh daily) is next added and the whole is shaken vigorously for 40 seconds. The chloroform layer is run into another separatory funnel and the aqueous phase is washed with 0.5 ml. of chloro-

[5] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, 14, 82 (1942). C. C. Cassil and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, 22, 436 (1939), used mercuric chloride solution alone for the absorption of arsine in a microvolumetric method for arsenic based on iodometric titration.

[6] M. B. Jacobs and J. Nagler, *Ind. Eng. Chem., Anal. Ed.*, 14, 442 (1942). Rogers and Heron (*loc. cit.*) mention the appearance of a disturbing greenish tint in the subsequent colorimetric determination as heteropoly molybdenum blue when hypobromite solution is used as an absorbent for arsine.

[7] A. K. Klein and F. A. Vorhes, *J. Assoc. Official Agr. Chem.*, 22, 121 (1939).

[8] N. Strafford, P. F. Wyatt, and F. G. Kershaw, *Analyst*, 70, 232 (1945).

form without mixing. The aqueous solution is extracted with another portion (2 ml.) of the carbamate reagent and washed as before. These amounts of reagent suffice for at least 25 γ of arsenic. The chloroform extracts and washings are shaken with 10 ml. of 1 *N* sulfuric acid to remove any entrained droplets that might contain phosphate. The chloroform now contains all the arsenic (less than 0.2 γ escapes extraction according to the authors). The arsenic can be brought into aqueous solution by evaporating the chloroform and oxidizing the residue with bromine water or with perchloric acid.

The extraction of arsenic is stated to be complete over the range 1 to 10 *N* sulfuric acid. Lead will not be extracted if the hydrochloric acid concentration is at least 2 *N*. Zinc, cadmium, nickel, and iron also are not extracted. Copper, mercury, and bismuth accompany arsenic.

D. Precipitation Methods

Occasionally, precipitation of elemental arsenic by such reducing agents as stannous chloride, hypophosphite, and copper in acid solution find application. Hypophosphite has been used for the precipitation of arsenic from 1:1 hydrochloric acid in its determination in copper and copper-base alloys as well as in lead and tin-base bearing metal.[9] The recovery of arsenic is not quite complete, averaging about 95 per cent. If copper is not originally present it must be added to catalyze the reduction of arsenic.

Arsenic in the quinquevalent state can be coprecipitated with ferric hydroxide or magnesium ammonium phosphate.

II. Methods of Determination

A. The Heteropoly Molybdenum Blue Method

In this method the isolated arsenic is brought into the quinquevalent state and ammonium molybdate is added to form a heteropoly molybdiarsenate which is then reduced by a suitable reducing agent to strongly colored "molybdenum blue," in which molybdenum is present in a lower valence, but whose constitution is uncertain. The conditions of reduction must be such that the molybdenum in the complex, but not the excess ammonium molybdate, which is more difficultly reducible, is attacked. Phosphate reacts in the same manner as arsenate and must be absent.

Stannous chloride[10] and a reduced molybdate reagent[11] have frequently

[9] O. P. Chase, *Anal. Chem.*, **20**, 902 (1948).

[10] See for example G. Denigès, *Compt. rend.*, **171**, 802 (1920); E. Truog and A. H. Meyer, *Ind. Eng. Chem., Anal. Ed.*, **1**, 136 (1929). Hydroquinone is recommended as reducing agent by B. Visintin and N. Gandolfo, *Ann. chim. applicata*, **33**, 111 (1943).

[11] C. Zinzadze, *Ind. Eng. Chem., Anal. Ed.*, **7**, 230 (1935); J. T. Woods and M. G. Mellon, *ibid.*, **13**, 760 (1941).

been used as reductants, but hydrazine sulfate is generally preferable.[12] With the latter a stable blue color (maximum absorption at 840 mμ)[13] is obtained which shows no appreciable change in 24 hours. Heating is necessary to develop the color with hydrazine sulfate, but the time of heating has no effect on the color intensity as long as it is sufficient to give the maximum color. The acid concentration of the solution must be controlled. If the acidity is too low silicate, or even molybdate alone, will give a blue

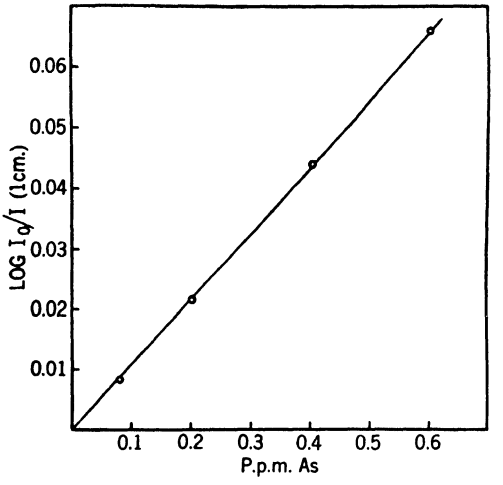


Fig. 23. Determination of arsenic by the molybdenum blue method (red filter).

color, and if it is too high the color due to arsenic is decreased in intensity. The approximate optimum concentrations of sulfuric acid and ammonium molybdate in the final solution are stated to be 0.25 *N* and 0.05 per cent respectively.[14]

Two molybdenum blue procedures for the determination of arsenic are given below, one for use after distillation of arsenious chloride, the other after evolution as arsine. Hydrazine sulfate is used as reducing agent in both procedures, but the composition of the molybdate-hydrazine sulfate reagent is different in the two cases. In the first procedure the arsenious chloride distillate is treated with nitric acid and evaporated to dryness to

[12] H. J. Morris and H. O. Calvery, *Ind. Eng. Chem., Anal. Ed.*, 9, 447 (1937); E. H. Maechling and F. B. Flinn, *J. Lab. Clin. Med.*, 15, 779 (1930).

[13] According to J. A. Sultzaberger, *Ind. Eng. Chem., Anal. Ed.*, 15, 408 (1943), who gives the absorption curve of heteropoly molybdenum blue.

[14] A. L. Chaney and H. J. Magnuson, *Ind. Eng. Chem., Anal. Ed.*, 12, 693 (1940). In the procedure of C. J. Rodden, *J. Research Natl. Bur. Standards*, 24, 7 (1940), the acid concentration is 0.5 *N* in sulfuric acid and the ammonium molybdate concentration is 0.1 per cent. These are the conditions originally prescribed by Morris and Calvery.[12]

oxidize arsenic to the quinquevalent state and remove the excess acid.[15] In the second procedure the mercuric chloride–potassium permanganate solution which is used to absorb and oxidize the arsine to arsenic acid may be treated directly with the molybdate-hydrazine sulfate reagent to develop the blue color; a small amount of mercurous chloride which is formed by reduction may be removed by rapid filtration.[16] Beer's law is followed in both procedures. As already mentioned, Method 1 is the most generally applicable, whereas Method 2 is restricted to samples not containing such heavy metals as lead and mercury, which prevent the complete liberation

TABLE 30

DETERMINATION OF ARSENIC IN ALLOYS BY THE MOLYBDENUM BLUE METHOD AFTER DISTILLATION AS THE CHLORIDE[a]

Arsenic present %	Arsenic found %	Sample
0.009	0.008 0.009 0.009	Steel
0.024	0.024 0.025	Ferromanganese
0.071	0.068 0.070 0.071	Cast iron
0.19	0.17 0.18	Phosphor-bronze bearing metal

[a] Figures from results reported by Rodden.[17]

[15] In addition there is given on p. 191 a procedure which is more or less the equivalent of the arsenious chloride distillation, namely distillation of quinquevalent arsenic from sulfuric-hydrobromic acid medium. This procedure is simpler and more rapid than the arsenious chloride distillation, but it requires a still of special design.

[16] Another arsine-molybdenum blue method has been described by R. Milton and W. D. Duffield, *Analyst*, 67, 279 (1942). In their procedure the arsine is absorbed in a sodium bicarbonate solution of iodine and the molybdenum blue is produced by reduction with stannous chloride. This method is slightly simpler than the one given above since no filtration is required. The authors, however, give no figures for the determination of very small quantities of arsenic (for larger quantities satisfactory recoveries of arsenic are shown to be obtained) and therefore we retain the original directions for the molybdenum blue method.

of arsine in the evolution flask, or lead to incomplete absorption of arsine by causing too vigorous evolution of hydrogen.

The accuracy of the methods may be judged from the figures given in Tables 30, 31, and 32.

TABLE 31

DETERMINATION OF ARSENIC BY THE MOLYBDENUM BLUE METHOD AFTER EVOLUTION AS ARSINE[a]

Arsenic taken, γ....	1.0	1.0	2.0	2.0	5.0	5.0	10.0	15.0	10.0[b]	10.0[c]
Arsenic found, γ.....	0.9	0.9	1.8	2.0	4.8	5.2	9.8	15.1	9.5	9.8

[a] Data of the writer. Absorption vessel shown in Fig. 25 used.
[b] In the presence of 10 γ Sb.
[c] In the presence of 60 mg. Fe.

TABLE 32

DETERMINATION OF ARSENIC BY THE MOLYBDENUM BLUE METHOD AFTER EVOLUTION AS ARSINE[a]

(Solution in evolution flask heated for 10 minutes at the end of the half-hour evolution period. Volume of final solution 10 ml.; 1 cm. cell.)

Addition	As taken, γ	As found, γ
	1.0	1.0
	1.5	1.4
	2 0	2.2
	3 0	3.0
	4.0	3.8
	5.0	4.9
	7 0	6.9
	7 0	7.2
	7.5	7 4
	10.0	10.1
50 mg. Pb	5.0	5.0
10 mg. Ag	8 0	8.0
50 mg. Fe (III)	8.0	7.8
50 mg. Cr (III)	8 0	7.9
10 mg. Mo (VI)	8.0	7.8
50 mg. Cu (II)	8.0	6.4
50 mg. Cu (II)	9.0	7.2
50 mg. Ni, 50 mg. Co[b]	6.0	3.8
50 mg. Ni, 50 mg. Co[b]	8.0	5.0

[a] Data obtained by J. J. Neumayer, University of Minnesota, 1947, using absorption vessel shown in Fig. 26.
[b] Evolution flask cooled in ice water for 5 minutes at beginning to slow down vigorous evolution of hydrogen.

Method 1: Determination of Arsenic after Distillation of Arsenious Chloride[17]

Apparatus

The distillation of arsenic trichloride should be made from an all-glass distilling apparatus such as that of Scherrer[18] shown in Fig. 24. The flask may have a volume of 250 ml.

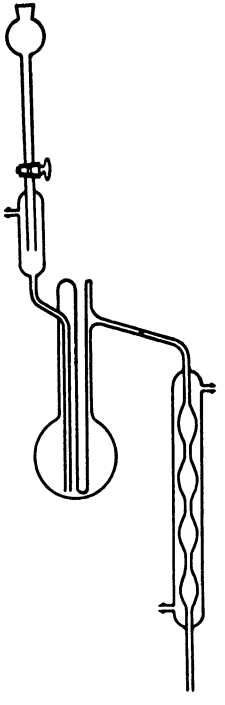


Fig. 24. Scherrer distillation apparatus.

Special Solutions

Hydrazine sulfate-ammonium molybdate. Dissolve (*a*) 1 g. of ammonium molybdate in 100 ml. of 5 *N* sulfuric acid, and (*b*) 0.15 g. of hydrazine sulfate in 100 ml. of water. Dilute 10 ml. of solution (*a*) to 90 ml. with water, add 1 ml. of solution (*b*), and dilute to 100 ml. with water. The mixed solution should be prepared fresh daily. Alternatively, appropriate volumes of the individual solutions may be added separately to the sample solution, to avoid the frequent preparation of the mixed solution which is not stable.

Standard arsenic solution. Dissolve 0.132 g. of arsenic trioxide in 2 ml. of 1 *N* sodium hydroxide, dilute with water, make slightly acid with hydrochloric acid, and dilute to 100 ml. From this stock solution (1.00 mg. As per ml.) prepare a standard solution containing 0.010 mg. of arsenic per ml.

§ Procedure

Transfer the sample to the distilling flask with concentrated hydrochloric acid. The volume of the solution in the flask may be 10–15 ml. Then add 2 ml. of hydrobromic acid and a mixture of 0.3 g. (or more if required) of hydrazine sulfate and 10 ml. concentrated hydrochloric acid. Dip the end of the condenser into 10 ml. of cold water in a small beaker. Pass a slow stream of carbon dioxide or nitrogen through the solution (2–3 bubbles per second), and boil gently until the temperature reaches 111° C. This requires about 15 minutes, and the flask will then contain approximately 10 ml. of solution.

Add 10 ml. of concentrated nitric acid to the distillate and evaporate to dryness. Then heat at 130° C. (not higher than 140°) for ½ to 1 hour to remove nitric acid. Add 10 ml. of hydrazine sulfate-ammonium molybdate solution for each 30 γ of arsenic and heat the solution on a steam

[17] C. J. Rodden, *J. Research Natl. Bur. Standards*, **24**, 7 (1940). This procedure was worked out with special reference to the determination of arsenic in ferrous and nonferrous alloys, but it may be applied quite generally to inorganic samples free from strong oxidizing agents such as nitric acid.

[18] J. A. Scherrer, *J. Research Natl. Bur. Standards*, **16**, 253 (1936); **21**, 95 (1938).

bath for 15 minutes.[19] Cool, and dilute to volume with hydrazine sulfate-molybdate solution. The final solution should not contain more than 3 γ of arsenic per ml. Obtain the transmittancy of the solution with a photometer, using a filter with maximum transmission at 700 mμ or above (840 mμ is the optimum). Construct the standard curve from known amounts of arsenic treated in the same way as the unknown. Correct the results for a blank carried through all the steps of the procedure.

Method 2: Determination of Arsenic after Evolution as Arsine

Apparatus[20]

The evolution vessel is a 50 ml. Erlenmeyer flask closed by a one-hole rubber stopper from which leads a tube *A* (Fig. 25) containing at its lower end one or two plugs of glass wool impregnated with lead acetate. This tube is connected by means of a short section of rubber tubing to the delivery tube *B* which is drawn down to a tip having an opening of about 0.5 mm. The absorption vessel *C* is drawn from a test tube, and should have a capacity of 8 to 10 ml. with the tapered portion of such dimensions that the 1.35 ml. of absorbing solution will have a depth of 6–7 cm. A short piece of glass tubing, *D*, having an internal diameter approximately 1 mm. greater than the external diameter of *B* is placed in the absorption vessel to break up the gas bubbles and provide more absorption surface. Alternatively, the absorption vessel can have the form shown in Fig. 26; the collar *D* is then not necessary. The apparatus should be tested for its ability to completely absorb arsine by running a known quantity of arsenic.

Reagents

Stannous chloride, 40 g. of $SnCl_2 \cdot 2H_2O$ in 100 ml. of concentrated hydrochloric acid.

Potassium iodide, 15 g. in 100 ml. of water.

Zinc, 20 to 30 mesh, arsenic-free. Zinc metal containing less than 0.005 p.p.m. of arsenic is commercially available. Any surface-contaminating arsenic can be removed by rinsing the metal with dilute hydrochloric acid and water.

Hydrochloric acid, concentrated. Analytical-reagent acid will serve satisfactorily in the great majority of cases. A special arsenic-free acid is available commercially; it is supplied in Pyrex bottles and contains less than 0.002 p.p.m. of arsenic.

Mercuric chloride, 1.5 g. in 100 ml. of water.

Potassium permanganate, 0.03 *N*. 0.10 g. in 100 ml. of water. Discard the solution when a precipitate of manganese dioxide forms.

Ammonium molybdate-hydrazine sulfate. Prepare fresh daily by mixing 10.0 ml. each of solutions (*a*) and (*b*) and diluting to 100 ml. with water. *Solution* (*a*): Dissolve 1.0 g. of ammonium molybdate in 10 ml. of water and add 90 ml. of 6 *N* sulfuric acid. *Solu-*

[19] If the approximate amount of arsenic is unknown add 10 ml. of hydrazine sulfate-molybdate solution, develop the color, and obtain the transmittancy of the solution. If the arsenic content exceeds 3 γ per ml., add 10–15 ml. of reagent, develop the color and obtain the transmittancy, and proceed in this manner until the arsenic concentration is less than 3 γ per ml.

[20] Instead of the apparatus described, that of C. C. Cassil and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **22**, 436 (1939) can perhaps be used. The procedure of these authors involves heating the acid solution with zinc so that the evolution time is much reduced.

tion (*b*): Dissolve 0.15 g. of hydrazine sulfate in 100 ml. of water. If desired, solutions (*a*) and (*b*) can be added separately to the sample solution to avoid the necessity of preparing the unstable mixture.

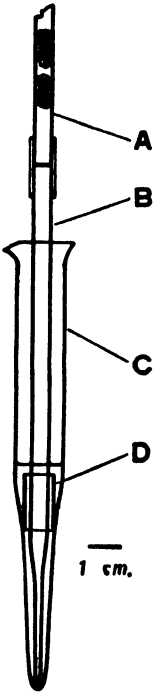


Fig. 25. Apparatus for the absorption of arsine in the molybdenum blue method.

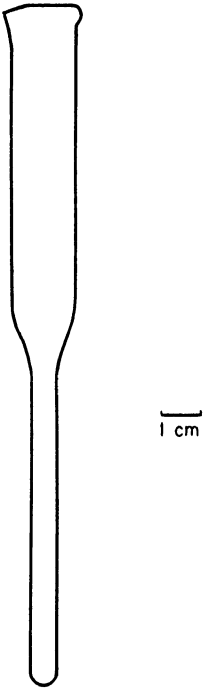


Fig. 26. Alternative absorption tube for arsine.

§ Procedure

The prepared sample must be free from substances that prevent the complete evolution of arsine.

Transfer the solution of the sample, conveniently having a volume of 25 ml. and containing not more than 15 micrograms of arsenic (20 micrograms of arsenious oxide), to the 50 ml. Erlenmeyer flask and add sufficient concentrated hydrochloric acid to make its total volume present 5 ml., 2 ml. of potassium iodide solution, and 0.5 ml. of stannous chloride solution. Allow the mixture to stand at room temperature for 15 to 30 minutes to assure the complete reduction of arsenic from the quinquevalent to the trivalent condition. Alternatively heat to 80–90° C., keep at this temperature for 5 minutes, and then cool to room temperature.

Measure 1.0 ml. of mercuric chloride solution, 0.2 ml. of 6 *N* sulfuric

acid, and 0.15 ml. of potassium permanganate solution into the absorption vessel. Mix with a thin glass rod. Connect the drawn-out delivery tube to the tube passing through the rubber stopper and lower the former into the absorption vessel so that its tip nearly touches the surface of the solution. The absorbing solution should not be allowed to enter the delivery tube, for then a coating of mercury arsenide is likely to be formed later on the interior of the tube.

When all is in readiness quickly add 2.0 g. of zinc to the flask, immediately insert the stopper, and lower the delivery tube into the absorbing solution so that its tip barely touches the bottom of the vessel. Allow the gases to bubble through the solution for 25 or 30 minutes without heating the flask. At the end of this time the solution should still contain some permanganate. With larger amounts of arsenic (10 micrograms) the solution will be more or less turbid because of the separation of hydrated manganese dioxide; this does no harm. Disconnect the delivery tube from the rest of the apparatus, leave it in the absorption vessel, add 5.0 ml. of ammonium molybdate-hydrazine sulfate reagent, and mix well. Heat for 15 minutes in a water bath at 95–100°, cool, transfer the solution to a 10 or 25 ml. volumetric flask, and make up to volume with water. Filter the solution through a small plug of fine glass wool in a small funnel and reject the first portion of the filtrate.

Obtain the transmittancy of the clear solution with a photometer, using a red filter (preferably one showing maximum transmission at 700 mμ or higher). In the reference cell place a comparison solution obtained as follows. Mix 1 ml. of mercuric chloride solution, 0.2 ml. of 6 *N* sulfuric acid and 0.10 ml. of potassium permanganate, and heat in a water bath for 5 minutes. Add 5.0 ml. of ammonium molybdate-hydrazine sulfate and heat for 15 minutes at 95°. Cool to room temperature, make up to the same volume as the unknown and filter.

Since Beer's law holds for the color system, the reference curve can be constructed by finding the transmittancy of one or two solutions of known arsenic concentration. Mix respectively 1.00 and 2.00 ml. of 0.001 per cent arsenic (as arsenious oxide) solution with 1.0 ml. of mercuric chloride, 0.2 ml. 6 *N* sulfuric acid and 0.10 ml. of potassium permanganate solution, and heat at 95° for 5 minutes. Then add 5.0 ml. of the molybdate-hydrazine reagent and proceed as already described for the unknown.

Correct the result for a blank carried through the procedure.

B. The Gutzeit Method

In this old but still much-used method, arsenic (III) is reduced to arsine by the action of zinc in hydrochloric or sulfuric acid solution and the evolved gases are led over a strip of paper impregnated with mercuric bromide or

chloride which is placed in a narrow tube. Instead of a paper strip, a string similarly impregnated and placed in a capillary tube may be used. Superior to either of these is the use of an impregnated paper disk.[21] The stain produced is compared with a series of standard stains, generally indirectly in the case of a strip or string by making use of a graph in which the length of the stain is plotted against the quantity of arsenic. When a paper disk is used, the spot is intensified with ammonia and evaluated by reference to a standardized photographic step-scale print having 20 bands of graded reflection densities, which have been photometrically calibrated against spots given by known amounts of arsenic (Satterlee and Blodgett).

The Gutzeit method is highly sensitive (as little as 0.1 γ of arsenic can be detected under the proper conditions), but except for very minute amounts it is neither as precise nor as accurate as the molybdenum blue method. It is rather troublesome to carry out, and extreme care must be taken to maintain conditions constant. Thus, to mention only one factor, the rate of hydrogen evolution must be kept constant or the length of the stain (in the paper strip method) will vary from one determination to another. To do full justice to the method, a discussion of nearly monographic proportions would be required. The reader is referred for full experimental details to the procedure given in *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists*, or to the procedures of How and of Cahill and Walters,[22] and especially to that of Satterlee and Blodgett.

C. Other Methods

A number of nephelometric methods for arsenic based on the formation of colloidal dispersions of alkaloid arsenomolybdates have been described. Cocaine,[23] strychnine,[24] and quinine[25] have been used as reagents. These methods are inferior to the colorimetric method (IIA).

Nephelometric methods have also been based on the formation of colloidal suspensions of elemental arsenic obtained by reduction with sodium hypophosphite[26] in hydrochloric acid solution.

[21] See especially the work of H. S. Satterlee and G. Blodgett, *Ind. Eng. Chem., Anal. Ed.*, **16**, 400 (1944), who have developed a refined Gutzeit method for amounts of arsenic in the range 0.04 to *ca.* 1 γ. The hydrogen is evolved at room temperature in a system in which the pressure is reduced to 0.25–0.5 atmosphere, and the gases are drawn through sensitized paper having an exposed circular area 0.125 or 0.25 inch in diameter.

[22] A. E. How, *Ind. Eng. Chem., Anal. Ed.*, **10**, 226 (1938); Sister Emily Cahill and Sister Louisella Walters, *ibid.*, **14**, 90 (1942).

[23] H. Kleinmann and F. Pangritz, *Biochem. Z.*, **185**, 14 (1927).

[24] L. Belladen, U. Scazzola, and R. Scazzola, *Ann. chim. applicata*, **23**, 517 (1933).

[25] D. Chouchak, *Ann. chim. anal. chim. appl.*, **4**, 138 (1922).

[26] M. Delaville and J. Belin, *Bull. soc. chim. biol.*, **9**, 91 (1927).

Stannous chloride in acid solution reduces arsenic, giving a reddish brown sol. The reduction takes place more easily if a minute trace of mercury is present.[27]

III. Applications

A. Metals and Alloys[17]

§ Procedure

Carbon Steel, Cast Iron, Ferromanganese, etc.—Dissolve 0.1 g. of sample in 10 ml. of 1:1 nitric acid, evaporate the solution to dryness on a hot plate at a temperature not exceeding 130°. Cool, add 5 ml. of concentrated hydrochloric acid, and transfer the solution to the Scherrer distilling apparatus with the aid of 10 ml. of hydrochloric acid. Add hydrobromic acid and hydrazine sulfate as described in the directions on p. 182, distil, and finish the determination according to Method 1 above.

High-Chromium Steel. Dissolve 0.1 g. in a mixture of 5 ml. of concentrated nitric and 5 ml. of concentrated hydrochloric acids. Evaporate to dryness and proceed as in the case of carbon steel.

Brass, Bronze, and Bearing Metals. Dissolve 0.1 g. of sample in 5 ml. of concentrated nitric acid, cool, add 8 ml. of 1:1 sulfuric acid and evaporate to fumes of sulfuric acid. Cool, add 5 ml. of water, transfer the solution to the distilling flask with hydrochloric acid and proceed as described on p. 182.

Alternative Procedure for Copper or Brass.[9] Dissolve a 5 g. sample (for 0.002–0.012 per cent As) in 35 ml. of 1:1 nitric acid, add 8 ml. of concentrated sulfuric acid, and evaporate to near dryness. Dissolve the residue in 60 ml. of water, and add 75 ml. of concentrated hydrochloric acid and 15 ml. of 50 per cent hypophosphorous acid (or 12 g. of sodium hypophosphite). Digest at 80–90° for 30 minutes or longer and then boil for 5 minutes.

Filter off the precipitate on a sintered-glass crucible of fine porosity and wash beaker and crucible with small portions of hot freshly boiled water. Dissolve the arsenic in 10 ml. of iodine solution (2.54 g. of iodine and 8 g. of potassium iodide dissolved in 25 ml. of water and diluted to 1 liter) containing 1 drop of "Aerosol," which is drawn through the filter crucible into a 200 ml. volumetric flask. Wash with water, dilute the solution to the mark, and transfer a 20 ml. aliquot to a 25 ml. volumetric flask. Add 2.5 ml. of ammonium molybdate solution (1 per cent in 5 *N* sulfuric acid) and 1.0 ml. of hydrazine sulfate (0.15 per cent aqueous solution). Heat the mixed solution in a water bath at 90–100° for 10 minutes. Cool

[27] W. B. King and F. E. Brown, *Ind. Eng. Chem., Anal. Ed.*, **5**, 168 (1933).

to room temperature, make up to volume, and obtain the transmittancy of the solution at 840 mμ (or above 700 mμ).

To construct the standard curve, dissolve arsenic-free copper in nitric-sulfuric acid, add suitable amounts of standard arsenic solution to cover the desired range, and treat as above.

The method may also be applied to lead and tin-base bearing metals.

Pig Lead. To 5 g. of sample in a 400 ml. beaker add 100 ml of 1:3 nitric acid and warm until the lead has all dissolved. Cool, add 15 ml. of concentrated sulfuric acid, and evaporate to dense fumes. Add 20 ml. of water to the cold mixture and transfer to the distilling flask with 50 ml. of concentrated hydrochloric acid. Add 10 ml. of hydrobromic acid and 1 g. of hydrazine sulfate with an additional 50 ml. portion of hydrochloric acid. Catch the distillate in 10 ml. of water contained in a 250 ml. beaker. Distil until approximately 90 ml. of distillate have been collected. Add 30 ml. of nitric acid to the distillate, evaporate to dryness on the steam bath and complete the determination as described on p. 182.

B. Soils

Acid-soluble arsenic in soils can be determined by either of the two following procedures.

§ Procedure 1[1]

Transfer 50 g. of air-dry soil to a special distillation apparatus, which consists of a 500 ml. round-bottomed flask provided with a thistle tube reaching to the bottom and a condenser with a downward-curved adapter (all connections glass). Add slowly 100 ml. of 48 per cent hydrobromic acid containing 2 to 3 ml. of bromine. After any frothing due to evolution of carbon dioxide has subsided, connect the condenser so that the adapter dips below the surface of 5 ml. of bromine water in the receiving flask. Boil gently and collect 50 to 60 ml. of distillate. (If sufficient bromine was not added to the soil to give some in the distillate, remove the flame and add more bromine in hydrobromic acid solution.)

Add the distillate slowly to an excess of arsenic-free nitric acid to destroy hydrobromic acid. This is best done by adding 5 to 10 ml. portions of the solution to nitric acid in a casserole and expelling most of the bromine on a steam bath before adding the next portion. Finally evaporate to dryness on the steam bath, wash down the sides of the casserole with water, and again evaporate to dryness. Dissolve the residue in water and make up to 50 or 100 ml. in a volumetric flask. Determine arsenic in a suitable aliquot according to the directions on p. 182.

§ Procedure 2[28]

Transfer 5 g. of air-dry soil to a 200 ml. Kjeldahl flask, add 20 ml. of sulfuric acid, mix well, and then add 5 ml. of nitric acid and 0.1 g. of potassium chlorate. Heat gently at first and then more strongly until the solution boils; digest at this temperature until all organic matter is destroyed, adding more nitric acid if necessary. Cool, dilute the solution with 50 ml. of water and boil until fumes of sulfur trioxide are given off. Repeat this operation twice to expel all nitric acid. Dilute the solution in the flask with water and decant into an all-glass distilling apparatus (Fig. 24), rinsing the residue with water; an aliquot portion may of course be taken if thought desirable. Add hydrochloric acid, hydrobromic acid and hydrazine sulfate to the distilling flask, distil as already described (p. 182), and finish the determination according to the directions in the general procedure.

C. Silicate Rocks[29]

The determination of the minute amounts (0.000n per cent) of arsenic usually occurring in silicate rocks has not been investigated thoroughly but the following method has been shown to give fair results for the very small quantities of arsenic encountered. Approximately 80 per cent of the arsenic present in the sample is recovered, the remainder apparently being lost in the decomposition.

§ Procedure

Mix and fuse 0.50 g. of 100-mesh sample with a mixture of 1.0 g. sodium carbonate and 50 mg. sodium nitrate. Disintegrate the melt with water, add 2.5 ml. of 60–70 per cent perchloric acid and 5 ml. of hydrofluoric acid. Evaporate to a paste, add a few ml. of water, evaporate to dryness, and heat until fumes of perchloric acid cease to come off. Transfer the residue with 25 ml. of water to a 50 ml. Erlenmeyer flask, add 5 ml. of concentrated hydrochloric acid, and heat to about 80°. A practically clear solution should be obtained. Then add potassium iodide and stannous chloride

[28] *J. Assoc. Official Agr. Chem.*, 18, 62, 207 (1935).

[29] Based on unpublished work of the writer. The following papers may be mentioned as having a bearing on the determination of arsenic in minerals. H. N. Wilson, *Analyst*, 68, 361 (1943), decomposes glass by fusion with sodium hydroxide and isolates arsenic by distillation as the chloride from the hydrochloric acid solution of the melt; the method described is a volumetric one but it seems likely that it can be adapted to colorimetry. L. W. Strock, *Z. anal. Chem.*, 99, 321 (1934), found that iron ore was best decomposed for the determination of arsenic by fusion with sodium carbonate in combination with borax. Sodium carbonate fusion alone was found unsatisfactory. Nitric-sulfuric-hydrofluoric acid decomposition resulted in loss of arsenic. For the determination of arsenic in limestone see J. Wyllie, *Can. Pub. Health J.*, 32, 81 (1941).

and finish the determination as described on p. 184. The results are low and a more correct value for arsenic can be obtained by multiplying the apparent arsenic content by 10/8. Preferably the latter factor is determined by each analyst for his particular working conditions.

D. Sulfide Minerals

The finely powdered sample is brought into solution with a mixture of hydrochloric and nitric acids (*cf.* p. 518) or nitric acid alone, and the excess of nitric acid is expelled by addition of sulfuric acid and evaporation to thick fumes. The arsenic is then distilled as the trichloride as described on p. 182, or as the bromide.[1,2]

E. Bio Materials

The destruction of organic material must be done with suitable precautions to prevent loss of arsenic. A strong oxidizing wet attack with a mixture of nitric and sulfuric acids or of nitric-sulfuric-perchloric acid is usually employed for most organic samples. Charring or browning of the sample is to be avoided as possibly leading to loss of arsenic as arsenious oxide or as arsenious chloride if chloride is present. As a precautionary measure, the liquid which is boiled off in the first part of the digestion can be condensed and returned to the mixture for the recovery of any volatilized arsenic. If the digestion is carefully carried out, the loss of arsenic is negligible.[30]

In special cases, decomposition of the sample in an oxygen bomb or in a stream of oxygen may be desirable or necessary.[31] Oils, fats, tobacco,[32] and certain other materials are hard to decompose completely by wet oxidation.

The most rapid method for the determination of arsenic in the acid digest consists of the distillation of quinquevalent arsenic after the addition

[30] Under conditions similar to those of the procedure above, D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, **13**, 915 (1941), found that the distillate from the digestion of 100 ml. of urine containing 4 mg. of arsenic showed 12 γ of arsenic, corresponding to a loss of 0.3 per cent.

[31] Consult, for example, F. P. Carey, G. Blodgett, and H. S. Satterlee, *Ind. Eng. Chem., Anal. Ed.*, **6**, 327 (1934), and R. E. Remington, E. J. Coulson, and H. von Kolnitz, *ibid.*, **6**, 280 (1934); H. S. Satterlee and G. Blodgett, *ibid.*, **16**, 400 (1944). The last named authors have pointed out the existence of loosely bound arsenic in blood and other bio material, which is, or becomes, volatile at as low a temperature as 56° C. They describe a procedure for the recovery of such loosely bound arsenic.

[32] Pyridine and other nitrogen ring compounds resist oxidation and interfere by inhibiting the evolution of arsine. See C. R. Gross, *Ind. Eng. Chem., Anal. Ed.*, **5**, 58 (1933).

of bromide followed by the direct application of the molybdenum blue method. The procedure is given in detail below.[33]

Alternatively, arsenic can be isolated from the digest by distillation as the trichloride (Sultzaberger, *loc. cit.*) or by evolution as arsine according to the general procedures on pp. 182–183. If arsenic is to be evolved as arsine, it is best to dilute the digest to 50 ml. and take a 20 or 25 ml. aliquot, no further addition of hydrochloric acid being necessary.

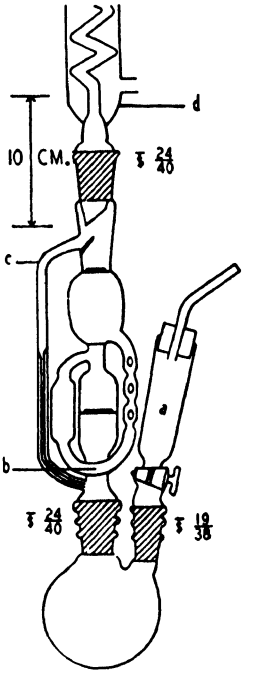


Fig. 27. Magnuson and Watson distillation apparatus for arsenic.

Apparatus

A special distillation apparatus is required (Fig. 27). This consists of a 250-ml. round-bottomed flask with two necks, one for the reception of a dropping funnel, the other for a still head (commercially available), which is in turn connected to a reflux condenser, coil type, 200 mm. in length.

Special Solutions

Ammonium molybdate. Dissolve 1.0 g. of ammonium molybdate in 100 ml. of 1:9 sulfuric acid, and add 50 ml. of 1 *N* hydrochloric acid.

Hydrazine sulfate, 0.05 per cent aqueous solution.

Standard arsenic solution. Dissolve 1.53 g. of reagent-quality arsenic pentoxide (≡ 1.00 g. As) in 100 ml. of 1 *N* sodium hydroxide, dilute with water to about 500 ml., neutralize with hydrochloric acid (add 100 ml. 1 *N* acid), and dilute to 1 liter. The strength of the solution is preferably checked by iodometric titration. Dilute this stock solution to give a solution containing 10 γ arsenic per milliliter.

§ Procedure

Transfer a suitable weight of sample (*e.g.*, 5–10 g., or less for relatively high arsenic contents) to a 250 ml. Erlenmeyer flask[34] with a small funnel in its mouth. Add 10 ml. of concentrated nitric acid and 5 ml. of concentrated sulfuric acid.[35] Heat gently at first and add more

[33] Directions of Magnuson and Watson, *loc. cit.*, as modified by T. H. Maren, *Ind. Eng. Chem., Anal. Ed.*, 18, 521 (1946). The latter worker showed that not less than 2.5 milliequivalents of acid should be present in the distillate in order that molybdenum not combined with arsenic be not reduced. Since the amount of hydrobromic acid in the distillate varies somewhat with the exact conditions of distillation, additional acid is added with the molybdate reagent to provide a safe excess.

[34] If desired, the decomposition can be carried out in a round-bottomed 1-liter Pyrex flask having three necks: one connected to a vertical condenser for downward distillation and the other two fitted with funnels for addition of acids. This arrangement permits collection of the distillate in the early stages of the digestion if it is feared some arsenic may be volatilized (Morris and Calvery).

[35] Sulfuric acid containing less than 0.05 γ arsenic in 10 ml. is commercially available.

nitric acid at intervals so that the mixture does not darken at any time. Continue the digestion until all organic material has been destroyed and the mixture does not show more than a very pale yellow color when evaporated to fumes of sulfuric acid.[36] Add 10 ml. of water to the cooled digest and again evaporate to fumes of sulfuric acid to expel all nitric acid. Avoid undue loss of sulfuric acid.

Transfer the solution to the special distillation flask (Fig. 27) with 5 ml. of water. Add 2 ml. of 30 per cent potassium bromide solution to the dropping funnel. Attach the distilling head and place the flask in an already hot "Hot Cone" heater. When boiling has started and steam has begun to condense in the trap *b*, add 3 ml. of water through the top of the still and put the condenser into place so that condensed vapor will drip down the capillary tube *c*. Now blow the potassium bromide solution into the flask, followed by 2 ml. of water as a rinse. Continue the distillation for 4 minutes after the bromide has been added. Then disconnect the still from the flask and condenser and pour the distillate through the top of the still into a test tube. Rinse two or three times with 2 ml. of water.

To the solution in the tube, now having a volume of 15 to 20 ml., add 3.0 ml. of ammonium molybdate solution and 2.0 ml. of hydrazine sulfate solution, avoiding contact of the solutions with the side of the tube. Mix thoroughly and heat in a water bath at 90–100° C. for 10 minutes. Cool and dilute the solution to 25 or 30 ml. Obtain the transmittancy of the solution at 840 mμ in a spectrophotometer; use a filter with maximum transmission at 700 mμ (or higher) with a filter photometer.

Construct the standard curve by taking various amounts of pentavalent arsenic (*e.g.*, 0–50 γ), adding 3 ml. of 1 *N* hydrochloric acid, and developing the color as described. Run a reagent blank.

[36] Perchloric acid may be added in small portions in the later stages of the digestion to hasten the oxidation.

CHAPTER VIII

BARIUM

I. Separations

For the isolation of barium, chief reliance is placed on the slight solubility of the sulfate and the chromate (0.29 mg. $BaSO_4$ and 0.46 mg. $BaCrO_4$ in 100 ml. of water at 30°), whose precipitation may be made more complete by the addition of alcohol or acetone. Precipitation of the chromate requires a nearly neutral medium, whereas the sulfate may be successfully separated from a slightly acid solution if an excess of sulfate is present. Isolation of barium as sulfate has the disadvantage that in order to bring barium into solution the precipitate must be fused with sodium carbonate and the melt leached with water to obtain barium carbonate which is then dissolved in acid after washing.

Lead will be precipitated or coprecipitated with barium sulfate and chromate, and strontium with barium sulfate. A fair separation of barium from strontium[1] can be effected by the use of chromate as precipitant because of the relatively high solubility of strontium chromate[2] (96 mg. $SrCrO_4$ in 100 g. of water at 25°). Double precipitation is necessary if an appreciable amount of strontium is present. Calcium chromate is very soluble (18.2 g. $CaCrO_4 \cdot 2H_2O$ in 100 ml. of solution at 45°). In the presence of lead it is best first to separate this metal electrolytically if it is present in appreciable amounts, and then to extract the solution with dithizone, after making alkaline, to remove any residual traces of lead.[3]

II. Methods of Determination

A. The Chromate Method[4]

Barium may be determined indirectly by precipitating as the chromate, dissolving the washed precipitate in acid, and comparing the color with

[1] A. Skrabal and L. Neustadl, *Z. anal. Chem.*, **44**, 742 (1905). The procedure has been improved by G. L. Beyer and W. Rieman, *Anal. Chem.*, **19**, 35 (1947).

[2] T. W. Davis, *Ind. Eng. Chem., Anal., Ed.*, **14**, 709 (1942).

[3] From the similarity in the ionic radii of barium and lead (1.43 and 1.32 Å. respectively) it may be expected that lead chromate or sulfate can be used to gather small amounts of barium.

[4] H. A. Frediani and B. J. Babler, *Ind. Eng. Chem., Anal. Ed.*, **11**, 487 (1939).

an acidified chromate solution, preferably obtained by dissolving barium chromate precipitated from a known amount of barium.[5] The weakness of the method lies in the appreciable solubility of barium chromate, especially in the presence of foreign salts, and the non-specificity of the reaction (precipitation of lead and possibly strontium). Separation and concentration of the barium will frequently be necessary before the method can be applied. Double precipitation usually suffices to separate barium from strontium.

Data on the performance of the method for trace quantities of barium are meager and the procedure must be given in a brief generalized form. A thorough study of the method is greatly needed, especially since it is the only satisfactory one at present for the colorimetric determination of barium.

§ Procedure

Add 0.05 ml. of glacial acetic acid and 5 ml. of 25 per cent ammonium acetate solution to the neutral sample solution of appropriately small volume. Heat to boiling and add a moderate excess of 10 per cent ammonium or potassium chromate solution. Allow the solution to cool to room temperature and filter through a small sintered-glass or porous porcelain filter crucible (or use a filter stick, p. 500). Wash with cold water to remove all excess chromate. Dissolve the precipitate in 5 ml. of 4 *N* hydrochloric acid and dilute the solution to a convenient volume. Compare the solution in a Duboscq colorimeter against a similar one containing a comparable amount of barium chromate or determine the transmittancy with a photometer. Use a blue filter (maximum transmission <500 mμ).

In the presence of more than an equal amount of strontium, dissolve the precipitate of barium chromate in dilute hydrochloric acid, neutralize the solution with ammonia, and add ammonium acetate solution equal to about one-tenth the volume of the solution. Heat to boiling, add a drop or two of ammonium chromate, allow the solution to cool to room temperature and proceed as before.

Note. The chromate in the barium chromate precipitate can also be determined with diphenylcarbazide after solution in dilute hydrochloric acid (see p. 260).

B. Other Methods

Tannic acid (10 per cent aqueous solution) gives a transitory yellow or yellow-green color with an alkaline solution of barium, strontium, and

[5] In another method, barium is precipitated with a known amount of chromate and the excess of the latter is found from the optical density of the solution. This procedure can be applied to milligram quantities of barium. See S. Christow, *Z. anal. Chem.*, **125**, 278 (1943).

calcium.[6] The colored barium salts of rhodizonic acid[7] and tetrahydroxyquinone are too soluble to be of much value in colorimetric trace analysis.

A method for the determination of 5 to 150 γ of barium in atmospheric dusts has been described, in which use is made of mixed crystal formation between barium sulfate and potassium permanganate.[8] Barium is precipitated as the sulfate in the presence of permanganate, and, after the destruction of the excess permanganate, the precipitate is collected on a "confined spot test paper," which restricts the precipitate to a definite area. A series of standards is prepared in like manner. The color intensity of the spots is proportional to the amount of the barium precipitate. Lead, calcium, strontium, and iron (III) interfere.

It may be expected that barium can be determined turbidimetrically or nephelometrically as barium sulfate, but no data seem to be available.

[6] Ammer and Schmitz, *Wasser*, **8**, Part II, 161 (1934); *Chem. Abstracts*, **29**, 4285 (1935).

[7] Friedrich and Rapoport, *Mikrochemie*, **14**, 41 (1933).

[8] H. Yagoda, *J. Ind. Hyg. Toxicol.*, **26**, 224 (1944).

CHAPTER IX

BERYLLIUM

I. Separations

A. Ammonia Precipitation in the Presence of Mercaptoacetate Followed by Sodium Hydroxide Fusion of Precipitate

The most generally useful methods for the fluorimetric or colorimetric determination of beryllium require the absence of iron, manganese, magnesium, and other metals whose hydroxides are insoluble in strongly basic medium. Sodium hydroxide precipitation of these metals, when present in appreciable amount, is not satisfactory because of the strong coprecipitation of beryllium.[1] Fusion with sodium hydroxide gives a better separation, but even it is not satisfactory if comparatively large quantities of these elements are present. In such a case it is usually best to make an ammonia precipitation of beryllium hydroxide first to effect a separation from the alkaline earths, magnesium, and manganese. Iron also can be kept in solution if mercaptoacetic (thioglycolic) acid is added. The complete precipitation of beryllium is assured by having a sufficient amount (*e.g.*, 20 mg.) of aluminum present; this metal does not react with the preferred fluorimetric or colorimetric reagents for beryllium. Less than 0.1 γ of beryllium remains in 25 ml. of solution after ammonia precipitation if as little as 3 mg. of aluminum is also present.

The ammonia precipitate is then subjected to double fusion with sodium hydroxide. Since ordinarily the aluminum-beryllium hydroxide precipitate will contain only little titanium hydroxide and small amounts of coprecipitated iron hydroxide, there is little tendency for beryllium to be retained in the residue from the fusion, and satisfactory recoveries of beryllium are obtained. Titanium, if present in relatively large amount, should first be separated by one of the methods described under section B below. The sodium hydroxide fusion separates small amounts of such metals as magnesium, calcium, nickel, and cobalt, which may have been coprecipitated in the ammonia precipitation. The rare earth metals remain in the residue when the sodium hydroxide melt is leached with water.

[1] Better separation of beryllium from iron and manganese can be had by precipitating the latter as sulfides by adding the sample solution dropwise to a boiling solution of sodium hydroxide-sulfide (10 per cent of each) and digesting for an hour before filtration.

Scandium, if alone, would dissolve to some extent, since its hydroxide is slightly soluble in strong alkali, but this tendency is decreased in the presence of small amounts of iron or other metals whose hydroxides are insoluble under the conditions. Chromium (III) is oxidized to chromate in the hydroxide fusion and leads to difficulties (especially in the fluorimetric determination). In some cases it may be possible to oxidize chromium to chromate (as with persulfate) before the ammonia precipitation is made, and thus keep almost all of the chromium in solution when ammonia is later added. If only a small amount of chromate is present in the leach of the sodium hydroxide melt it may perhaps be reduced with a little stannite before the mixture is filtered.

The ammonia precipitate should be ignited at as low a temperature as possible in burning off the paper before the sodium hydroxide fusion, because strongly ignited beryllium oxide is not easily attacked by the molten hydroxide.[2]

TABLE 33

DETERMINATION OF BERYLLIUM WITH MORIN AFTER SEPARATION BY AMMONIA PRECIPITATION IN THE PRESENCE OF MERCAPTOACETATE FOLLOWED BY DOUBLE FUSION WITH SODIUM HYDROXIDE[a]

(Solution contained 48 mg. Al_2O_3, 38 mg. Fe_2O_3, 25 mg. MgO, 25 mg. CaO, 0.6 mg. MnO, 3 mg. TiO_2, and 1.2 mg. P_2O_5)

	Be found, p.p.m.		
Be present, p.p.m.[b]	First fusion	Second fusion	Total
0.0	0.0	0.0	0.0
0.5	0.3	0.1	0.4
0.5	—	—	0.45
1.0	0.75	0.2	0.95
1.0	—	—	1.0
2.0	1.35	0.4	1.75

[a] Data of the writer.

[b] P.p.m. refers to sum of the oxides.

The separation described in the preceding paragraphs has been studied especially from the standpoint of determining less than 10 p.p.m. of beryllium in silicate rocks, and detailed directions are given under that heading (p. 206). For results see Tables 33 and 34.[6]

[2] Experiments by G. Wirths (quoted by Fischer and Wernet) have shown that as much as 30 per cent of the beryllium may remain in the leached residue when the precipitate is ignited at 850°.

[6] W. Fischer and J. Wernet, *Angew. Chem.*, **A60**, 729 (1948), give results showing very satisfactory recovery of beryllium by sodium hydroxide fusion when used in conjunction with preliminary ammonia precipitation and other separations.

B. Other Methods

Electrolysis with a mercury cathode should be a useful method for the elimination of many interfering metals (p. 144), but it must be combined with other separations when the alkaline earth metals, magnesium, manganese, titanium, etc. are present. Copper can be removed by electrolysis with a platinum cathode.

Cupferron precipitation in mineral acid medium (2 *N* hydrochloric acid) separates ferric iron, titanium, zirconium, and some other metals. The insoluble cupferrates and the excess cupferron can be extracted with chloroform (*cf.* p. 142).

Much iron can be largely removed by extraction of ferric chloride from hydrochloric acid solution by ethyl or isopropyl ether. Small amounts of ferric iron can be precipitated with ferrocyanide in acid medium (p. 209).

Separation of aluminum from beryllium will rarely be required. The former, with other metals such as ferric iron, copper, and zinc (p. 115), can be precipitated with 8-hydroxyquinoline in acetic acid-acetate medium; traces of unprecipitated metals can be extracted with chloroform. Beryllium shows little tendency to be carried down in an aluminum hydroxyquinolate precipitate. Excess oxine in the solution can be destroyed with sulfuric-nitric acid.

Large amounts of aluminum and titanium can be separated by saturating an aqueous solution containing ammonium chloride (4 g. in 75 ml.) with gaseous hydrogen chloride at 0° C.[4] These metals are precipitated as $AlCl_3 \cdot 6H_2O$ and $(NH_4)_2TiCl_6$, whereas beryllium remains in solution. There is very little tendency for beryllium to be coprecipitated. Thus, Fischer and Wernet recovered 60 γ of BeO within ± 5 γ when applying this separation to a mixture containing 3 g. of Al and 0.18 g. of TiO_2. Approximately 1 mg. of aluminum and 1.5 mg. of titanium remain in 100 ml. of solution following this precipitation. The beryllium in the filtrate can be recovered by ammonia precipitation (a few mg. of ferric iron are added as collector if not already present). The precipitate is then fused with sodium hydroxide.

Beryllium can be separated from calcium and magnesium by precipitation as phosphate at *p*H 4.5 if aluminum phosphate is used as collector (p. 209). As little as 0.75 mg. of aluminum phosphate is stated to be sufficient for complete gathering of microgram quantities of beryllium.

[4] W. Fischer and J. Wernet, *Angew. Chem.*, **A60**, 729 (1948); W. Fischer and W. Seidel, *Z. anorg. allgem. Chem.*, **247**, 333 (1941); Seidel and Fischer, *ibid.*, **247**, 367 (1941).

II. Methods of Determination

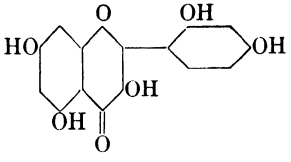
The fluorimetric methods for beryllium are more sensitive than the colorimetric and the former are therefore given first place in the following treatment.

A. Fluorimetric Methods

Morin has perhaps been investigated more thoroughly than any other fluorescence reagent for beryllium. It appears to be more sensitive and specific than others which have been proposed.

1. Morin as Reagent

In sodium hydroxide solution, morin, a tetrahydroxy flavanol having the formula



yields a compound with beryllium which shows a strong yellow-green fluorescence.[5] This reaction may be made the basis of a very sensitive fluorimetric method for the determination of beryllium.[6] As little as 0.001 p.p.m. of Be in solution can be detected. Metals yielding slightly soluble hydroxides must naturally be separated before the determination can be made.

The intensity of the fluorescence given by beryllium depends on the sodium hydroxide concentration, being less at higher concentrations, and therefore the alkalinity must be controlled. In 0.3 *N* sodium hydroxide medium the fluorescence is about 10 per cent weaker than in 0.24 *N* solution. On standing, the fluorescence intensity slowly decreases; it remains more constant at higher morin concentrations.

Aluminum has no effect on the reaction except insofar as it reduces the alkalinity by aluminate formation. For the most accurate results, aluminum should be added to the standards to give a concentration approximately the same as in the sample solution. When less than the equivalent of 10 mg. of Al_2O_3 is present the error can usually be neglected (*cf.* p. 208).

With the exception of lithium, calcium, and zinc, the metals not precipitated by sodium hydroxide do not react with morin. Lithium gives a weak fluorescence with morin in basic solution, which is approximately

[5] H. L. J. Zermatten, *Proc. Acad. Sci. Amsterdam*, **36**, 899 (1933); E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 762 (1940).

[6] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 674 (1940).

one-thousandth as strong as the beryllium fluorescence (the value depends upon the alkalinity) when radiation in the near ultraviolet is used for excitation. Zinc also fluoresces weakly in basic medium, but can easily be prevented from interfering by the addition of cyanide. In daylight, amounts of zinc less than about 0.2 mg. do not show a fluorescence. The fluorescence of small amounts of calcium can be destroyed by the addition of sodium pyrophosphate. Certain of the rare earth hydroxides and also scandium hydroxide are sufficiently soluble in excess sodium hydroxide to yield a distinct fluorescence with morin, but pyrophosphate greatly weakens or destroys the fluorescence. Small quantities of copper, silver, and gold in basic solution oxidize morin and prevent the determination of beryllium; the same is true of manganese as manganate, but the latter can be destroyed readily, for instance by heating with a little alcohol.

Phosphate, fluoride, and borate are without effect, and likewise silicate if the solution is not turbid. Chromate except in minute amounts must be absent because it diminishes or destroys the beryllium fluorescence, presumably by absorbing the ultraviolet radiation.

Special Solutions

Sodium hydroxide, 1 or 2 *N*.

Sodium pyrophosphate, saturated aqueous solution.

Morin, 0.05 per cent in acetone. The solution may be kept for months.[7]

Standard beryllium solution, 0.00050 per cent. Dissolve 0.0246 g. of $BeSO_4 \cdot 4H_2O$ (tested purity) in water, add 1.0 ml. of concentrated hydrochloric acid and dilute to 250 ml. with water. The standard solution may also be prepared from pure BeO, by fusing the latter with potassium pyrosulfate and dissolving the melt in 0.1 *N* sulfuric acid.

§ Procedure

The following directions for the determination of beryllium by the standard series method may be applied to a solution free from metals that are precipitated by sodium hydroxide in excess. Lithium in large amounts should be absent, at least if the comparison is made in the ultraviolet. Calcium may be present up to at least 0.5 mg. when the comparison is made in daylight.

The sample solution may conveniently have a volume of 5 or 10 ml. and may contain 0.1 to 1 γ of beryllium. A flat-bottomed tube of 25 ml. capacity (p. 52) should be used to hold the solution. Add 5 ml. of sodium pyrophosphate solution and sufficient sodium hydroxide to make its concentration 0.1 *N* if metals precipitated by alkali are absent. If aluminum, lead, and other metals giving precipitates soluble in excess hydroxide are

[7] If only technical-grade morin is available, extract it with acetone, filter, evaporate the extract to dryness, and powder the residue.

present, add enough sodium hydroxide to give a clear solution. In such a case approximately the same amount of the metal should be present in the standards to keep the alkalinity the same. If zinc is present and the comparison is to be made in the ultraviolet, add 2 ml. of 5 per cent potassium cyanide (sufficient for a few milligrams of zinc). Then add 0.20 ml. of morin solution and mix. Treat similarly a series of standards, containing the same concentration of sodium hydroxide as the sample and having the same volume. Compare the tubes axially in strong daylight against a dark background. If preferred the comparison can be made in the near ultraviolet. The tubes are then conveniently held above the source and examined transversely. Solutions differing in concentration by 10 per cent show a perceptible difference in fluorescence intensity.

2. 1-Amino-4-hydroxyanthraquinone and 1,4-Dihydroxyanthraquinone as Reagents[8]

The first of these substances is soluble in alcoholic, alkaline, and acid solutions. In neutral or acidic solution it shows a red fluorescence, in basic solution none. In basic medium (about 0.2 *N* in sodium hydroxide) beryllium gives a red fluorescence. The limit of detectability of beryllium is given as 0.025 p.p.m. The sensitivity decreases as the hydroxyl ion concentration is increased. Even in 0.3 *N* sodium hydroxide the decrease is appreciable. Lithium in concentrations greater than 700 p.p.m. gives a fluorescence like that of beryllium. A saturated solution of calcium hydroxide produces a faint fluorescence; in 0.2 *N* sodium hydroxide the amount of calcium remaining in solution is said to be too small to yield a fluorescence. Other ions not precipitated in basic solution seem to have no effect in reasonable quantities. High concentrations of sodium chloride destroy the fluorescence of beryllium. Small amounts of iron are said to be made harmless by the addition of tartrate, but the sensitivity of the beryllium reaction is then decreased. The reagent has been applied in the determination of beryllium in tissues (p. 209).

1,4-Dihydroxyanthraquinone (quinizarin) also gives a red fluorescence with beryllium (p. 209), the intensity being of the same order as that given by the above reagent. A relatively weak fluorescence is produced by 1,8-dihydroxyanthraquinone. The 1,4 compound has been used by Fletcher, White, and Sheftel as a fluorimetric reagent for beryllium in sodium hydroxide-citrate medium. Iron, manganese, magnesium, ca[1]·

[8] C. E. White and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.*, **13**, 809 (1941); M. H. Fletcher, C. E. White, and M. S. Sheftel, *ibid.*, **18**, 179 (1946) (determination of beryllium in ores with 1,4-dihydroxyanthraquinone).

cium, and other elements precipitated under the conditions must be absent. Lithium also yields a fluorescence, but reacts less sensitively than beryllium. A limited amount of aluminum may be present. This reagent is said to be more satisfactory than 1-amino-4-hydroxyanthraquinone.

B. Colorimetric Methods

The color reactions of beryllium are of two types. In one the *p*H of the solution is adjusted to a value which will cause precipitation of beryllium hydroxide, which then absorbs the reagent (dye) with a change in color. This is lake formation (4 and 5 below). The other type probably involves reaction between the dye and beryllate, the alkalinity being great enough to dissolve beryllium hydroxide. The nature of the colored product is not certain. On the whole, this type of reaction (1 and 2 below) is to be preferred as being more specific. Aluminum, for example, does not react in strongly basic medium.

1. Quinalizarin as Reagent

Quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) yields a blue color with beryllium in sodium hydroxide solution[9]; in the absence of beryllium the dye has a violet color in basic medium. The colored compound is reported to contain beryllium and quinalizarin in the molar ratio 2:1. Beryllium can thus be determined by the mixed-color method, *i.e.*, by treating the alkaline sample solution with a sufficient excess of reagent to furnish a blue-violet color whose hue can be matched in a standard series or by colorimetric titration. A photometric procedure may also be used, although data concerning suitable wave lengths are lacking.

The quinalizarin method has been investigated in detail by W. Fischer and Wernet.[4] They found that very small amounts of magnesium, rare earths, scandium, cobalt, and nickel, in the absence or presence of tartrate, give a blue color similar to that produced by beryllium. Various other metals, such as lithium, the alkaline earths, zinc, mercury, lead, and thorium, react less sensitively, also giving a blue color. Many heavy metals are of course precipitated in the basic medium required for the reaction. Some of these (ferric iron, titanium, and zirconium, for example) produce more or less reddish colors, especially when they are kept in solution by the addition of tartrate. In amounts less than 2 mg., aluminum gives no color; above this quantity it tends to impart a reddish coloration to the solution, which is much more pronounced in the presence of tartrate.

As much as 800 mg. of sodium chloride does not affect the color intensity of the beryllium compound. Sodium fluoride in large amounts (500 mg.)

[9] H. Fischer, *Z. anal. Chem.*, **73**, 54 (1928).

produces flocculation in 5 minutes. Sodium sulfate (500 mg.) deepens the blue color very slightly. Sodium phosphate in small quantities (10 mg.) is without effect. Small amounts of vanadate and molybdate are harmless. It is known that borate, tungstate, gallium, indium, germanium, arsenic, antimony, selenium, and tellurium do not give a color with quinalizarin, but their effect, if any, on the determination of beryllium has not been investigated. If the amount of aluminum exceeds 5–10 mg., a like amount should be added to the standards.

Full directions for the determination of beryllium in the presence of interfering elements will be found in the paper already cited.[4] Large amounts of iron are removed by ether extraction of ferric chloride, aluminum and titanium are precipitated with hydrogen chloride as described on p. 198, and finally a sodium hydroxide fusion is made. The following general directions are similar to those of Fischer and Wernet.

Quinalizarin in unstable in strongly basic solution (slow fading of the color). The beryllium quinalizarin compound is rather stable, so that on standing the hue of a solution containing excess quinalizarin changes from the violet to the blue side. Therefore the color comparison should be made soon after the addition of the quinalizarin.

Reagent

Quinalizarin, 0.01 per cent in acetone. Shake 10 mg. of finely powdered quinalizarin with 100 ml. of acetone until all or nearly all of the powder has dissolved. The substance goes into solution slowly. Decant off the clear supernatant liquid and store in the dark. The solution is quite stable.

§ Procedure

The sample solution may conveniently have a volume of 5 to 10 ml. and may contain from 1 to 5 γ of beryllium.[10] Add sufficient sodium hydroxide solution to make its concentration 0.2 to 0.3 N; in the presence of relatively much aluminum the alkali concentration may be increased to 0.5 N or more. Prepare a series of standards having the same volume and sodium hydroxide concentration as the unknown. Add 1.0 ml. of quinalizarin solution and compare without undue delay in flat-bottomed tubes (1.8 × 15 cm.). Alternatively make the comparison by colorimetric titration, adding 0.005 per cent beryllium solution from a microburet to a solution having the same volume as the unknown and containing the same amounts of quinalizarin and sodium hydroxide, until the hues of the two solutions match.

[10] Under the conditions described 0.5 γ of beryllium can readily be detected.

2. p-Nitrobenzeneazo-orcinol as Reagent

This compound was first used for the detection of beryllium by the spot technique.[11] Lately it has been used in the photometric determination of beryllium, with special reference to aluminum and its alloys[12] and to beryllium minerals.[13] The dye is yellow in basic medium; in the presence of beryllium the color changes to reddish brown. The zone of optimum alkalinity is rather critical and narrow. With increasing alkalinity the color intensity of the reagent increases whereas that of the beryllium compound decreases. Buffering with boric acid increases the reproducibility. There is a small temperature coefficient (0.005 in extinction per 1° C. under the conditions below with a 2 cm. stratum of solution). The sensitivity is high, being about 0.005 γ of Be per square centimeter for 0.001 extinction at about 525 mμ. The extinction-concentration curve is not a straight line except over a limited range. The color develops instantaneously and shows little tendency to fade.

Zinc produces a color which is roughly $^1/_{100}$ as strong as that of beryllium. Copper interferes seriously, even in such small amounts as are soluble in sodium hydroxide solution. Aluminum in concentrations up to 1 per cent has practically no effect, provided an excess of 1 mole of sodium hydroxide is added for each mole of aluminum present. Other elements which might interfere are removed by preliminary treatment with sodium hydroxide, but the possible coprecipitation of beryllium must be considered (p. 196).

§ Procedure[14]

Transfer the almost neutral beryllium solution (volume approximately 10 ml. and containing 5 to 80 γ of the element) to a 25 ml. volumetric flask. Add 2.7 ml. of 2.0 *N* sodium hydroxide solution,[15] 5 ml. of 0.64 *M* boric acid solution, and exactly 6 ml. of dye solution (prepared by stirring mechanically for several hours 0.025 g. of *p*-nitrobenzeneazo-orcinol with 100 ml.

[11] A. S. Komarovsky and N. S. Poluektov, *Mikrochemie*, **14**, 315 (1933).

[12] W. Stross and G. H. Osborn, *J. Soc. Chem. Ind.*, **63**, 249 (1944).

[13] G. H. Osborn and W. Stross, *Metallurgia*, **30**, No. 175, 3 (1944).

[14] This general procedure is based on statements in the paper of Stross and Osborn, *loc. cit.* The procedure there given for the determination of beryllium in aluminum alloys is omitted here since it falls outside the scope of this book, being intended for relatively much beryllium (more than 0.01–0.02 per cent). For a method of determining beryllium in its minerals, which likewise falls outside the field of this book, see Osborn and Stross, *loc. cit.* This latter paper also contains a method for the determination of beryllium in rocks, which it is stated "seemed to give positive and reproducible results on some granite pegmatites from the Mourne Mountains (average Be content 0.00077%), and also satisfactory recovery of small amounts of euclase added to these granites."

[15] If much aluminum is present more sodium hydroxide is required in accordance with the statement in the preceding paragraph above.

of 0.10 *N* sodium hydroxide and then filtering). Make up to the mark with water, mix, and find the transmittancy at about 525 mμ preferably using a 2 cm. cell.

Note. For traces of beryllium it would seem to be desirable to decrease the amount of reagent to increase the reproducibility. Since the blank itself is strongly colored (extinction about 0.2 in a 1 cm. cell under the above conditions), small variations in volume of the dye solution added or in the alkali concentration will lead to relatively large percentage errors with low beryllium concentrations.

3. Naphthochrome Azurine 2B and Naphthochrome Green G as Reagents

These dyes react with beryllium, but not aluminum, at *p*H 11.5–12.3.[16] The latter reagent has been used for the determination of beryllium in bio material. Beryllium produces a color change from green to red. The *p*H must be regulated very precisely. Above *p*H 12.3 the color due to beryllium is diminished and at *p*H 13 there is hardly any coloration. Phosphate prevents the reaction with azurine.

4. 1,4-Dihydroxyanthraquinone-2-sulfonic acid (Quinizarin-2-sulfonic Acid) as Reagent[17]

This compound gives a red lake with beryllium in a solution of *p*H 7 (ammonium acetate as buffer). The color reaches full intensity in 5 minutes and does not fade for several hours. The most satisfactory range for visual colorimetry is said to be 0.1 to 1 p.p.m. The effect of other metals is not mentioned but it is clear that many must interfere.

5. Curcumin as Reagent[18]

In faintly alkaline solution beryllium hydroxide adsorbs curcumin, giving an orange-red lake. A blank shows a yellow to brown color. Metals precipitated by ammonia must not be present. Fluoride and magnesium reduce the color intensity. The method has not been studied in detail.

§ Procedure

To 10 ml. of slightly acid or neutral solution containing 0.05 to 1 part per million of beryllium, add 0.05 ml. of a 0.1 per cent alcoholic solution of

[16] W. N. Aldridge and H. F. Liddell, *Analyst*, **73**, 607 (1948).

[17] F. Hyslop, E. D. Palmes, W. C. Alford, A. R. Monaco, and L. T. Fairhall, *Natl. Inst. Health Bull.* No. 181, p. 10 (1943). The method has lately been studied in detail by M. W. Cucci, W. F. Neuman, and B. J. Mulryan, *Anal. Chem.*, **21**, 1358 (1949). For the use of alkannin and naphthazarin as colorimetric beryllium reagents, see A. L. Underwood and W. F. Neuman, *ibid.*, **21**, 1348 (1949).

[18] I. M. Kolthoff, *J. Am. Chem. Soc.*, **50**, 393 (1928).

curcumin, 0.5 ml. of 4 *N* ammonium chloride solution, and 0.5 ml. of 4 *N* ammonia. Compare against a series of standards prepared simultaneously

III. Applications

A. Silicates and Silicate Rocks

The sample is decomposed with sulfuric-hydrofluoric acid and separations are made as outlined under section IA, p. 196. The morin fluorimetric method is then applied.[19] The major and minor constituents of silicate rocks, in the amounts that they are likely to occur, are without effect, except chromium (for effect of aluminum, see p. 199). Relatively much chromium is likely to lead to low results because it will be present in the final solution as chromate, which absorbs U. V. radiation. As much as 0.02 per cent Cr_2O_3 is permissible, however. The presence of chromium will be revealed by the color of the final solution.

Special Solutions

Mercaptoacetic acid, at least 80 per cent strength.

Wash solution. Dilute 10 ml. of concentrated hydrochloric acid and 10 ml. of concentrated ammonium hydroxide to 1 liter with water. Shortly before use, add 2 ml. of mercaptoacetic acid which has been neutralized with ammonia to 100 ml. of this solution.

Sodium pyrophosphate, saturated solution in water at room temperature. Filter to remove any suspended material.

Methyl orange indicator solution, 0.01 per cent. Dilute the usual laboratory solution (0.1 per cent) ten times with water.

Sodium hydroxide, 3.0 g. in 100 ml. of solution.

Sodium chloride solution (for addition to standards to make the composition the same as the sample solution). Dissolve 3 g. of sodium hydroxide in about 50 ml. of water, add 1 ml. of methyl orange solution, and neutralize with 1:1 hydrochloric acid, making the final adjustment with the sodium hydroxide solution if necessary, and dilute to 100 ml. with water.

Aluminum sulfate, 0.05 g. of Al_2O_3 per ml. Dissolve 32.6 g. of $Al_2(SO_4)_3 \cdot 18H_2O$ in water containing 2 ml. of 6 *N* sulfuric acid and dilute to 100 ml. Filter if not entirely clear. Test the solution for beryllium by treating 0.5 ml. with 5 ml. of sodium hydroxide and 5 ml. of sodium pyrophosphate, diluting to 20 ml., adding 0.2 ml. of morin, and comparing against a similar blank solution. The fluorescence, if any, should be less than that of 0.05 γ of beryllium in the comparison solution.

Morin, 0.05 per cent. Dissolve 50 mg. of solid in 100 ml. of reagent-grade acetone.

Standard beryllium solution, 0.001 per cent, or a lower concentration if preferred, in 0.2 *N* hydrochloric acid. Air-dried recrystallized beryllium sulfate tetrahydrate may be used as the source of beryllium ($BeSO_4 \cdot 4\ H_2O/Be = 19.7$).

[19] E. B. Sandell, *Anal. Chim. Acta*, **3**, 89 (1949). In an earlier procedure (*Ind. Eng. Chem., Anal. Ed.*, **12**, 674 (1940)), the rock was fused twice with sodium hydroxide, the melts leached, and beryllium determined in the filtrates with morin. This method is restricted in application to silicic rocks. With subsilicic rocks there is too much retention of beryllium in the large amount of residue from the leaching.

§ Procedure

Add 2 ml. of 6 *N* sulfuric acid and 3 ml. of hydrofluoric acid to 0.25 g. of 100-mesh rock sample in a platinum dish or crucible. Evaporate to dryness on a hot plate and raise the temperature to expel the excess of sulfuric acid. Add 0.5 ml. of 6 *N* sulfuric acid and a few milliliters of water, evaporate to dryness, and again drive off the free sulfuric acid. Treat the residue with 2 ml. of concentrated hydrochloric acid and 20 ml. of water and heat near the boiling point with stirring until complete or almost complete solution has been obtained. A turbidity due to barium sulfate or a small residue of quartz may be disregarded. Most of any insoluble material will be decomposed in the sodium hydroxide fusion to follow, but if there is reason to believe that appreciable amounts of minerals resistant to such treatment remain, the residue should be given appropriate treatment. Transfer the solution to a small beaker.

Ammonia precipitation. Add 1:1 ammonium hydroxide to the cold solution until a faint permanent precipitate is obtained and bring it into solution by the addition of a drop or two of hydrochloric acid. Heat to boiling. Disregard any precipitate formed on heating. Next add 2.5 ml. of mercaptoacetic acid and then 1:1 ammonium hydroxide until a slight excess is present as indicated by odor or by spotting the solution on phenol red paper (distinct red color). Keep the mixture near the boiling point for a few minutes and then filter through a 9-cm. paper of medium or coarse texture. Wash the precipitate with four 5-ml. portions of hot wash solution and once with water. When much iron is present in the sample, the washed precipitate may not be entirely white, but this does not matter.

Open the filter paper and allow it to dry in the air overnight. Carefully scrape the dried precipitate from the paper with a spatula and transfer to a nickel crucible. Any small amount of precipitate remaining adhering to the paper may usually be neglected in the case of basic rocks with low beryllium contents. With silicic rocks it is safest to ignite (in platinum) the paper from which most of the precipitate has been removed and to add the ash to the nickel crucible.

Sodium hydroxide fusion. Add 0.75 g. (5 pellets) of sodium hydroxide to the nickel crucible. It is advisable to weigh the 5 pellets of sodium hydroxide rapidly to be certain that the weight is within 10 per cent of 0.75 g. If the difference is greater, allowance for the variation should be made later by adding a corresponding amount of sodium hydroxide to the standards. Heat gently at first to the fusion point of sodium hydroxide, keep at this temperature for a few minutes, and then heat to medium redness. Keep at the latter temperature for 10 minutes. Swirl the melt while it is cooling so that it will solidify as a shell on the walls of the crucible.

When the contents are cold, add 13 ml. of water and 2 or 3 drops of ethyl alcohol to reduce any manganate which may be present. Allow to stand for 15 to 30 minutes after the sodium hydroxide has dissolved. Transfer the solution to a small beaker.

Filter through a small (5-cm.) retentive filter paper. It is best to refilter the first few milliliters of the solution to be certain that an entirely clear filtrate will be obtained. Catch the filtrate in a 50 ml. volumetric flask. Wash with small portions of cold water totaling 8 or 9 ml. Ignite the paper and its contents (best in a platinum crucible) and fuse the residue in a nickel crucible as before with 5 pellets of sodium hydroxide. Extract the melt with water, filter, and wash as already described, but collect the filtrate and washings in a small beaker. Add 0.1 ml. of methyl orange solution and neutralize with 1:1 hydrochloric acid. Combine the neutralized solution with the solution in the volumetric flask and dilute to the mark with water.

Fluorimetric comparison. Transfer 20 ml. of the mixed solution to a 1.8 × 15 cm. glass-stoppered flat-bottomed tube (capacity slightly greater than 25 ml.) and add 5 ml. of sodium pyrophosphate solution. Prepare a series of standards by taking 10 ml. of sodium chloride solution, the volume of aluminum solution to furnish the amount of aluminum present in the $^2/_5$ aliquot of the sample (in most cases it suffices to assume that the alumina content of the rock is 15 per cent and to add the corresponding amount of aluminum to the standards), 10 ml. of sodium hydroxide (or slightly different volume if the amount of sodium hydroxide in the sample aliquot is not exactly 0.3 g.), 5 ml. of sodium pyrophosphate solution, and suitable amounts of beryllium. For basic rocks the series 0, 0.05, 0.1, and 0.15 γ of beryllium is suggested, and for acidic rocks the series 0.1, 0.2, 0.3, and 0.4 γ. Add 0.20 ml. of morin solution to each tube and mix by inversion. Remove the stoppers and compare the fluorescences by examining the tubes axially in strong daylight against a dark background. If desired the approximate beryllium content of the aliquot can first be obtained by

TABLE 34

DETERMINATION OF BERYLLIUM IN SILICATE ROCKS

	Be present, p.p.m.	Be found, p.p.m.
Granite + 0.006% Sc	3.5	3
Granite + 0.2% La	3.5	3
Diabase I	5.1	4.8, 5.0
Diabase I	9.1	8.0, 7.5
Diabase II	5.8	5.6
Diabase II	9.8	8.9

adding standard beryllium solution to a comparison tube until the fluorescence matches that of the sample tube. Then the final comparison is made by using a fresh aliquot and a series of standards, the number of which can now be small. If the beryllium content of the sample is 3 p.p.m. and greater, a 10 ml. aliquot is sufficiently large; the volume of the final solution should then be increased to 20–25 ml. by dilution with water.

B. Bio Material

Published procedures for the determination of beryllium in materials of bio origin are not entirely satisfactory (although useful for certain purposes) and it is believed that improved methods can be developed.

Decomposition of organic material can be carried out by oxidation with sulfuric-nitric acid, with or without perchloric acid.[20]

The use of the colorimetric reagent 1,4-dihydroxyanthraquinone-2-sulfonic acid has been described.[21] It is necessary to remove phosphate with zirconyl nitrate and the excess of the latter with selenious acid. The fluorimetric reagents 1-amino-4-hydroxyanthraquinone and 1,4-dihydroxyanthraquinone have also been applied.[17]

In another procedure, naphthochrome green G is employed as reagent after beryllium has been isolated by coprecipitation with aluminum phosphate at *p*H 4.5 (separation from calcium and magnesium); ferric iron must first be removed by precipitation as ferrocyanide in mineral acid medium.[16] Much calcium causes difficulties.

[20] According to J. Cholak and D. M. Hubbard, *Anal. Chem.*, **20**, 75 (1948), dry ashing at 500° leads to loss of beryllium. The reason for this is not evident. Others (Hyslop et al.) have used dry ashing.

[21] F. Hyslop et al., *op. cit.*, p. 13; R. Lesko, *U. S. Atomic Energy Commission Document* **1857** (1948).

CHAPTER X

BISMUTH

I. Separations

The chief methods coming into consideration for the isolation of minute quantities of bismuth are those involving the use of hydrogen sulfide and of dithizone.

A. Sulfide Precipitation

Precipitation with hydrogen sulfide may be applied to bio materials and other samples not containing large amounts of metals giving sulfides insoluble in dilute mineral acid medium. Copper may be added as a collector if bismuth is finally to be determined by the dithizone method; possibly cadmium will serve as a collector if bismuth is determined by the iodide method. The acidity should be as low as feasible, say 0.1–0.3 *N*. The results shown in Table 35 (p. 213) indicate that microgram quantities of bismuth can be satisfactorily recovered in this way from as much as 50–100 ml. of solution. The sulfide precipitate should be allowed to stand overnight before filtration.

B. Dithizone Extraction

There is some contradiction in the literature concerning the completeness of extraction of bismuth with dithizone from basic citrate solutions containing high concentrations of salts. Some authors[1] report incomplete recovery of bismuth under these conditions. On the other hand, Haddock[2] gives results that apparently show complete extraction of bismuth in the presence of much citrate and even cyanide. A further study of the extraction would be desirable (effect of citrate, cyanide, and dithizone concentration, and of *p*H). The extraction of bismuth becomes less complete in strongly basic solution. Fischer[3] recommends a *p*H of 7–8 for the extrac-

[1] D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, 11, 343 (1939); J. F. Reith and C. P. van Dijk, *Chem. Weekblad*, 36, 343 (1939). In a later paper, Hubbard (p. 224) has shown that good recovery of bismuth from a citrate-cyanide solution can be obtained by diluting the solution considerably, extracting at a sufficiently high *p*H, and using a comparatively strong dithizone solution.

[2] L. A. Haddock, *Analyst*, 59, 163 (1934).

[3] H. Fischer, *Angew. Chem.*, 50, 928 (1937).

tion with a carbon tetrachloride dithizone solution. When a chloroform solution of dithizone is used, a *p*H of 10 is recommended by Hubbard (p. 224).

In the presence of cyanide, the number of metals reacting with dithizone is greatly reduced and bismuth can thus be separated from copper, silver, cadmium, zinc, etc. Lead, thallium (I), and tin (II) also react with dithizone in basic cyanide solution. A separation of bismuth from lead (and thallium) in not too greatly preponderant amounts may be based on the comparative stability of bismuth dithizonate at low *p*H. By extracting an aqueous solution of *p*H 3.0 a sufficient number of times with a carbon tetrachloride solution of dithizone, bismuth can be completely brought into the carbon tetrachloride phase; practically all of the lead will remain in the aqueous phase.[4] At *p*H 4 the extraction of lead becomes appreciable. An alternative method consists in shaking the organic solvent, containing both bismuth and lead dithizonates, with a buffer solution having a *p*H such that lead is brought into the aqueous phase while bismuth is left unaffected in the organic phase. For a chloroform solution of bismuth and lead dithizonates, a buffer of *p*H 3.4 is recommended (p. 225).

From the equation

$$Bi^{+++} + 3\ Dz \rightleftharpoons BiDz_3' + 3\ H^+$$

it is evident that both the concentration of dithizone in the organic solvent and the *p*H of the solution will have a tremendous effect on the amount of bismuth extracted.[5] A more exact treatment of the separation of bismuth and lead by dithizone must await the determination of the equilibrium constants of bismuth and lead dithizonates.

C. Miscellaneous Separations

Bismuth diethyldithiocarbamate can be extracted by ethyl ether from slightly acidic solution.[6] Bismuth diethylammonium diethyldithiocarbamate can be extracted quantitatively by chloroform from 2 *M* hydrochloric acid solution[7]; arsenic (III), copper, and mercury accompany bismuth, but lead and ferrous iron remain in the aqueous phase.

In special cases, preliminary separation of bismuth by extraction of the

[4] H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **119**, 182, 184 (1940). See also p. 389 of this book.

[5] For graphs showing percentages of bismuth extracted at various *p*H's with various amounts of excess dithizone see C. A. Greenleaf, *J. Assoc. Official Agr. Chem.*, **24**, 341 (1941).

[6] S. L. Tompsett, *Analyst*, **63**, 250 (1938).

[7] N. Strafford, P. F. Wyatt, and F. G. Kershaw, *Analyst*, **70**, 232 (1945).

iodide complex by amyl alcohol-ethyl acetate or higher ketones may be of value.

Ammonium hydroxide precipitation has been used to separate bismuth from much copper; aluminum or ferric hydroxide (p. 219) is used as collector.[8] Bismuth may be separated from metals whose hydroxides are soluble in excess alkali hydroxide by precipitation as the metal by the use of stannite as the reducing agent. This separation has been applied in the determination of bismuth in metallic tin.[9]

Bismuth may be coprecipitated as a basic salt with hydrous manganese dioxide obtained by adding potassium permanganate to a hot, very slightly acid solution containing a manganous salt.[10] Park[11] makes the precipitation in the presence of bromide (0.2 per cent) in about 0.015 *N* nitric acid solution; the *p*H of the solution after precipitation is 2–2.6. Practically all of the bismuth, together with tin, antimony, and molybdenum, is found in the precipitated manganese dioxide. A second precipitation may be carried out in the filtrate to recover the remainder of the bismuth. With 0.1 mg. of bismuth in a liter of solution containing 100 g. of copper, all of the metal was found in the first manganese dioxide precipitate; with 2 mg. in the same volume, some bismuth was found spectrographically in the second precipitate but none in the third. This method permits the separation of as little as 1 p.p.m. of bismuth in copper. Bismuth may also be coprecipitated in ferric hydroxide.

The similarity in the ionic radii of trivalent bismuth and calcium may possibly find some application in the isolation of traces of bismuth by coprecipitation with slightly soluble calcium salts.

Bismuth may be separated from lead and tin by internal electrolysis.[12] It has also been isolated by deposition on metallic copper.[13]

Bismuth has been separated from metallic copper by volatilization in a stream of hydrogen or nitrogen at about 1000°.[14]

II. Methods of Determination

When less than 10 γ of bismuth is to be determined, the dithizone method is recommended. Its sensitivity is so great that even 1 γ of the

[8] A. I. Kokorin and I. G. Dermanova, *Zavodskaya Lab.*, **12**, 59 (1946); *Chem. Abst.*, **40**, 7050 (1946). The isolated bismuth is determined with thiocyanate.

[9] H. J. Tabor, *Analyst*, **68**, 305 (1943).

[10] H. Blumenthal, *Z. anal. Chem.*, **74**, 33 (1928); S. Kallman and F. Pristera, *Ind. Eng. Chem., Anal. Ed.*, **13**, 8 (1941).

[11] B. Park, *Ind. Eng. Chem., Anal. Ed.*, **6**, 188 (1934).

[12] B. L. Clarke, L. A. Wooten, and C. L. Luke, *Ind. Eng. Chem., Anal. Ed.*, **8**, 411 (1936); E. M. Collin, *Analyst*, **55**, 312, 680 (1930).

[13] S. Kaye and J. C. Castillo, *Am. J. Clin. Path., Tech. Sect.*, **8**, 81 (1944).

[14] E. W. Colbeck, S. W. Craven, and W. Murray, *Analyst*, **59**, 395 (1934); C. O. Bannister and W. M. Doyle, *ibid.*, **60**, 33 (1935).

element can be determined with fair accuracy. For amounts greater than 10 γ the iodide method will frequently be satisfactory. The dithizone method requires the separation of bismuth from other metals, particularly lead which reacts in the same manner as bismuth under the conditions of the determination, whereas the iodide method can be applied directly in the presence of small amounts of lead as well as other metals such as iron.

A. The Dithizone Method

This method has been worked out in the greatest detail for the determination of bismuth in bio material and detailed directions are therefore given under that heading (p. 223). The procedure given there can be adapted to other samples. The dithizone separation of bismuth from such metals as copper, which can be complexed with cyanide, and from lead which accompanies bismuth in this step, has already been discussed in section IB. The isolated bismuth is determined by shaking the aqueous solution, containing a little cyanide and having a *p*H of 11.5, with a chloroform solution of dithizone. At this *p*H most of the excess dithizone remains in the aqueous phase and the method is essentially a mono-color method. A carbon tetrachloride solution of dithizone can be used at a lower *p*H, the exact value of which has not been ascertained.

For a mixed-color procedure in acidic medium see p. 222.

Table 35

Determination of Bismuth by the Dithizone Method[a]

In urine (*100 ml.*)	Bi added, γ	0	1 0	5	15	50	500
	Bi found, γ	0.1	1 1	4.9	15	49	470
In blood (*10 g.*)	Bi added, γ	0	1.0	5 0	15	50	
	Bi found, γ	0.1	1.2	5.0	14.5	48	

[a] Representative results taken from tables given by D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, **11**, 344 (1939). Bismuth was first isolated by precipitation with hydrogen sulfide (p. 226) and then determined by a procedure similar to the one described on p. 225. The accuracy of the later method of Hubbard, described in detail on p. 224, is somewhat better than this, especially with 50–500 γ of bismuth, which were recovered within ±1 per cent.

B. The Iodide Method[15]

The addition of an excess of a soluble iodide to an acid solution of bismuth produces a yellow to orange color due to iodobismuthite ion. The color intensity increases with iodide concentration up to about 1 per cent

[15] H. Baggesgaard-Rasmussen, K. A. Jackerott, and S. A. Schou, *Dansk. Tids. Farm.*, **1**, 391 (1927); R. C. Sproull and A. O. Gettler, *Ind. Eng. Chem., Anal. Ed.*, **13**, 462 (1941); C. J. W. Wiegand, G. H. Lann, and F. V. Kalich, *ibid.*, **13**, 912 (1941).

potassium iodide and then remains practically constant (Wiegand, Lann, and Kalich, *loc. cit.*). Beer's law is followed. The reaction is a sensitive one, but is subject to interference from a number of substances. Platinum, palladium, and, to a lesser extent, antimony and tin give colored compounds with iodide. Metals giving insoluble iodides must naturally be absent, or present in amounts not yielding a precipitate. Lead and thallous iodides carry down large quantities of bismuth, but silver and cuprous iodides show a much smaller tendency to occlude bismuth. Oxidizing agents such as ferric iron liberating iodine must be reduced or the iodine formed by them destroyed. Sulfurous acid or sulfite is frequently used

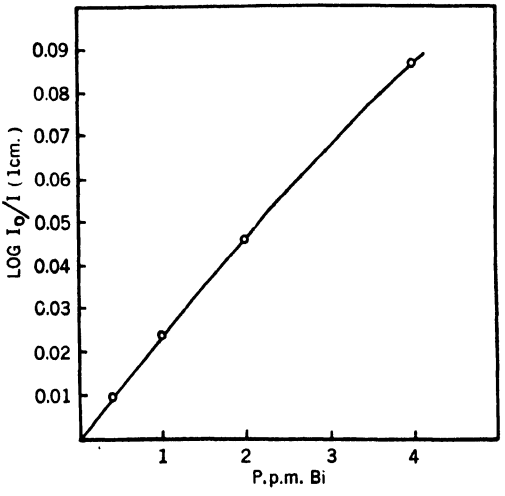


Fig. 28. Determination of bismuth by the iodide method (aqueous solution). The slight deviation from linearity is due to the comparatively wide band of wave lengths transmitted by the blue filter used (Wratten 47). Transmittancy of the blank solution was 95.6% under the conditions.

for this purpose but care must be taken to avoid any large excess because, in sufficient concentration, sulfite alone produces a yellow color with iodide, probably owing to the formation of an iodo-sulfinic acid, $I(HSO)_2$. Hypophosphorus acid can often be used instead of sulfurous, although it acts slowly.[16] A combination of sulfurous and ascorbic acids has also been recommended as reducing agent.[17] High concentrations of acid (more than 50 per cent of sulfuric or hydrochloric acid) yield a weak yellow color in the absence of bismuth because of the formation of complex iodo acids,

[16] A mixture of hypophosphorous and sulfurous acids as recommended by some is not permissible because the latter is reduced by the former to finely divided sulfur.

[17] N. J. Giacomino, *Ind. Eng. Chem., Anal. Ed.*, **17**, 456 (1945). It is stated that ascorbic acid alone does not exert sufficient reducing action.

but dilute acids (less than 1–2 *N*) do not.[18] In 2 *N* sulfuric acid solution the color is very slightly stronger than in 0.2 *N* solution.

Chloride ion reduces the intensity of the bismuth color. Fluoride in high concentration also reduces the color intensity. Sulfate ion in reasonable amounts is without effect and therefore sulfuric acid is ordinarily used for acidification, but nitric acid may also be used if its concentration in the solution is not too high. Cadmium in large amounts bleaches the bismuth color (formation of complex cadmium iodide) but the effect can be largely overcome by adding more iodide. A number of other elements such as arsenic and the rare earths in high concentration reduce the color intensity.

The colored product can be extracted by higher alcohols and esters. A mixture of amyl alcohol and ethyl acetate has been recommended for the purpose. The extraction procedure enables bismuth to be determined in the presence of colored ions such as nickel, cobalt, chromium, and uranium and, moreover, increases the sensitivity. The organic solvent solution of the bismuth-iodide compound obeys Beer's law.

The procedure below is similar to Haddock's.[18] The determination of bismuth may be made directly in the presence of considerable quantities

TABLE 36

DETERMINATION OF BISMUTH BY EXTRACTION OF THE BISMUTH-IODIDE COMPOUND WITH AMYL ALCOHOL-ETHYL ACETATE[18]

Foreign Element	Bi Added γ	Bi Found γ
1g. Sb[a]	30	33
1g Cu[a]	20	18
2g. "Di"[a]	10	12
1g. Fe^{III}	10	12.8
1g. Hg[a]	50	50
1g. Ag[a]	20	20
1g. Sn^{IV}[a]	20	17.5
1g. Co	10	11
1g. Ni	10	12
1g. Cr	10	12.5
1g. Zn	10	10

[a] Preliminary separation of bismuth with dithizone.

of the alkali metals, alkaline earth metals, magnesium, manganese, zinc cobalt, nickel, chromium, aluminum, etc. Lead and thallium do not interfere if present in such small amounts that no precipitate forms. In

[18] L. A. Haddock, *Analyst*, **59**, 163 (1934).

the presence of antimony, copper, iron, silver, etc., Haddock first isolates bismuth by extraction with dithizone from an ammoniacal cyanide solution. Some of the results obtained by Haddock in the application of the extraction procedure are given in Table 36.

Special Solutions

Potassium iodide, 10 per cent aqueous solution, preferably freshly prepared.

Hypophosphorous acid, 30 per cent. A solution of sodium hypophosphite of the same concentration may be used instead.

Ascorbic acid, 1 per cent in water. Prepare daily.

Sodium sulfite, 1 per cent in water. Prepare fresh every day or two.

Amyl alcohol-ethyl acetate, 3:1 mixture by volume of the best grade products.

Standard bismuth solution, 0.0010 per cent in 1:100 nitric acid. Prepare by dilution of a 0.100 per cent bismuth solution obtained by dissolving pure bismuth metal in nitric acid.

§ Procedure

The sample solution may conveniently have a volume of 10 or 15 ml. and should be about 2 *N* in sulfuric acid. At least 5 γ of bismuth should be present (1 cm. absorption cell). Add 1 ml. of hypophosphorous acid (alternatively add 5 ml. of ascorbic acid together with 1 ml. of sulfite solution), and 1 ml. of potassium iodide solution. Dilute to 25 ml. and determine the transmittancy at or near 460 mμ. If oxidizing agents such as ferric iron are present it is advisable to measure again after 5 or 10 minutes to be sure that any free iodine liberated has been destroyed and constant transmittancy has been attained.

Extraction Procedure. In this case it appears best to use ascorbic acid and sulfite as reducing agents. After the addition of iodide, allow the solution to stand for 10 minutes and then extract in a separatory funnel with 2 or 3 ml. portions of amyl alcohol-ethyl acetate until the last extract is colorless or virtually so. Make up the combined extracts to a definite volume (5 ml. for 5–25 γ of bismuth) with the organic solvent and filter through a small plug of cotton-wool into the absorption cell. Obtain the transmittancy of the solution at once (460 mμ). The standard curve should be constructed by extracting known amounts of bismuth under the same conditions as the sample.

Note. The aqueous bismuth solution to be extracted with amyl alcohol-ethy acetate should have a volume less than 40 ml. In general, 2 extractions will remove 5 to 20 γ of bismuth and 4 extractions 50 to 80 γ. For 100 γ, 5 extractions should be made. By adding a known amount of bismuth to the extracted sample solution and extracting as before, any error due to slight coloration of the organic solvent resulting from a high concentration of neutral salts or from solution of small amounts of cobalt, nickel or chromium is largely compensated.

C. The Thiourea Method[19]

In acid solution, thiourea forms a soluble yellow-colored complex with bismuth. The reaction is of rather low sensitivity. Silver, mercury, lead, copper, cadmium, and tin give white precipitates if present in considerable amounts, but none at low concentrations (copper is then decolorized). Ferric iron must be reduced, for example, by heating the solution with hydrazine sulfate. Antimony also gives a yellow color with thiourea. Fluoride destroys the antimony color but not that of bismuth.

Beer's law holds in the range 0.2 to 5 mg. of metal per 100 ml.

§ Procedure[20]

The bismuth solution should be 0.7–1.3 *N* in nitric acid and should contain no chloride. Iron must previously have been reduced to the ferrous condition. Add 10 to 12 g. of thiourea for 50 ml. of solution, warm gently to dissolve, cool to 18 ± 3°, and filter through a sintered-glass crucible (G4) to remove excess thiourea and any precipitated metal complexes. Wash with saturated thiourea solution and make up to volume with the same solution. Use a filter showing maximum transmission at 420 mμ in determining the color intensity.

The solution becomes turbid on standing from the separation of sulfur, especially when lead and copper are present. This can be prevented by adding hydrazine sulfate to the solution and keeping it cool.

The color intensity of the solution decreases with a rise in temperature and the temperature at which the transmittancy of the sample solution is determined must be the same as that existing when the standard curve was established.

D. Other Methods

Among the many other methods which have been described for the colorimetric or nephelometric determination of bismuth the following may be noted:

1. Formation of slightly soluble red compounds in dilute nitric acid medium with dimercaptothiobiazole and phenyldithiobiazolonethiol.[21] The suspension is stabilized with gum acacia. The presence of chloride reduces the sensitivity. Beer's law holds. As little as

[19] C. Mahr, *Z. anal. Chem.*, 94, 161 (1933); 97, 96 (1934). S. L. Tompsett, *Analyst*, 63, 250 (1938).

[20] C. Mahr, *Z. anal. Chem.*, 97, 96 (1934). The thiourea procedure is used for bismuth in aluminum (Aluminum Research Institute, *Analytical Methods for Aluminum Alloys*, p. 69). A final thiourea concentration of 2 per cent is recommended.

[21] A. K. Majumdar, *J. Indian Chem. Soc.*, 21, 240, 347 (1944).

3 γ of bismuth in 20 ml. is stated to be determinable. The bismuth compound of both reagents is soluble in isoamyl alcohol, ethyl acetate, and ether; in addition, the compound with phenyldithiobiazolonethiol is soluble in chloroform. Many metals, particularly those of the hydrogen sulfide group, give precipitates with the reagents; most of these are paler in color than the bismuth compounds.

2. Formation of an orange double iodide with 8-hydroxyquinoline, which can be extracted with a mixture of acetone and amyl alcohol or with cyclohexanol.[22]
3. Formation of a slightly soluble bismuth quinine iodide, which is made the basis of a nephelometric method.[23]
4. Production of a yellow color with thiocyanate in acid solution similar to that produced by thiourea.[24]
5. Precipitation of bismuth with pyrogallol or 8-hydroxyquinoline and subsequent reduction of phosphomolybdic acid to molybdenum blue.[25]
6. Formation of a colloidal suspension of bismuth sulfide in dilute acid solution in the presence of gelatin,[26] or in basic solution in the presence of gum arabic.[27]
7. Formation of a colloidal suspension of bismuth with stannite.[28]

III. Applications

A. Metals

1. Antimony, Mercury, Silver, Iron, Etc.

Haddock[18] has shown that small amounts of bismuth, of the order of a few thousandths of a per cent, can be determined in the presence of these metals by separating bismuth by dithizone extraction from a basic cyanide medium and making the final determination by the iodide method (Table 36). The absence of appreciable amounts of lead and thallium is presupposed. Bismuth can thus be determined in the presence of metals forming stable cyanide complexes in alkaline solution (mercury, silver, gold, and copper) as well as those not reacting with dithizone (arsenic, antimony, and iron). More specific directions for determining bismuth in copper in this way are given on p. 220.

[22] R. Sazerac and J. Pouzergues, *Compt. rend. soc. biol.*, **109**, 79, 370 (1932).
[23] S. Kaye and J. C. Castillo[13]; Kaye, *Am. J. Clin. Path., Tech. Sect.*, **8**, 83 (1944).
[24] H. Heinrichs and M. Hertrich, *Glastech. Ber.*, **1924**, 112.
[25] M. Teitelbaum, *Z. anal. Chem.*, **82**, 366 (1930).
[26] F. Malengreau and G. Delrue, *Arch. intern. méd. exptl.*, **1**, 35 (1924).
[27] T. Yamamoto, *Bull. Inst. Phys. Chem. Research Tokyo*, **13**, 1265 (1934).
[28] L. Malossi, *Rend. accad. sci. Napoli*, **2**, 83 (1932).

§ Procedure

Bring a 0.5 to 1 g. sample of metal (Bi < 0.01 per cent) into solution by appropriate treatment with acid. If there is a possibility of a little stannous tin being present in the solution, add a small amount of a ferric salt to oxidize it to the stannic condition. Boil out oxides of nitrogen if nitric acid has been used. Add 1 to 2 g. of ammonium citrate[29] to the solution (volume about 25 ml.), neutralize with ammonia, and add 2 g. of potassium cyanide[30] and 5 ml. of 10 per cent ammonia. Extract in a separatory funnel with four 15 ml. portions of 0.1 per cent (weight/volume) dithizone solution in chloroform. Combine the dithizone extracts and wash with two 10 ml. portions of water. Transfer the washed chloroform phase to a small Erlenmeyer flask, evaporate to dryness, and add 1 ml. of concentrated sulfuric acid. Heat carefully over a small flame and add dropwise 30 per cent hydrogen peroxide until all organic matter has been destroyed.[31] Dilute with 15–20 ml. of water, cool, and add a dilute iodine solution in very slight excess to destroy any sulfur dioxide. Then determine bismuth by the iodide method (p. 216).

2. Copper

There is no dearth of procedures for the determination of minute quantities of bismuth in metallic copper, but there is some doubt about the accuracy of a number of these procedures, especially when the percentage of bismuth is less than 0.001 per cent. Most of the methods call for the final determination of bismuth by the iodide method after isolation of bismuth by coprecipitation with collectors such as hydrous manganese dioxide or ferric hydroxide,[32] or by extraction with dithizone from cyanide medium. In one procedure copper is precipitated as cuprous iodide.[33] The directions in Procedure A are essentially those of the Fiscal Policy Joint Committee of the (British) Brass, Copper and Nickel Silver Industries.[34] The

[29] In the presence of much iron a larger amount of citrate may be necessary. The quantity of citrate added should not be much greater than that required to keep the metals in solution when the mixture is made basic. The addition of hydroxylamine hydrochloride may be advantageous when much iron is present (prevention of oxidation of dithizone by ferricyanide).

[30] When much copper, silver and other metals forming cyanide complexes are present, the quantity of potassium cyanide may have to be increased to 5 or 10 g. to prevent these metals from reacting with dithizone.

[31] Sulfuric and perchloric acids may also be used for the destruction of organic matter (p. 314).

[32] See, for example, A. J. G. Smout and J. L. Smith, *Analyst*, **58**, 475 (1933); C. O. Bannister and W. M. Doyle, *ibid.*, **60**, 33 (1935).

[33] H. R. Fitter, *Analyst*, **63**, 107 (1938).

[34] *Analyst*, **60**, 554 (1935).

procedure is suitable for samples containing from 0.0002 to 0.005 per cent bismuth.

A method for the determination of bismuth in copper based on extractive titration with dithizone has been described.[35] Very likely this volumetric method can be transformed into a colorimetric method by altering the last step in the procedure. Bismuth is first separated from the bulk of the copper by coprecipitation with hydrous manganese dioxide according to Park. Isolation of bismuth by dithizone extraction from cyanide medium then follows and finally the determination is made in weakly acidic medium. See Procedure B. Yao was able to determine 10 to 100 p.p.m. of bismuth in copper (as pure copper sulfate) with an accuracy of 5 to 10 per cent (6 out of 7 results were low).

§ Procedure A

Dissolve 2 g. of drillings in 20 ml. 1:1 nitric acid in a 250 ml. Erlenmeyer flask (see Note 1 for treatment of any insoluble material). Evaporate the solution until it becomes viscous, add 3 ml. of concentrated sulfuric acid, and continue the evaporation until white fumes are evolved. Cool, add 30 ml. of water and 20 ml. of 5 per cent citric acid, and make slightly ammoniacal so as to bring all copper salt into solution (usually 12–15 ml. of ammonia of sp. gr. 0.88 are required). Cool and add 50 ml. of fresh 20 per cent potassium cyanide solution.[36] Transfer the solution to a 250 ml. separatory funnel, dilute to 20 ml. with water, and shake with successive 10 ml. portions of 0.1 per cent dithizone in chloroform until all the bismuth has been extracted. Usually 3 or 4 portions suffice, unless much lead is present (red extract). Finally shake the aqueous solution with 5 ml. of chloroform and add this to the combined chloroform extracts. Shake this combined solution with 50 ml. of water. Run the washed chloroform into a small (150 ml.) flask and evaporate to practical dryness.[37] Add 1 ml. of concentrated sulfuric acid, heat until thick fumes are evolved, cool, and add 2–3 ml. of 20-volume hydrogen peroxide. Continue the heating until the solution is colorless, adding more hydrogen peroxide if necessary. Cool and add 15 ml. of water. Filter off any residue of lead sulfate (see Note 2 for treatment of the precipitate).

Determine bismuth in the solution by the iodide method in any con-

[35] Yu-lin Yao, *Ind. Eng. Chem., Anal. Ed.*, **17**, 114 (1945).

[36] H. Fischer, *Angew. Chem.*, **50**, 929 (1937), recommends adjusting the *p*H of the solution to 7–8 at this point by buffering with an ammonium salt (*e. g.*, ammonium nitrate).

[37] Fischer, *loc. cit.*, recommends that the dithizone extracts be shaken with 10 per cent sulfuric acid to transfer the bismuth to the aqueous phase. The latter is then evaporated to a small volume, and traces of organic material are destroyed by adding hydrogen peroxide and heating to fumes of sulfuric acid.

venient way, for example by the photometric procedure (p. 216) after transferring the solution to a 25 ml. volumetric flask. Alternatively transfer the solution to a comparison tube and add sulfurous acid and potassium iodide (*cf.* p. 216). In a second tube prepare a solution having the same composition as the sample and add a dilute standard bismuth solution until the colors match.

Notes. 1. Any metastannic acid or other insoluble material remaining after solution of the sample should be fused with potassium pyrosulfate, the melt leached with dilute sulfuric acid and the filtered solution added to the main solution.

2. Any lead sulfate precipitated should be filtered off, ignited, and dissolved in 10 ml. of hot concentrated hydrochloric acid. The resulting solution is cooled, 1 g. of tartaric acid, and 1 ml. each of concentrated nitric and sulfuric acids are added. The mixture is evaporated to expel the volatile acids (until red fumes cease to come off). Fifteen ml. of water are added, the solution is filtered, and the filtrate combined with the main solution.

§ Procedure B

Dissolve a suitable weight of copper, containing 5 to 25 γ of bismuth in 1:1 nitric acid. Boil the solution to expel oxides of nitrogen, cool, and treat with ammonia until basic to methyl orange. Add enough nitric acid to make the acidity 0.02 *N*, heat the solution to boiling, add 5 ml. of 20 per cent potassium bromide and 3 ml. of 3 per cent potassium permanganate, and boil until the color of the permanganate disappears. Collect the manganese dioxide precipitate in a sintered glass or Gooch crucible and wash twice with 5 ml. portions of water. Treat the filtrate as before with bromide and permanganate to obtain a second precipitate of manganese dioxide. Dissolve the two precipitates in 5 ml. of a mixture composed of equal volumes of 6 *N* sulfuric acid and 20 per cent sodium sulfite solution, and add 4 ml. of 50 per cent citric acid solution, enough dilute ammonia to give a barely perceptible odor, and 8 ml. of 25 per cent potassium cyanide solution (sulfide-free).

Transfer this mixture to a separatory funnel and extract with successive 5 ml. portions of dithizone in carbon tetrachloride (5 mg. in 100 ml.) until the last portion remains an unchanged green after a minute's shaking. Wash the combined extracts with 5 ml. of water. Care must be taken to see that any aqueous solution which may contain copper does not remain with the carbon tetrachloride phase. Bring bismuth into the aqueous phase by shaking the carbon tetrachloride with two successive 5 ml. portions of 1:20 nitric acid. To the combined water phases add 1:10 ammonia until *m*-cresol purple (2 drops 0.04 per cent) becomes almost orange. Extract with one or more portions of pure carbon tetrachloride to remove any foreign coloring material (no dithizone may be present at this stage, else there will be loss of bismuth). Add 0.2 g. of hydroxylamine hydro-

chloride (to minimize oxidation of dithizone) and readjust the pH of the solution to 3.[38]

Dilute the solution to a definite volume (20–25 ml.) and shake the whole or an aliquot, containing up to 12 or 15 γ of bismuth, with 5.0 ml. of 0.001 per cent (1 mg. in 100 ml.) dithizone in analytical reagent carbon tetrachloride for two minutes. Compare the mixed color (orange plus green) with that of a series of standards prepared by shaking various amounts of bismuth in a solution of the same composition with 5.0 ml. of dithizone solution. The transmittancy of the mixture of bismuth dithizonate and dithizone may also be determined and the concentration of bismuth found from a standard curve, but the optimum wave length for measurement is not known (perhaps it lies near 500 mμ). When only a few micrograms of bismuth are present, the volume of dithizone should be proportionately reduced to maintain the precision.

3. Lead

§ Procedure[39]

Dissolve 20 g. of sample in a mixture of 25 ml. nitric acid and 50 ml. of water. Add 30 ml. of hydrochloric acid to precipitate lead chloride,[40] cool to at least 20°, filter and wash the precipitate with cold 1:1 hydrochloric acid. To the filtrate add 5 mg. of iron as ferric salt followed by 20 ml. of 20 per cent ammonium acetate solution. Add sodium hydroxide solution until a small amount of lead hydroxide is precipitated, and just bring the latter into solution by the dropwise addition of hydrochloric acid, finally adding an excess of 1 ml. of the acid (Note 3). Filter off the ferric hydroxide immediately on an asbestos mat and wash three times with water. Dissolve the precipitate in 50 ml. of warm 1:20 sulfuric acid containing 3 g. of tartaric acid, allowing the solution to flow slowly through the filter. Wash twice with a little water. Treat the filtrate and washings with 5 ml. of hypophosphorous acid (sp. gr. 1.135) and dilute with water to 100 ml. Pour the solution into a dry flask containing 1.5 g. of potassium iodide. Heat to 70°, cool to 20° and determine the color intensity of the solution.

Notes. 1. With the acidity specified above, antimony in small amounts (5 mg.) does not interfere in the colorimetric determination. At higher acidities antimony gives a yellow color.

[38] Up to this point the directions have been essentially those of Yao. The directions following for the mixed-color method have not been tested, but are suggested on the basis of available information.

[39] R. G. Robinson, *Analyst*, **64**, 402 (1939). For the use of thiourea as reagent see C. Zischkau, *Proc. Am. Soc. Testing Materials*, **44**, 767 (1945).

[40] Precipitation of lead as sulfate leads to large losses of bismuth.

2. The accuracy of the method is attested by the fact that samples of lead containing 0.0005, 0.0010, and 0.0015 per cent of bismuth gave the respective values 0.0005, 0.0011, and 0.0014 per cent.

3. As shown by C. W. Ballard and E. J. Ballard, *Analyst*, **74**, 53 (1949), the precipitation of ferric hyroxide must be made at *p*H 6–6.5 for complete recovery of bismuth at room temperature. If the solution is boiled, the precipitation of bismuth is complete at *p*H 5.

B. Bio Materials

If the bismuth content of the sample is greater than 5 to 10 p.p.m. the iodide method can generally be applied directly after destruction of organic matter. This method has the advantage of simplicity and rapidity. Such small amounts of lead, copper, iron, and other metals as are likely to be present in most samples will not interfere. On the other hand, if the bismuth content is so low that the final aliquot of solution contains less than 10 γ, the dithizone method is probably preferable.

However, it is possible to determine a few p.p.m. of bismuth by the iodide method with fair precision if the whole sample is used in the final determination, if the iodide complex is extracted with an organic solvent, and if a 3 to 5 cm. cell is available for the transmittancy measurement.

The destruction of organic matter is usually effected by digestion with sulfuric and nitric acids, often together with perchloric acid.[41] Typical procedures have been given by Wiegand, Lann, and Kalich[42] and by Sproull and Gettler.[43] The procedure given below for the acid digestion is similar to that of the latter authors.

§ Procedure

1. Iodide Method. *Tissue.* Transfer 10 g. of sample to an Erlenmeyer flask and add 20 ml. of concentrated nitric acid. Heat on the steam bath until a clear yellow or brown solution is obtained. Cool, and if fat separates filter it off on glass wool, collecting the filtrate in a small Kjeldahl flask and washing with a little nitric acid. Add 3 ml. of concentrated sulfuric acid and evaporate to fumes of the latter. Then add dropwise a 1:2 mixture of nitric-perchloric acid and continue heating until the color is destroyed. Next add 0.5 ml. of 30 per cent hydrogen peroxide dropwise and boil to destroy the excess. Cool, add 5 ml. of water, and evaporate to

[41] J. Cholak, *Ind. Eng. Chem., Anal. Ed.*, **9**, 26 (1937), and D. M. Hubbard, *ibid.*, **11**, 344 (1939), decompose organic samples by digesting with nitric acid, evaporating to dryness and then heating at 450–500° C. in a muffle for several hours; if a gray ash is obtained, it is moistened with nitric acid and again ignited until it is white. When much phosphorus is present, the ash is likely to fuse and the procedure is not suitable.

[42] C. J. Wiegand, G. H. Lann, and F. V. Kalich, *Ind. Eng. Chem., Anal. Ed.*, **13**, 912 (1941).

[43] R. C. Sproull and A. O. Gettler, *Ind. Eng. Chem., Anal. Ed.*, **13**, 462 (1941).

fumes of sulfuric acid. Repeat the evaporation to fumes after adding 5 ml. of water. After cooling dilute with water, transfer to a 25 ml. volumetric flask, and make up to the mark. Determine bismuth in a 10 ml. aliquot according to the directions on p. 216. If the amount of bismuth is less than 10 γ it is advisable to take the whole solution and apply the extraction procedure. For low bismuth concentrations use a 2 or 5 cm. cell in obtaining the transmittancy. The standards for the establishment of the reference curve should have the same acidity as the unknown solution. For the greatest accuracy known amounts of bismuth should be added to a bismuth-free material of the same nature as the sample and carried through the procedure to obtain the standard curve.

Urine. Add 5 ml. of nitric acid and 3 ml. of sulfuric acid to a 50 ml. sample, and evaporate to fumes of sulfuric acid. Then add a mixture of nitric and perchloric acids as described in the preceding paragraph and continue according to the directions given there.

Blood serum.[44] To 10 ml. of serum or plasma in a 100 ml. Kjeldahl flask add 1.2 ml. of concentrated sulfuric acid and 5 ml. of concentrated nitric acid, heat over a burner until fumes of sulfuric acid appear, add dropwise a 1:2 mixture of nitric and perchloric acids until all color is destroyed, and then 1 ml. of 30 per cent hydrogen peroxide dropwise to the hot mixture. Boil vigorously to destroy peroxide, cool, add 10 ml. of water, and evaporate to fumes; repeat the evaporation to fumes after the addition of another 10 ml. portion of water. Transfer the digest to a 50 ml. separatory funnel with 15 ml. of water and add 5 ml. of ascorbic acid, 1 ml. of potassium iodide, and 1 ml. of sodium sulfite (see p. 216 for concentrations). After 10 minutes extract with 6 ml. of amyl alcohol-ethyl acetate (p. 216), shaking for two minutes, and filter the organic solvent layer through a small plug of cotton-wool into an absorption cell having a length of 4 cm. Determine the transmittancy at once at wave length 460 mμ.

2. Dithizone Method.[45] Take 100 ml. or less of urine, or 20 g. or less of blood or tissue, and destroy organic matter by digesting with 20 ml. of concentrated sulfuric acid, 5 ml. of perchloric acid (70 per cent), and 20 ml. or more of concentrated nitric acid (*cf.* p. 385). Add 50 ml. of water to the cooled digest and transfer to a 400 ml. beaker. Cool in an ice bath and add 15 ml. of 40 per cent w/v ammonium citrate solution, 50 ml. of 20 per cent sodium sulfite solution and, with stirring, 100 ml. of concentrated ammonium hydroxide.

[44] Giacomino, *loc. cit.* The figures given by him show that the negative error may amount to 20 per cent for 1 γ to about 10 per cent for 5–10 γ of bismuth.

[45] D. M. Hubbard, *Anal. Chem.*, 20, 363 (1948). Another dithizone procedure for bismuth in bio material is described by E. F. Kluchesky, B. J. Longley, and F. L. Kozelka, *J. Pharmacol.*, 74, 395 (1942).

Extraction of bismuth and lead. Transfer the mixture to a 500 ml. separatory funnel, add 5 ml. of 10 per cent potassium cyanide solution (sulfide-free), dilute to 400 ml. with water, and extract the whole with successive 10 ml. portions of a chloroform solution of dithizone (60 mg. per liter) until the last portion shows no color change. If the amount of bismuth is less than 10 γ, three portions of dithizone should suffice; for 10–50 γ of bismuth, four portions are necessary.

Depending upon the amount of bismuth present, take the whole or an aliquot of the combined extracts to furnish not more than 50 γ of bismuth. Wash the chloroform solution with 50 ml. of water and draw off the chloroform into a small separatory funnel. Shake the aqueous phase with 5 ml. of dithizone in chloroform and add the latter to the main portion.

Separation of bismuth and lead. Shake the chloroform solution of bismuth and lead dithizonates for one-half minute with 50 ml. of biphthalate buffer solution of *p*H 3.4. Draw off the chloroform into another separatory funnel and shake the aqueous phase with 5 ml. of dithizone; combine the latter with the main chloroform fraction. In the presence of large amounts of lead the treatment of the chloroform phase with fresh buffer solution should be repeated.

Shake the chloroform solution of bismuth dithizonate with 25 ml. of 1:100 nitric acid for one-half minute, draw off the chloroform phase into another separatory funnel, and repeat the shaking with a fresh portion of acid. Discard the chloroform. Combine the acid fractions and wash with 5 ml. of chloroform to remove droplets of dithizone.

Determination of bismuth. Add 20 ml. of pure concentrated ammonium hydroxide containing 0.2 g. of potassium cyanide (sulfide-free) and 15 ml. of dithizone (60 mg. per liter of redistilled chloroform) to the 50 ml. of aqueous solution containing the bismuth. Shake the mixture for one minute. Place a small plug of cotton in the tip of the stem of the separatory funnel and run about 5 ml. of the chloroform layer through it. Discard this chloroform and fill a cell of suitable thickness with filtered chloroform solution. Find the extinction of the solution at 505 mμ. Run a blank on 50 ml. of 1:100 nitric acid (procedure as in this paragraph) to obtain the zero reading.

Construct the standard curve by taking 0 to 50 γ of bismuth and treating as above.

Notes. 1. Thallium (III) is not extracted at *p*H 10, in the first step. If any thallium should be extracted, it would subsequently be separated from bismuth by treatment with the buffer solution at *p*H 3.4.

2. Tin is not extracted by dithizone because it is oxidized to the stannic state in the preparation of the sample.

3. If unusually large amounts of lead are present, bismuth may not be completely

brought into the aqueous phase on shaking with the 1:100 nitric acid, because of the large amount of dithizone liberated in the treatment with the buffer. In such a case 1:20 nitric acid should be used and bismuth then re-extracted (including the wash with *p*H 3.4 buffer).

4. When bismuth must be determined in the presence of much calcium and phosphorus, as in bone, it is best to isolate it as the sulfide. Adjust the acidity of the solution of the decomposed sample to 0.2–0.3 *N* (as by the addition of sodium hydroxide solution). Add 1 mg. of copper to the solution (50–100 ml. in volume) to furnish copper sulfide and pass in hydrogen sulfide for one-half hour. Allow the mixture to stand overnight and filter off the precipitate on a small dense filter paper. Wash once or twice with 5 ml. of 0.1 *N* hydrochloric acid saturated with hydrogen sulfide. Transfer the filter paper to the precipitation vessel and heat gently with 10 ml. of 1:3 nitric acid to dissolve the sulfides. Filter off the disintegrated paper and sulfur by the use of a fine sintered-glass filter crucible and wash with hot dilute nitric acid. Evaporate the filtrate to a small volume to remove most of the nitric acid. Dilute with water and determine bismuth according to the directions on p. 224, using either the whole solution or an aliquot of it.

5. Another approach to the determination of bismuth in bio material by the use of dithizone has been described by Laug,[46] who decomposes the sample by ignition, dissolves the ash in nitric acid, and then extracts bismuth (as well as copper and some zinc) at *p*H 2.5 in the presence of 20 per cent (*w/v*) acetic acid with a 0.01 per cent solution of dithizone in carbon tetrachloride. Bismuth is transferred to the aqueous phase from the carbon tetrachloride by shaking the latter with 0.2 per cent nitric acid containing bromide. The colorimetric determination is made at *p*H 9.5 with a chloroform solution of dithizone in the presence of cyanide. Phosphate and chloride (both in amounts up to 1 g.) are reported to be without hindrance on the extraction of bismuth from the acid solution of the ash. More than small amounts of ferric iron in the presence of phosphate cause trouble by giving a precipitate of ferric phosphate.

[46] E. P. Laug, *Anal. Chem.*, 21, 188 (1949).

CHAPTER XI

CADMIUM

I. Separations

A. Extraction Methods

When it is a matter of isolating cadmium from a solution containing only small amounts of heavy metals such as copper, silver, zinc, etc., dithizone is the reagent of choice. Cadmium dithizonate may be extracted quantitatively in faintly basic solution. It is easily decomposed by shaking the organic solvent solution with dilute acid (0.01 *N* hydrochloric acid suffices for a carbon tetrachloride solution). A separation can thus be effected from copper, mercury, and other metals whose dithizonates are hardly affected by weak mineral acid.[1] The separation from cobalt in this way is quite satisfactory, but the separation from nickel is imperfect because nickel dithizonate is appreciably decomposed by the dilute acid. The great stability of cadmium dithizonate in strongly basic solutions makes possible the separation from lead, zinc, and bismuth. Cadmium can be extracted with a carbon tetrachloride solution of dithizone from an aqueous solution 1 to 2 *N* in sodium hydroxide. At this high alkalinity, the metals mentioned are extracted hardly at all, even if present in relatively high concentrations (see Table 38). Much zinc tends to give low results. Other metals extracted with cadmium under these conditions include copper, silver, mercury, cobalt, and nickel.

An extraction method for the separation of traces of cadmium from nickel is based on the use 2-mercaptobenzothiazole.[2] The cadmium complex of this reagent can be extracted from ammoniacal medium by chloroform; a little tartrate can be added to prevent precipitation of the hydrous oxides of such metals as manganese. After the chloroform extract has been washed with ammoniacal mercaptobenzothiazole solution, cadmium can be returned to the aqueous phase by shaking the chloroform with 6 *N* hydrochloric acid. It appears that traces of nickel accompany cadmium, but they can be made harmless in the subsequent determination of cadmium by dithizone if dimethylglyoxime is added. From 10 to 60 γ of

[1] It should also be possible to pre-extract these metals from a mineral acid solution (*e.g.*, 0.05 *N*) with dithizone.

[2] E. J. Serfass et al., *Plating*, **35**, 456 (1948).

cadmium can be recovered within *ca.* 5 per cent in the presence of 60 mg. of nickel. The interference of iron and copper can be prevented by extraction of their cupferrates with chloroform before the mercaptobenzothiazole extraction of cadmium is applied.

Cadmium pyridine thiocyanate can be extracted by chloroform and a separation of cadmium thus made from silver, mercury, and copper (reduced to the cuprous state).[3] See p. 233.

Nickel can be separated from cadmium by dimethylglyoxime precipitation or by chloroform extraction of nickel dimethylglyoxime.

B. Sulfide Precipitation

Precipitation of cadmium as sulfide is a useful separation method in some instances. For complete recovery of cadmium the solution should be very slightly acid and a collector should be used.[4] High concentrations of the halides hinder the precipitation of cadmium sulfide in acid solution. Presumably hydrogen sulfide will provide a separation of little cadmium from much nickel and cobalt at low acidities. Fractional precipitation of cadmium sulfide may be applied to isolate cadmium from large quantities of zinc. A restricted amount of sodium sulfide is added to the solution to give a precipitate of zinc sulfide which contains virtually all of the cadmium present. The cadmium thus enriched may be separated with dithizone from the zinc in the precipitate if required.

II. Methods of Determination

A. The Dithizone Method

Two more or less general procedures for the determination of cadmium are given below in the belief that each has features of merit.

The procedure of Church[5] gives good results in the presence of relatively much silver, mercury, nickel, cobalt, copper, zinc, and lead, as shown by the figures in Table 37. An extraction from strongly basic medium with a chloroform solution of dithizone separates cadmium, silver, copper, etc. from lead and apparently zinc, which remain in the aqueous phase. The chloroform phase is then shaken with a buffer of *p*H 2 to bring cadmium into the aqueous layer; the other metals remain in the chloroform (p. 227).

[3] H. Fischer and G. Leopoldi, *Mikrochim. Acta*, **1**, 30 (1937).

[4] L. T. Fairhall and L. Prodan, *J. Am. Chem. Soc.*, **53**, 1321 (1931), in isolating cadmium from a solution of acid-digested organic material make the hydrogen sulfide precipitation at *p*H 3 in the presence of about 2 per cent sodium citrate and a little copper salt.

[5] F. W. Church, *J. Ind. Hygiene Toxicol.*, **29**, 34 (1947).

Finally cadmium is determined by a mixed color method in weakly basic medium, a chloroform solution of dithizone being used.[6]

The following procedure is generalized from directions given by Church.

1. *Method of Church*

Reagents

Citrate buffer. Dissolve 30 g. of boric acid, 65 g. of potassium hydroxide, and 20 g. of citric acid in a minimum volume of water and add 100 ml. of 20 per cent hydroxylamine hydrochloride solution. Shake this solution with successive portions of dithizone solution until the last remains green, indicating the removal of reacting heavy metals. Remove residual dithizone by shaking with a little chloroform and make up to 1 liter.

Hydroxylamine hydrochloride, 20 per cent solution. If thought necessary, it may be purified as described on p. 395.

Sodium potassium tartrate, 200 g. in 1 liter of solution.

TABLE 37

DETERMINATION OF CADMIUM BY MIXED COLOR METHOD OF CHURCH[a]

Foreign metal	Cd taken, γ	Cd found, γ
Ag, 2 mg	5.0	5.0, 4.9
Ag, 100 mg	10.0	10.6, 10.9
Hg, 2 mg	5.0	4.9, 4.9
Hg, 100 mg	10.0	10.5, 10.7
Ni, 2 mg	5.0	4.9, 4.9
Ni, 50 mg	10.0	9.8, 9.7
Co, 2 mg	5.0	5 0, 4.8
Co, 100 mg	10.0	10.2, 10.4
Cu, 2 mg	5.0	5.1, 5.0
Cu, 100 mg	10.0	10.4, 10.2
Zn, 2 mg	5.0	5.0, 4.8
Zn, 100 mg	10.0	10.6, 10.5
Pb, 2 mg	5.0	4.9, 5.0
Pb, 100 mg	10.0	10.1, 10.5

[a] Selection of figures from lower cadmium ranges.

[6] Further work to establish the best conditions for the final determination of cadmium appears to be required. The use of a carbon tetrachloride solution of dithizone and a higher *p*H as in the procedure of Fischer and Leopoldi may have advantages because of greater specificity (especially as concerns zinc). According to A. K. Klein and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **28**, 257 (1945), cadmium dithizonate solutions in carbon tetrachloride, obtained by extraction from strongly basic aqueous medium, are as stable as any other dithizonate solutions if the carbon tetrachloride is of high purity. The use of amber glassware is of aid in protecting the solution from the decomposing effect of light, as shown by Shirley et al.[16] Purification of carbon tetrachloride by refluxing with 5 per cent sodium hydroxide for several hours, followed by washing with water, drying with calcium chloride, and distilling over calcium oxide has been recommended by A. K. Klein, *J. Assoc. Official Agr. Chem.*, **32**, 349 (1949).

Acid buffer, pH 2. Make up according to Clark and Lubs, except double strength.

Stock dithizone solution, 200 mg. in 1 liter redistilled chloroform. The chloroform may be treated with hydroxylamine hydrochloride to give a more stable solution (p. 241). Dilute this stock solution with pure chloroform to obtain weaker solutions as needed.

Standard cadmium solution, 10 γ Cd per ml. in 0.1 *N* hydrochloric acid. This is best obtained by diluting a stronger solution, say 0.1 per cent, prepared from cadmium metal.

§ Procedure

Add 5 ml. of sodium potassium tartrate solution and 1 ml. of hydroxylamine hydrochloride solution to the sample solution having a volume near 50 ml. and containing as much as 50 γ of cadmium.[7] Make the solution basic with potassium hydroxide and add an excess of 5 ml. of 25 per cent solution. Shake for 1 minute with 5 ml. of dithizone solution (20 mg. per liter). If the aqueous layer is brown to light brown, add a 10 ml. portion of dithizone, shake for a minute, and draw off the chloroform into another separatory funnel. Add another 10 ml. portion of dithizone to the first funnel, shake for a minute and draw off the chloroform into the second funnel.

If the aqueous layer was not at least a light brown, add another 5 ml. portion of the 20 mg./liter dithizone, shake for a minute, and note the color of the aqueous layer. If the latter is brown to light brown, add 10 ml. of dithizone, shake for 1 minute, and repeat the steps given at the end of the last paragraph. By continuing in this way the amount of cadmium present can be approximated (if other reacting metals are practically absent):

Dz added, ml.	Color of aqueous phase	Color of $CHCl_3$ phase	Range of Cd, γ
5	Brown	Faint pink	0–5
5	Light brown	Pink	5–10
10	Light brown	Pink	10–20
20	Light brown	Pink	20–50
30	Light brown	Pink	50–75

Add 5 ml. of 200 mg./liter dithizone solution to the combined chloroform extracts and wash with a 50 ml. portion of water to remove all entrained base. Run the chloroform layer into another separatory funnel and use a

[7] If the sample contains appreciable amounts of copper, mercury, nickel, or cobalt, it is best to extract all the reacting metals by shaking the ammoniacal (pH 8–9) solution, containing about 5 per cent of an alkali citrate, with successive 5 ml. portions of dithizone (200 mg. per liter) until the last portion remains green. The combined chloroform extracts are shaken with two successive 25 ml. portions of 0.2 *N* hydrochloric acid (1 *N* according to Church). Cadmium, lead, and zinc are thus brought into the aqueous phase; copper and the other acid-resistant dithizonates remain almost entirely in the chloroform; cobalt should also remain to a large extent in the chloroform, but nickel divides. The water solution is then treated according to the above procedure.

few milliliters of pure chloroform to recover any remaining dithizonate from the water layer. Shake the chloroform solution with 50 ml. of *p*H 2 buffer for at least 2 minutes. Discard the chloroform layer if the original approximation of the amount of cadmium was 60 γ or less. Otherwise, shake the separated chloroform with another portion of buffer. Combine the aqueous solutions, now containing all the cadmium, and wash with a few milliliters of chloroform. (If the color of the dithizone layer indicates the presence of large amounts of acid-resistant dithizonates, it may be advisable to shake the separated buffer solution with a little dithizone solution to remove traces of these metals which may have gone into the acid phase.) If necessary, allow droplets of chloroform on the surface of the aqueous layer to evaporate.

Now add 20 ml. of citrate buffer to the solution, mix, and add the proper volume and strength of dithizone solution according to the estimated amount of cadmium:

Cd range, γ	Dz concn., mg./liter	Volume of Dz, ml.
0–5	4	10
5–10	8	10
10–20	8	20
20–50	8	50

Shake well for 2 minutes. Allow the phases to separate and displace any aqueous solution in the bore of the stopcock with a few drops of chloroform solution; dry the stem of the funnel with a roll of filter paper or a cotton swab. If the chloroform solution is free of water droplets, run it directly into a dry absorption cell (1 or 2 cm. thick), else filter it through a small plug of glass wool. Find the transmittancy at 515 mμ.

Prepare standard curves for each range of cadmium concentration (4 or 5 points for each). Mix 20 ml. of citrate buffer solution and 50 ml. of acid buffer of *p*H 2 and shake with a small volume of dithizone solution (20 mg./liter) to remove traces of heavy metals; wash out droplets of remaining dithizone with chloroform. Then add standard cadmium solution, shake with dithizone solution, and proceed as described above. Extinction plotted against concentration should give a straight line.

Run a blank through the procedure.

2. Method of Fischer and Leopoldi

The following procedure[8] can be applied directly in the presence of lead, bismuth, tin (II), and moderate amounts of zinc (Zn:Cd less than 3000)

[8] A preferable method of separation when the amounts of these metals are small may be based on the undecomposability of copper, silver, and mercury dithizonates by dilute acid (see page 230); a separation from cobalt and the most of any nickel is effected at the same time.

TABLE 38

DETERMINATION OF CADMIUM BY THE MONO COLOR DITHIZONE METHOD[a]

Foreign metal	Cd taken γ	Cd found γ	Error γ	Remarks
	5.6	5.8	+0.2	
	7.4	7.4	0.0	
	18.5	18.2	−0.3	
	33.3	33.0	−0.3	
50 mg. Fe (III)	7.4	7.8	+0.4	5 ml. 25% Rochelle salt
200 mg. As (V)	5.6	5.3	−0.3	
100 mg. Sb (III)	5.6	5.3	−0.3	
75 mg. Pb	5.6	5.3	−0.3	1 ml. 25% Rochelle salt
50 mg. Bi	7.4	7.0	−0.4	1 ml. 25% Rochelle salt
25 mg. Sn (II)	5.6	5.3	−0.3	1 ml. 25% Rochelle salt
30 mg. Zn	7.4	7.0	−0.4	
60 mg. Zn	7.4	5.5	−1.9	
30 mg. Ag	7.4	7.8	+0.4	Cd separated by extraction of the pyridine thiocyanate with chloroform
30 mg. Hg (II)	7.4	7.8	+0.4	
30 mg. Cu	7.4	8.2	+0.8	
30 mg. Cu	7.4	7.8	+0.4	
25 g. Zn	0.030%	0.031%	+0.001%	Preliminary concentration of cadmium as sulfide. Determination on aliquot ≡ 1 g. Zn
	0.0074%	0.0071%	−0.0003%	
	0.0022%	0.0021%	−0.0001%	

[a] Selection of figures from data of H. Fischer and G. Leopoldi, *Mikrochim. Acta*, **1**, 30 (1937), especially from the lower ranges of cadmium.

by extracting with dithizone from an approximately 5 per cent sodium hydroxide solution. A carbon tetrachloride, not chloroform, solution of dithizone must be used if zinc is present. When copper, silver, and mercury are present, cadmium must first be separated by the pyridine-thiocyanate method already referred to.[3] This procedure does not provide for the presence of nickel and cobalt. The figures in Table 38 will give some idea of the accuracy of the method.

Reagents

Dithizone, 5 mg. in 100 ml. of carbon tetrachloride.

Sodium hydroxide solution, 10 per cent. The solution should be tested by diluting with an equal volume of water and shaking with dithizone. The carbon tetrachloride layer must become colorless or at most slightly yellowish.

Sodium hydroxide solution, 2 per cent. The solution must give no reaction with dithizone.

Sodium potassium tartrate solution, 20 per cent. The solution must show no reaction with dithizone when mixed with an equal volume of 10 per cent sodium hydroxide.

Ammonium thiocyanate solution, (*a*) 25 g. in 100 ml. of water, (*b*) 2 g. in 100 ml. of water.

Pyridine-chloroform. A mixture of 5 ml. of pyridine and 100 ml. of chloroform.

Sulfurous acid, 1 per cent SO_2 in water.

Nitric acid, concentrated.

Sodium acetate solution, 5 per cent.

Standard cadmium solution, 0.001 per cent Cd in 0.1 *N* hydrochloric acid. Prepare fresh by diluting a stronger solution (0.01 or 0.1 per cent) obtained by weighing out pure cadmium metal.

§ Procedure

In Pure Solution or in the Presence of the Alkali and Alkaline Earth Metals, Aluminum, Manganese, Iron, Arsenic, Antimony, Zinc, Lead, Bismuth, and Tin. The solution may have a volume of 5 to 10 ml. and may contain 3 to 30 γ of cadmium. Add an equal volume of 10 per cent sodium hydroxide solution to the approximately neutral sample solution which has been treated with sufficient sodium potassium tartrate to keep metals precipitated by alkalies in solution (5 ml. of 20 per cent sodium potassium tartrate suffices to prevent the precipitation of 50 mg. of iron). Extract in a separatory funnel with small portions of dithizone until the last portion becomes colorless (see Note 3). Collect the extracts in a separatory funnel, and wash the extracted aqueous solution with a few milliliters of carbon tetrachloride.

Shake the carbon tetrachloride extract with two successive portions of 2 per cent sodium hydroxide solution having approximately one-half the volume of the carbon tetrachloride, wash once with a small volume of water, and transfer the carbon tetrachloride to a small volumetric flask (*e.g.*, 25 ml.) and make up to volume with the same solvent. Since cadmium dithizonate solution in carbon tetrachloride is not very stable (the stability depends upon the purity of the carbon tetrachloride[6]), transform the complex into free dithizone by shaking with 0.5 *N* hydrochloric acid.[9] Compare against a standard solution of dithizone prepared in the same manner as the unknown or determine the transmittancy at 620 mμ with a photometer.

In the Presence of Silver, Mercury, and Copper. When silver and mercury are present in the sample proceed as follows. To the slightly acid solution add sufficient ammonium thiocyanate (25 per cent solution) to redissolve the silver thiocyanate first precipitated. If mercury is present, a greater excess of thiocyanate is required (approximately 5 ml. of ammonium thiocyanate per 10 mg. of mercury). Add sodium acetate solution until blue Congo paper just turns red (*p*H 5). Extract with small portions of pyridine-chloroform totaling 15 ml. Wash the combined extracts once with an equal volume of 2 per cent ammonium thiocyanate solution.

[9] For the determination of very small amounts of cadmium, however, comparison as cadmium dithizonate is permissible and indeed preferable. See p. 238. The transmittancy may be measured at 520 mμ.

Evaporate the chloroform extract to dryness on the water bath, add 3 ml. of concentrated nitric acid, and again evaporate to dryness. Take up the residue in 2 or 3 ml. of 1 per cent sulfuric acid, transfer to a separatory funnel, and rinse with a little water. Extract with small portions of dithizone to remove traces of silver and mercury. Dilute the aqueous solution with water to 10 ml. and determine cadmium as described above.

In the presence of copper proceed as follows. Add sodium carbonate solution to the acid sample solution until a turbidity appears and then clear the solution with a few drops of sulfurous acid. Heat nearly to boiling, add 5–6 ml. sulfurous acid (for 30 mg. Cu), boil briefly, and cool to room temperature. In this way most of the copper is reduced to the cuprous condition. Reduce the acidity of the solution by the addition of sodium acetate as already described above and add sufficient ammonium thiocyanate to dissolve the precipitated cuprous thiocyanate. Extract with chloroform-pyridine and proceed as already described. Since some copper is extracted by pyridine-chloroform, it must be removed by shaking with dithizone in acid solution before the cadmium determination.

Notes. 1. Cadmium dithizonate has only a limited solubility in carbon tetrachloride, and if much cadmium is present yellow flocs of the dithizonate may separate. The solubility in chloroform is much greater, and a chloroform solution of the reagent may be used except when appreciable amounts of zinc are present. The stability of cadmium dithizonate is said to be greater in chloroform than in carbon tetrachloride.

2. If an appreciable quantity of manganese is present, hydroxylamine hydrochloride should be added to prevent oxidation of the dithizone and the obtaining of low results for cadmium.

3. When much zinc is present it may be slightly coextracted with the cadmium so that on successive extraction with dithizone a point is never reached at which the carbon tetrachloride becomes colorless. In such a case the extract must be shaken with 2 per cent sodium hydroxide solution before being added to the previous extracts. If the red color then disappears it was due to zinc dithizonate and cadmium has been completely extracted from the solution.

4. The removal of the noble metals and copper from solution by precipitation with a suitable reducing agent (hydroxylamine hydrochloride, hypophosphorous acid) is not admissible because the precipitated metals carry down cadmium.

5. By using the glass-stoppered comparison tubes described on p. 52 and extracting with a small volume of dithizone, much less than 1 γ of cadmium can be determined (*cf.* p. 238). With 1 ml. of carbon tetrachloride, 0.03 γ cadmium can then be detected.

B. Di-β-naphthylthiocarbazone Method[10]

The naphthyl analog of dithizone has been used for the determination of cadmium in bio material (for procedure see p. 239). The method described involves essentially three steps:

1. The ammoniacal citrate solution of the decomposed sample is ex-

[10] J. Cholak and D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, **16**, 333 (1944).

tracted with a chloroform solution of di-β-naphthylthiocarbazone to isolate cadmium and all other reacting heavy metals. The chloroform solution is shaken with 0.2 *N* hydrochloric acid to bring cadmium, zinc, lead, some of the nickel, etc. into the aqueous phase; copper and cobalt largely remain in the chloroform.

2. The acid solution from (1) is treated with tartrate and made strongly basic with sodium hydroxide. The resulting solution is extracted with a chloroform solution of *dithizone* to isolate cadmium; zinc, lead, and bismuth are left in the aqueous phase. Cadmium is brought into aqueous solution by shaking the chloroform with 0.2 *N* hydrochloric acid.
3. Cadmium is determined by the mixed color technique in ammoniacal solution with di-β-naphthylthiocarbazone as reagent.

It is said that di-β-naphthylthiocarbazone is superior to dithizone in the initial extraction because of more rapid removal of heavy metals in this step. However, no particular difficulty is encountered in the complete extraction of cadmium by dithizone, even in strongly basic solutions, and this reagent may be used as well (*cf.* p. 232). In the second step, di-β-naphthylthiocarbazone cannot be used in place of dithizone because zinc, lead, etc. would then also be extracted and no separation would result. The use of the naphthylthiocarbazone in the final step has a distinct advantage over the use of dithizone, since the former reagent does not dissolve in a basic aqueous solution and hence the *p*H need not be regulated closely in obtaining the mixed color.

Probably the most serious source of error in the method described lies in the separation of cadmium from zinc in step 2. Apparently some zinc accompanies cadmium in the chloroform-dithizone extraction of the sodium hydroxide solution.[11] Therefore it is necessary to wash the chloroform extracts with water, which becomes sufficiently basic from the entrained sodium hydroxide solution to remove the zinc according to the authors. In this process some of the cadmium may pass into the aqueous phase. Such loss of cadmium is prevented by adding dithizone to the chloroform before washing. The amount added must be such that some remains in the chloroform after the washing has been completed.

According to the authors, weak cadmium dithizonate solutions are unstable in the absence of excess dithizone (or naphthythiocarbazone) and it is therefore necessary to use a mixed color method in the final determination of cadmium (but see p. 229). In this mixed color procedure, other metals if present would react and be counted as cadmium. Therefore the

[11] A carbon tetrachloride solution of dithizone provides a better separation of cadmium from zinc than does a chloroform solution as shown by H. Fischer (p. 232).

preliminary separation of cadmium must be carefully made and one must guard against the introduction of zinc from the glassware in the final step.

C. The Sulfide Method

This method is based on the formation of a colloidal suspension of cadmium sulfide. It is inferior to the dithizone method in sensitivity and specificity. If the suspensions are compared in ultraviolet radiation from a mercury arc instead of in daylight, the sensitivity is increased ten-fold.[12] Juza and Langheim[13] use gelatin to stabilize the suspension, and make the determination photometrically. They find that Beer's law holds. In the presence of cyanide, 10 times as much copper and cobalt, 100 times as much nickel, and 1000 times as much zinc as cadmium may be present.

III. Applications of the Dithizone and Naphthylthiocarbazone Methods

A. Silicate Rocks[14]

The rock sample is decomposed with hydrofluoric-perchloric acid and the ammoniacal citrate solution of the residue is extracted with dithizone in carbon tetrachloride to isolate cadmium, zinc, lead, copper, etc. The carbon tetrachloride solution is shaken with very dilute hydrochloric acid to transfer cadmium, zinc, etc. to the aqueous phase; copper and cobalt remain in the carbon tetrachloride. Cadmium can then be determined in the aqueous phase after making strongly basic with sodium hydroxide.

The cadmium content of igneous rocks is of the order of 10^{-5} per cent. The method described permits the detection of 5×10^{-6} per cent of cadmium when a 0.5 g. sample is taken. The only metal likely to give trouble is nickel. If the sample contains more than 0.03–0.04 per cent of nickel, some of this metal will find its way into the final solution and impart a brownish color to the carbon tetrachloride solution.

Although the directions call for comparison by the standard series method, a photometer can be used to determine the transmittancy (520 mμ) if a suitable cell is available.

Special Reagents

Dithizone, 0.02 per cent (weight by volume) in carbon tetrachloride.

Dithizone, 0.001 per cent (weight by volume) in carbon tetrachloride. One milliliter of this solution shaken with 10 ml. of redistilled water and 2 to 3 ml. of 25 per cent sodium hydroxide solution should yield a colorless carbon tetrachloride layer. This solution should be prepared shortly before use by diluting the stronger dithizone solution.

[12] L. T. Fairhall and L. Prodan, *J. Am. Chem. Soc.*, **53**, 1321 (1931).
[13] R. Juza and R. Langheim, *Angew. Chem.*, **50**, 255 (1937).
[14] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **11**, 364 (1939).

Sodium citrate, 10 per cent. The solution should be freed from heavy metals by adding a few drops of concentrated ammonium hydroxide to 100 ml. and shaking with successive small portions of 0.01 or 0.02 per cent dithizone in carbon tetrachloride until the latter shows only a very faint pink color.

Sodium hydroxide, 25 grams in 100 ml. of solution.

Hydrochloric acid, approximately 0.01 *N*. Dilute 1 volume of concentrated acid with 1000 of redistilled water. The solution should be shaken with a few milliliters of 0.01 per cent dithizone in carbon tetrachloride and decanted from the latter before use.

§ Procedure

Weigh 0.5 gram of rock powder into a platinum dish and add a few milliliters of water, 1 ml. of 70 per cent perchloric acid, and 5 ml. of hydrofluoric acid. Evaporate to dryness, add 0.5 ml. of perchloric acid and a few milliliters of water to the residue, and again evaporate to dryness to expel excess perchloric acid. Moisten the residue with 1 ml. of concentrated hydrochloric acid, add 5 ml. of water, and heat near the boiling point until all soluble matter has been brought into solution.

Add 10 ml. of sodium citrate solution and 0.1 gram of hydroxylamine hydrochloride, neutralize with concentrated ammonium hydroxide using litmus paper, and add 2 drops in excess. If the solution is appreciably turbid at this point, filter through a small filter paper, wash with small portions of water, and ash the paper at a low temperature. Grind the residue with 0.15 to 0.2 gram of sodium carbonate in an agate mortar, transfer the powder to a platinum crucible, and fuse. Leach the melt with water, filter through paper, wash with a few milliliters of water, rinse the insoluble material out of the paper, and heat with dilute hydrochloric acid to effect as complete solution as possible. Add 2 or 3 ml. of sodium citrate and a small crystal of hydroxylamine hydrochloride, neutralize with ammonium hydroxide, and add 2 drops in excess.

Extract the main solution (filtrate from any insoluble material) as follows: Add 5 ml. of 0.02 per cent dithizone and shake in a separatory funnel for 0.5 to 1 minute; allow the carbon tetrachloride to settle and draw it off into another separatory funnel. If the carbon tetrachloride drawn off is not greenish, add 2 to 3 ml. more of dithizone to the main solution, shake, draw off, and repeat until the carbon tetrachloride layer shows a greenish color after shaking for 1 minute. In like manner extract the solution resulting from the sodium carbonate fusion, using 1 ml. portions of dithizone in this case.

Combine all the dithizone extracts and shake with 5 ml. of water; discard the water layer. Shake the carbon tetrachloride extract vigorously with 5 ml. of 0.01 *N* hydrochloric acid for 2 minutes. Draw off the carbon tetrachloride layer and repeat the shaking with a fresh 5 ml. portion of 0.01 *N* hydrochloric acid. Combine the acid extracts and discard the

carbon tetrachloride. Shake the hydrochloric acid extract with small portions of carbon tetrachloride to remove any colored droplets of carbon tetrachloride in the solution. Finally all droplets of carbon tetrachloride should be separated from the aqueous layer; care should be taken that a film of tetrachloride does not remain on the water surface. The loss of a drop or two of aqueous phase in removing carbon tetrachloride will do no harm.

Transfer the solution to a flat-bottomed glass-stoppered tube, 1.8 × 15 cm., and rinse the separatory funnel with a milliliter or two of water. Prepare a series of standards in similar tubes containing, for example, 0, 0.05, 0.1, 0.15 ... microgram of cadmium, dilute with 0.01 *N* hydrochloric acid to the same volume as the unknown, and mix. Add 2.5 ml. of 25 per cent sodium hydroxide solution to each tube and mix. Then add 1.0 ml. of 0.001 per cent dithizone solution and shake vigorously 10 to 15 times. Compare the colors of the carbon tetrachloride layers by viewing the tubes transversely against a white background. The colors fade on standing, and the hue also changes, so that the color comparison should be made immediately after shaking. The hue of the unknown should be the same as that of the standards.

Run a blank on the reagents, taking double the amounts used in the determination itself.

Notes. 1. Hydroxylamine hydrochloride is added to prevent air-oxidation of manganese to higher valences; such oxidation results in incomplete extraction of cadmium.

2. The excess of ammonia added prior to the dithizone extraction of the sample must not be too great, otherwise nickel is extracted in large amounts and later gives rise to difficulties in the color comparison.

3. The accuracy of the method may be judged from the following figures:

Cd present 10^{-5}%	Cd found 10^{-5}%	
2	1.5	
4	5, 4.5	
7	6.5	
3	3	(0.04% Ni)
4	4.5	(0.02% Ni)
4	3	(0.01% Ni, 0.2% Mn)

B. Zinc Metal

For the determination of less than 0.01 per cent of cadmium in zinc a preliminary concentration of cadmium by sulfide precipitation is necessary. The following procedure permits the determination of as little as 0.001–0.002 per cent cadmium with an accuracy of 5 to 10 per cent.

§ Procedure[15]

Dissolve 25 g. of zinc in dilute nitric acid, neutralize the solution with ammonia, warm, and add a dilute solution of sodium sulfide with stirring to precipitate a portion of the zinc and all or most of the cadmium. The zinc sulfide first precipitated is generally discolored by small amounts of other heavy metals present, and the precipitation of cadmium may be considered complete when further addition of sodium sulfide produces a pure white precipitate of zinc sulfide.

Filter off the precipitate, dissolve it in dilute nitric acid, evaporate the solution to a small volume to get rid of hydrogen sulfide and most of the acid, and transfer to a volumetric flask. Dilute the solution to volume with water and take for analysis an aliquot representing 1 or 2 g. of sample. Shake the dilute acid solution (*ca.* 0.05 *N*) with dithizone to remove copper and silver. Then determine cadmium as described on p. 233.

C. Air Samples

The general procedure described on p. 230 has been used to determine cadmium in samples collected with an electrostatic precipitator (deposit dissolved in warm 10 per cent nitric acid) or an impinger.[5]

D. Bio Material

Samples of organic origin can be decomposed by standard wet-oxidation procedures and cadmium determined according to the directions given on p. 230.[16] Good recoveries have been obtained in applying this method to urine.[5]

Directions are given below for determining cadmium by a mixed color method with naphthylthiocarbazone according to Cholak and Hubbard (p. 234). Recoveries are satisfactory (p. 9), and it has been shown that 100 γ each of nickel and zinc do not interfere in the determination of 10 γ of cadmium.

§ Procedure

Destroy organic matter in a suitable weight of sample (50–100 ml. of urine, 5–20 g. of tissue, blood, etc.) by oxidation with sulfuric-nitric acid

[15] H. Fischer and G. Leopoldi, *Mikrochim. Acta*, 1, 37 (1937).

[16] Another dithizone procedure for bio samples is described by Klein and Wichmann.[6] Good results were obtained, but later work (Klein, *J. Assoc. Official Agr. Chem.*, **30**, 455 (1947)) showed erratic and low recoveries of cadmium. The discrepancy has not yet been explained. A later procedure is that of R. L. Shirley, E. J. Benne, and E. J. Miller, *Anal. Chem.*, 21, 300 (1949). These authors remove copper and mercury by dithizone extraction from acid solution, and nickel by chloroform-dimethylglyoxime extraction (cobalt is complexed); cadmium is finally extracted by dithizone-carbon tetrachloride from 5 per cent sodium hydroxide solution.

(p. 320). Evaporate the digest to fumes of sulfuric acid, and destroy any char with repeated small additions of nitric and perchloric acids. Cool and rinse the sample into a 125 ml. separatory funnel. Add 15 ml. of ammonium citrate solution (400 g. of citric acid in 600 ml. of water made alkaline with ammonia and diluted to 1 liter), make up to 50 ml. with water, and add 2 drops of phenol red indicator. Adjust the *p*H to about 8.3 (first pink color) by adding concentrated ammonia.

Extract reacting heavy metals by shaking the solution with successive 5 ml. portions of di-β-naphthylthiocarbazone solution (200 mg. in 1 liter chloroform) until the last portion shows no change in color. Shake the combined extracts with 50 ml. of water and separate the phases; shake the aqueous layer with a few milliliters of chloroform and combine the latter with the chloroform extract. Remove the heavy metals from the chloroform extract by shaking it with 50 ml. of 0.2 *N* hydrochloric acid. Separate the phases and remove droplets of naphthylthiocarbazone from the aqueous layer by shaking with a little chloroform.

Separation of cadmium from zinc, lead, etc. To the hydrochloric acid solution containing cadmium and other metals, add 5 ml. of 25 per cent sodium tartrate solution and 20 ml. of sodium hydroxide solution (25 g. in 100 ml. of solution). Dilute to about 100 ml. with water. Extract with successive 5 ml. portions of dithizone (10 mg. in 1 liter chloroform) until the last portion is colorless or slightly yellowish.[17] Add 5 ml. of dithizone (100 mg. in 1 liter chloroform) to the combined extracts and shake with 50 ml. of water. Separate the chloroform layer and shake it with 50 ml. of 0.2 *N* zinc-free hydrochloric acid (obtained by absorbing hydrogen chloride in pure water). Draw off and discard the chloroform.

Determination of cadmium. Add to the acid extract 50 ml. of zinc-free ammonia solution obtained by diluting 50 ml. of concentrated ammonium hydroxide with water to 1 liter and shaking with 10 ml. portions of naphthylthiocarbazone solution in chloroform (20 mg. per liter) until the last portion shows no change in color (remove any entrained thiocarbazone with chloroform). Next add exactly 5 ml. of standard naphthylthiocarbazone solution (20 mg. per liter of chloroform) and shake for 1 minute. Allow the phases to separate completely, draw off the chloroform layer and dilute a portion of the latter exactly five-fold with pure chloroform. Obtain the transmittancy of the solution at 540 mμ, preferably using a 2.5 cm. cell.

Construct a standard curve by taking known amounts of cadmium in 50 ml. portions of 0.2 *N* hydrochloric acid and treating as described above. It is convenient to prepare curves for two concentration ranges—0 to 5

[17] Some commercial samples of dithizone have been found to contain semicarbazone, which imparts a pink color to the chloroform in the absence of cadmium. For purification of dithizone see p. 107.

and 0 to 50 micrograms of cadmium. In the latter case the strength of the naphthylthiocarbazone solution is increased to 200 mg. per liter, and the photometry is carried out in a 1 cm. cell after diluting the solution 20-fold with chloroform.

Notes. 1. Ashing the sample by ignition tends to give low results, especially when the ash content is small and when deflagration occurs. This is not an unexpected finding in view of the volatility of cadmium metal.

2. Dithizone may be used in place of naphthylthiocarbazone except in the removal of zinc from ammonium hydroxide in the purification of the latter.

3. Unless prepared immediately before use, dilute naphthylthiocarbazone solutions should be stabilized by the addition of alcohol to the extent of 0.5 per cent by volume and they should be kept in a refrigerator. Oxidizing substances in the chloroform used to make up the solutions may be destroyed by shaking 1 liter of chloroform with 100 ml. of water containing 0.5 g. of hydroxylamine hydrochloride and enough ammonia to give a basic color with phenol red.

CHAPTER XII

CALCIUM

I. Separations

Precipitation of calcium as oxalate is the most generally applicable method for its isolation. Magnesium oxalate is coprecipitated (or sometimes postprecipitated) with calcium oxalate and a double precipitation of the latter is likely to be required if magnesium preponderates over calcium. If magnesium greatly outweighs calcium, the oxalate separation becomes uncertain because of the difficulty of precipitating calcium completely.[1] It is then advisable to follow Hillebrand's method of precipitating calcium together with magnesium ammonium phosphate, dissolving the precipitate in sulfuric acid, and separating calcium as sulfate in alcoholic medium.[2] Fortunately in many materials (bio samples, water, etc.) the calcium-magnesium ratio is such that special attention need not be paid to the effect of magnesium. If the precipitation of calcium oxalate is carried out at a *p*H of 3 to 4, instead of in a slightly ammoniacal medium as is usually done, separation of calcium from iron, titanium, etc. as well as from much phosphate can be effected.[3] It may be calculated that the solubility of calcium oxalate in 0.1 *M* oxalate solution having a *p*H of 4 is less than 0.1 mg. Ca per liter.

For the separation of calcium from strontium, resort must be made to the extraction of the anhydrous nitrates with such solvents as absolute alcohol and ether, acetone,[4] or nitric acid (density 1.42), which dissolve calcium nitrate and leave most of the strontium (and barium) nitrate. This procedure has been applied particularly for the separation of little strontium from much calcium and there is little information available on its performance in the isolation of little calcium from much strontium. Barium is

[1] See I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, Macmillan, New York, 1943, p. 355, for a discussion of the oxalate method for the separation of calcium and magnesium.

[2] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*. Wiley, New York, 1929, p. 488.

[3] J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **20**, 607 (1938).

[4] According to M. M. Tillu and M. S. Telang, *J. Indian Chem. Soc.*, **19**, 231 (1942), the solubility of strontium nitrate in acetone is 1 part in 15,000 at 35° C.

quite readily separated from calcium by precipitation as the chromate (p. 193).

Electrolysis with a mercury cathode in acid solution provides a means of removing many heavy metals (p. 31).

II. Methods of Determination

Calcium must usually be determined by indirect colorimetric methods by making use of the reactivity of the anion of a slightly soluble calcium salt. Because of their indirect character the colorimetric methods for calcium are far from ideal, but nevertheless are useful for certain types of material, especially bio samples, in which the proportion of calcium is not too low. The two methods which have found the most favor are based on the precipitation of calcium as oxalate and phosphate respectively.

A. The Oxalate Method

Because of its low solubility, calcium oxalate recommends itself as the basis of a colorimetric method for calcium, especially since small amounts of magnesium will not interfere appreciably. Oxalate does not form colored compounds, but it readily reduces colored substances or those that can be made to yield strongly colored products. Ceric salts are probably best suited for the determination of calcium by the oxalate method.[5] Solutions of ceric salts are not sufficiently intensely colored to permit their concentration to be determined advantageously in this way for the present purpose, but it is a simple matter to add iodide and obtain a strong-colored solution of tri-iodide ion. This is the method used by Sendroy for the micro and ultramicro determination of calcium.[6] It will be noted that the method is very much an indirect one:

$$\underbrace{Ca \equiv C_2O_4}_{(1)} \underbrace{\equiv Ce^{IV}}_{(2)} \underbrace{\equiv I_3^-}_{(3)}$$

The most crucial step in the sequence is (1), *i.e.*, all the calcium must be precipitated, no appreciable amount of calcium oxalate must be lost in washing, and the precipitate must contain calcium and oxalate in a 1:1 ratio (if the standard curve is based on known quantities of a soluble oxalate such as sodium oxalate). If these conditions can be fulfilled, the other

[5] For a photometric method based on the reduction of potassium permanganate solution by calcium oxalate see R. E. Scott and C. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 504 (1945). The procedure described is intended for milligram amounts of calcium. Another colorimetric method for calcium following oxalate precipitation is based on ignition of the precipitate to carbonate, solution of the latter in hydrochloric acid, and determination of the excess of acid by reaction with iodide and iodate to liberate iodine. See H. A. De Luca, *Can. J. Research*, **25B**, 449 (1947).

[6] J. Sendroy, Jr., *J. Biol. Chem.*, **144**, 243 (1942).

steps should give little trouble, although in step (3) air-oxidation of the acid iodide solution may introduce error unless suitable precautions are taken.

So far as the requirements of the colorimetric method are concerned, the calcium oxalate precipitate formed in a slightly acid solution may be considered to have the theoretical ratio of calcium-oxalate, although actually it contains a little excess oxalate (coprecipitated ammonium oxalate or oxalic acid); a precipitate formed in an initially ammoniacal solution will contain a little less oxalate than it should (the ratio Ca/C_2O_4 is of the order 1.01). Sodium is fairly strongly coprecipitated with calcium oxalate and leads to slightly high results (*ca.* 1 per cent), if present in high concentrations. The effect of magnesium may be more serious, and the error may be positive or negative depending on its amount as already indicated. Sulfate in sufficient concentration gives rise to low results owing to the coprecipitation of calcium sulfate. Phosphate is not coprecipitated with calcium oxalate to any serious extent if the precipitation of the latter is made in a medium initially slightly acid.

The following procedure is essentially the same as that given by Sendroy (*loc. cit.*) for the determination of calcium in blood serum. The error should not exceed ± 2 per cent.

Reagents

Ammonium oxalate solution, saturated (4.5 per cent) at room temperature.

Ammonium hydroxide, 6 *N*.

Washing mixture. Mix equal volumes of water, absolute alcohol (or redistilled 95 per cent alcohol) and reagent-grade ethyl ether. This mixture on evaporation must not give a residue that reduces acid ceric solution.

Sulfuric acid, 1 *N*.

Ceric sulfate ca. 0.1 *N*. Dissolve 29 g. of anhydrous $Ce(HSO_4)_4$ of 92 per cent purity or the equivalent weight of $Ce(SO_4)_2$ in 500 ml. of 1 *N* sulfuric acid. The concentration of the solution should not differ too much from 0.1 *N*. Its strength may be checked by adding a suitable amount of the diluted solution to acidified potassium iodide solution and measuring the transmittancy (*cf.* p. 245). The calculated amount of water or ceric sulfate may then be added to make the solution more nearly 0.1 *N*.

Ceric sulfate, 0.005 *N* in 0.2 *N* sulfuric acid. Prepare from the 0.1 *N* ceric solution shortly before use.

Sodium oxalate, 0.1000 *N*. Dissolve 3.350 g. $Na_2C_2O_4$ in water, add 50 ml. of 1 *N* sulfuric acid and dilute to 500 ml. Protect the solution from the light. It should be stable for 6 months.

Sodium oxalate, 0.0025 *N*. Prepare fresh from the 0.1 *N* solution by dilution with water.

Potassium iodide, 1 per cent. Prepare immediately before use by dissolving 1.0 g. of analytical quality salt in 100 ml. of water.

Potassium iodate, 0.0005 *M*. Prepare from pure dry KIO_3, accurately weighed. This solution is used to furnish iodine by reaction with an acidified iodide solution, for the construction of the calibration curve.

§ Procedure

The following directions may be used for the determination of 0.05–0.15 mg. of calcium (for smaller amounts see Note 1) in the absence of such interfering substances as have been mentioned above.

To the neutral sample solution in a 10 to 15 ml. Pyrex conical bottomed centrifuge tube[7] add sufficient water to make the volume 5 ml., 1 or 2 drops of concentrated hydrochloric acid, 1 ml. of saturated ammonium oxalate solution, and then enough dilute ammonia to make the liquid basic to methyl orange (*p*H 4.5 or above). In the same manner treat two "standard" tubes containing 5 ml. of water. Allow the solutions to stand overnight.

Centrifuge each tube for 5 minutes, and by means of a capillary with an upturned tip draw off all but about 0.2 ml. of the supernatant liquid. Wash the entire inside of the tube with 3 ml. of water added from a pipet moved around the top of the tube. Mix the water with the residual solution by tapping the tube until the precipitate just starts to rise. Then centrifuge and withdraw the liquid as before. Next wash with the water-alcohol-ether mixture as follows. Add 1 ml. of the mixture, stir to mix well, add an additional 3 ml. and mix gently with the first 1 ml. portion so as not to bring much of the precipitate into the supernatant layer. Centrifuge and draw off the supernatant liquid. Repeat the washing and withdrawal. Dry the tubes for $^1/_2$ to 1 hour in an oven at 100–110°, inclining them at an angle of 15°.

At this point add 1.00 and 3.00 ml. of 0.0025 *N* sodium oxalate solution to the two standard tubes. Then add 2.0 ml. of 0.5 *N* sulfuric acid to all the tubes, and heat the latter for 5 minutes in a beaker of water kept below the boiling point. Cool to room temperature, add 2.00 ml. of 0.005 *N* ceric solution, mix and allow the covered tubes to stand for 30 minutes at room temperature, or alternatively in a water bath at 70° for 10 minutes.

Transfer the solutions to a 25 ml. volumetric flask and dilute to about 20 ml. Add 1.5 ml. of 1 per cent potassium iodide solution, mix, dilute to volume and mix again. Without undue delay determine the transmittancy of the solutions with the aid of a filter showing maximum transmission at 400 mμ, against a reagent blank containing the same concentration of sulfuric acid and potassium iodide as the sample and standard solutions, and which has been prepared at the same time as these. Error due to liberation of iodine by air-oxidation will be cancelled out by the use of such a solution as a reference liquid representing 100 per cent transmittancy.

[7] Instead of employing the centrifuge technique, one can as well work with the filter stick, using the apparatus illustrated on p. 500.

The concentration of calcium in the *diluted* sample is equal to

$$\frac{[C_2O_4^{=}]_{s_1} + [C_2O_4^{=}]_{s_2} + [I_2]_{s_1} + [I_2]_{s_2}}{2} - [I_2]_u,$$

where the brackets denote equivalent concentrations at the volume of dilution (25 ml.) and the subscripts s_1, s_2, and u refer to the standards and the sample solution.

Construct the iodine calibration curve by mixing from 1 to 10 ml. of 0.0005 *M* potassium iodate solution with 10 ml. of 0.5 *N* sulfuric acid and 6 ml. of 1 per cent potassium iodide solution, and diluting to 100 ml. with water in a volumetric flask; obtain the transmittancy, using a similar sulfuric acid-iodide solution prepared at the same time for reference (= 100 per cent transmission). Plot extinction versus iodine concentration.

Notes. 1. By appropriately reducing the volume and concentration of the solutions used, quantities of calcium much smaller than 0.1 mg. can be determined. Reference must be made to the paper of Sendroy, cited above, for details. When very small quantities of calcium are involved, it may be advantageous to augment the color of iodine-iodide solutions by the addition of ethyl alcohol. Moreover, starch suspension can be added to the iodine solution and the transmittancy of the blue solution determined by the use of a suitable filter, although the blue color is less stable than the yellow of I_3^- and more subject to variation from the effect of such factors as temperature.

2. The dilute (0.005 *N*) ceric sulfate solution is not stable for more than a few hours, but no error as the result of its decomposition is introduced when oxalate standards are used.

B. The Phosphate Method[8]

This method involves the precipitation of tri-calcium phosphate, solution of the washed precipitate in acid, and the determination of phosphate in the solution by the molybdenum blue method. The procedure described on p. 182 involving the use of hydrazine sulfate as reducing agent for arsenic may also be applied to the determination of phosphate. Alternatively an aminonaphthol sulfonic acid-sulfite reagent may be used for the reduction of phosphomolybdate to molybdenum blue. The procedure given below utilizes this reagent.

Reagents

Ammonium oxalate, 4 g. of the monohydrate in 100 ml. of water.

Sodium hydroxide, 6 *N*. Prepare by diluting 18 *N* carbonate-free sodium hydroxide; keep the solution in a paraffin-lined vessel. Obtain the 18 *N* sodium hydroxide by dissolving 500 g. of the C.P. solid in 450 ml. of water with cooling, allowing the suspended sodium carbonate (which is practically insoluble in the solution) to settle, and then filtering or drawing off the clear supernatant liquid; the latter must be kept in a paraffin-coated bottle protected from the carbon dioxide of the air.

[8] A. B. Briggs, *J. Biol. Chem.*, **59**, 255 (1924); J. H. Roe and B. S. Kahn, *ibid.*, **81**, 1 (1929); T. Kuttner and H. R. Cohen, *ibid.*, **75**, 517 (1927).

Tri-sodium phosphate, 1 per cent aqueous solution.

Alcoholic wash solution. Mix 58 ml. of ethyl alcohol with 10 ml. of amyl alcohol and dilute to 100 ml. with water. Add 1 drop of 6 *N* sodium hydroxide to make the solution neutral or very slightly basic.

Ammonium molybdate, 2.5 per cent in 6 *N* sulfuric acid.

Aminonaphthol sulfonic acid reagent. Dissolve 15 g. of sodium bisulfite and 0.5 g. of sodium sulfite in 100 ml. of water. Add 0.25 g. of 1-amino-2-naphthol-4-sulfonic acid and shake at intervals for a few hours. Filter the solution if it is not clear and keep it in a dark bottle. The solution should be made up fresh every 2–3 weeks.

Standard phosphate solution, 1.00 mg. P per ml. Dissolve 0.439 g. of pure dry KH_2PO_4 in water and dilute to 100 ml. This solution may be further diluted, as preferred, to give solutions containing 0.1 or 0.01 mg. P per ml.

§ Procedure

The sample may conveniently contain 0.2–0.5 mg. of calcium.

Magnesium if present in more than mere traces necessitates the isolation of calcium as the oxalate. The following directions may be used for the separation of calcium from magnesium when the latter is not greatly preponderant, and metals such as iron, aluminum, strontium, etc., which are precipitated by ammonia or oxalate, are absent. To 5 or 10 ml. of the solution add a drop of methyl orange and several drops of hydrochloric acid in excess of that required to make the solution acid. Heat to near boiling, add 1 ml. of ammonium oxalate solution and then 1:1 ammonium hydroxide dropwise until the solution becomes yellow. Allow the solution to cool to room temperature with occasional stirring, and filter (or centrifuge) after 1 or 2 hours. Wash the precipitate with cold 0.1 per cent ammonium oxalate, dissolve it in a few drops of hot 1:1 hydrochloric acid, wash the filter with water, and evaporate the filtrate and washings to a volume of a few drops. Destroy the oxalate by adding 0.5 ml. of 30 per cent hydrogen peroxide and heating for one-half hour on the steam bath. Alternatively the calcium oxalate may be transformed into calcium carbonate by ignition at low redness and the latter dissolved in a drop or two of dilute hydrochloric acid.

Dilute the solution to 3 to 5 ml. with water and add 0.5 ml. of 6 *N* sodium hydroxide. Allow the solution to stand for a few minutes to permit the precipitation of any traces of magnesium present, and then add 0.5 ml. of trisodium phosphate solution. Let the solution stand for an hour to assure complete precipitation. Collect the precipitate by filtering (small porous porcelain or sintered glass crucible) or centrifuging, and wash carefully with the alcoholic mixture. Usually three 2 ml. portions of wash solution suffice. Allow most of the alcohol to evaporate and dissolve the precipitate in 0.5 ml. of the acid molybdate solution, wash with a little water if a filter was used, add 1 ml. of the aminonaphthol sulfonic acid reagent, and dilute to 10.0 ml. with water. Mix, allow to stand in the dark for 10 minutes and

compare against a suitable phosphate standard prepared in a similar manner. For the most accurate results the standard phosphate solution should be obtained from a known amount of calcium treated in the same way as the sample.

C. Pyrogallol Carboxylic Acid Method

This reagent (2,3,4-trihydroxybenzene-1-carboxylic acid) reacts with the alkaline earth metals in basic medium, producing a blue-violet coloration. The reaction product is thought to be a colloidally dispersed basic calcium salt with the oxidized meriquinoid form of the reagent present in the adsorbed state.[9] The reaction with calcium is sensitive (1:200,000). The following procedure has been applied in the determination of calcium in water.[10] The sample (*ca.* 50 ml.) is treated with 1 or 2 ml. of 2 *N* sodium hydroxide, 1 ml. of gum arabic solution saturated with the reagent, and diluted to volume. Foreign metals can first be removed by sodium hydroxide precipitation. The color is said to be stable if the solution is kept in a closed container. Addition of sulfite makes the color more permanent.

D. The Oleate Method (Turbidimetric)

The following method for the determination of calcium in water is based on the formation of a colloidal suspension of calcium oleate, stabilized by the emulsifying agent "Duponol."[11] The latter substance also prevents the interference of magnesium in concentrations as high as 1000 p.p.m. Such amounts of copper, iron, manganese, aluminum, zinc, and lead as are likely to be encountered in water do not interfere. Various anions in concentrations less than 500 p.p.m. are without effect according to the authors. After 30 minutes the optical density of the calcium oleate suspension remains constant for as much as 24 hours. Temperature variation in the range 15 to 25° C. has no effect. The extinction-concentration curve is a straight line from 0.4 to 12 p.p.m. of calcium in the sample solution. It is said that the error is less than 10 per cent.

Special Solutions

Potassium oleate reagent. Shake 7.05 g. of oleic acid (Eastman) with 5 ml. of water containing 1.60 g. of potassium hydroxide and transfer with 50 ml. of 70 per cent alcohol to a flask. Reflux for 1 hour and dilute to 250 ml. with water.

[9] A. Okáč and J. Pech, *Coll. Czech. Chem. Comm.*, **13**, 515 (1948).

[10] Okáč and Pech, *ibid.*, **13**, 400 (1948).

[11] A. Saifer and F. D. Clark, *Ind. Eng. Chem., Anal. Ed.*, **17**, 757 (1945). For earlier applications of the oleate method see A. Gregoire, E. Carpiaux, E. Larose, and T. Sola, *Bull. soc. chim. Belg.*, **32**, 123 (1923); A. Gregoire and T. Sola, *ibid.*, **32**, 131 (1923); A. Gregoire, *J. Soc. Chem. Ind.*, **42**, 427A (1923); A. Romeo and V. Gambordella, *Chim. ind. agr. biol.*, **17**, 471 (1941).

Duponol, 3 per cent aqueous solution.

Potassium oleate-Duponol reagent. Add 20 ml. of potassium oleate solution to 100 ml. of Duponol solution. Allow to stand for 12 hours or longer and filter, or centrifuge, off any sediment. The solution is stable at room temperature.

Standard calcium solution. Dissolve 0.5 g. of pure calcium carbonate (calcite) in a little dilute hydrochloric acid. Boil off the carbon dioxide, transfer the solution to a 500 ml. volumetric flask, neutralize the excess acid with ammonia, and dilute to the mark with water. If the purity of the calcium carbonate is not assured, standardize the solution by one of the usual methods. Dilute this stock solution tenfold to obtain a solution containing 0.10 mg. of $CaCO_3$ (0.04 mg. Ca) per ml.

§ Procedure

Measure 45 ml. of sample into a 50 ml. volumetric flask and add concentrated ammonium hydroxide until the solution is just alkaline to litmus, followed by 1 ml. in excess. Dilute to the mark and mix. Allow to stand for 15 minutes. Filter off any precipitate formed. Transfer 2.00 and 5.00 ml. aliquots to a colorimeter tube (test tube) graduated at 5 and 10 ml., and dilute the 2 ml. portion to 5 ml. with water. Add exactly 5 ml. of potassium oleate-Duponol reagent, mix by inversion, and determine the transmittancy at 420 mμ (or use Corning filter No. 511, 3 mm. thickness) after 30 minutes. Prepare the standard curve by taking 0 to 0.28 mg. of calcium (0 to 0.7 mg. of calcium carbonate), adding 0.05 ml. of concentrated ammonium hydroxide to the solution, and then proceeding as with the sample.

E. Other Methods

Among other methods proposed for the colorimetric determination of calcium the following may be mentioned:

1. Precipitation as picrolonate,[12] solution of the precipitate in water and development of a red color by treatment with bromine and sodium hydroxide.
2. Precipitation as $K_2CaNi(NO_2)_6$[13] and determination of the nitrite in the precipitate.
3. Precipitation as tungstate[14] followed by determination of tungsten with titanous chloride.
4. Precipitation as 8-hydroxyquinolate[15] and determination of hydroxyquinoline in the precipitate with Folin's reagent.

[12] F. Alten, H. Weiland, and E. Knippenberg, *Biochem. Z.*, **265**, 85 (1933). *Cf.* G. Cohn and I. M. Kolthoff, *J. Biol. Chem.*, **147**, 705 (1943).

[13] M. Mousseron, *Bull. soc. chim. biol.*, 12, 1014 (1930); 13 831 (1931).

[14] M. Mousseron and N. Bouisson, *Bull. soc. chim. biol.*, 12, 482 (1930); E. Rinck and Ostertag, *Compt. rend.*, **224**, 1108 (1947).

[15] S. Yoshimatsu, *Tôhoku J. Exptl. Med.*, **15**, 355 (1930).

5. Precipitation as alizarinate[16] followed by colorimetric determination of alizarin in the precipitate.
6. Precipitation by chloranilic acid (2,5-dichloro-3,6-dihydroxyquinone) which forms a slightly soluble calcium salt, red-purple in color like the acid itself. A method for the determination of small amounts, but not trace quantities, of calcium has been described.[17]

Calcium may be determined nephelometrically as the oxalate.[18]

[16] P. P. Laidlaw and W. W. Payne, *Biochem. J.*, **16**, 494 (1922).
[17] E. H. Tyner, *Anal. Chem.*, **20**, 76 (1948).
[18] J. S. Sharpe, *Edinburgh Med. J.*, **33**, 27 (1926).

CHAPTER XIII

CERIUM

Cerium is distinguished from the other rare earth metals by its oxidizability in aqueous solution to the quadrivalent state, in which it shows a fairly strong yellow color (acid medium). It is thus possible to determine cerium directly in the presence of other rare earths as well as some of the common elements. The strong oxidizing character of ceric ion may be made the basis of an indirect colorimetric method by the formation of strongly colored oxidation products of various organic compounds. The indirect method gives promise of great sensitivity, but as yet it has not been developed as fully as might be desired.

I. Separations

Cerium (III) like the other rare earth metals forms an oxalate only slightly soluble in excess oxalic acid, and a fluoride very sparingly soluble in the presence of hydrofluoric acid. The latter precipitation form is generally considered the better one for the separation of cerium and the other rare earths from the metals of the ammonium hydroxide group. Calcium or strontium fluoride may perhaps be of value as collectors of cerous fluoride, but these precipitates are difficultly filterable (*cf.* p. 505).. Lanthanum has an ionic radius very close to that of cerium (III) and may be expected to function well as a collector for cerous fluoride or oxalate.

At times precipitation of cerium as the extremely slightly soluble ceric hydroxide should be of value in separations (for example from Cr^{VI}).

Ceric nitrate can be extracted by ether from solutions containing a high concentration of nitric acid. Uranyl and thorium are also extracted under these conditions. Extraction of cerium 8-hydroxyquinolate by chloroform from alkaline citrate medium as described on p. 254 may have value in separations.

Electrolysis with a mercury cathode serves to remove iron and many other heavy metals (p. 31).

II. Methods of Determination

A. The Persulfate Method (Color of Ceric Ion)

The color of quadrivalent cerium in acid medium is not as intense as might be desired, but it is strong enough to allow moderately small amounts

of cerium to be determined. At room temperature in 1 *N* sulfuric acid solution the visual sensitivity is approximately 10 γ Ce per square centimeter, and the photometric sensitivity (p. 49) with a blue filter is approximately 0.5 γ Ce per square centimeter. No doubt the sensitivity can be considerably increased by employing monochromatic light in the violet portion of the spectrum.[1] The color intensity of ceric solutions increases slightly with a rise in temperature. Beer's law is followed.

Cerous ion may conveniently be oxidized to ceric by ammonium persulfate in hot dilute sulfuric acid solution with silver ion as catalyst. Since chromium and manganese are also oxidized to strongly colored dichromate and permanganate under these conditions, no appreciable amounts of these metals may be present.[2] Chloride, fluoride, and phosphate must be absent. The effect of ferric iron and other colored ions in small quantities can be compensated by using an aliquot of the sample solution, not oxidized with persulfate, in the reference cell of the photometer. Alternatively, a drop of hydrogen peroxide or a little sodium azide can be added to reduce ceric ion to colorless cerous ion and the increase in transmittancy found.

The following procedure has been found to give satisfactory results. Three solutions containing respectively 0.080, 0.080, and 0.40 mg. of cerium gave the respective values 0.080, 0.088 and 0.40 ± 0.02 mg. by the standard series method (1.8 × 15 cm. tubes).

§ Procedure

The volume of the solution should be as small as practicable. Chloride and other interfering substances mentioned above must be absent. Add sufficient sulfuric acid to the sample solution to make its concentration 1 to 2 *N*, 0.2 g. of ammonium persulfate (for a 10 ml. volume), and 0.5 mg. of silver nitrate. Boil gently for 5 minutes, cool, dilute to volume with water, and determine the transmittancy with a violet filter. The solutions for the construction of the standard curve should have the same sulfuric acid concentration as the sample and the transmittancies should all be determined at the same temperature.

[1] See C. T. Kasline and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **8**, 463 (1936), for the transmission curve of ceric sulfate above 480 mμ.

[2] When a photometer is used, cerium can be determined in the presence of small amounts of dichromate by obtaining the transmittancy before and after adding sodium azide, which reduces cerium (IV) but not chromium (VI).

B. The Brucine Method

Ceric ion in acid solution oxidizes various organic compounds such as brucine, sulfanilic acid,[3] benzidine,[4] morphine, etc. to fairly intensely colored products.[5] The reaction with brucine has been proposed for the determination of quadrivalent cerium.[6] A strong red color is produced when brucine is added to an acid ceric solution, but this fades in the course

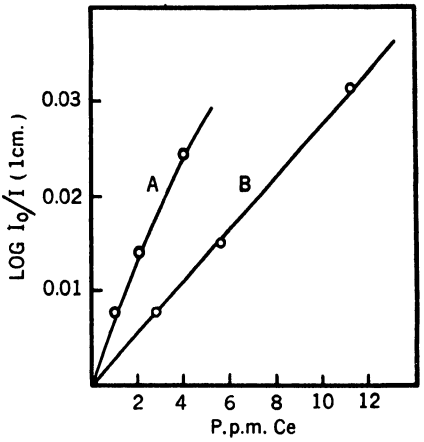


Fig. 29. Determination of cerium by (*A*) the peroxide method (1 ml. 3% H_2O_2 and 5 g. K_2CO_3 in a final volume of 25 ml.), and (*B*) as ceric sulfate in 1 *N* sulfuric acid solution; Wratten filter No. 47 used in both methods. (Data for the peroxide method obtained by R. A. Johnson, University of Minnesota.)

of a few seconds to an orange and finally a brownish color which is much less intense than the original. The color intensity becomes practically constant in 5 or 10 minutes, but decreases on long standing.[7] The color of the oxidized brucine is 4 or 5 times as strong as the ceric solution producing it. The color intensity is proportional to the concentration of cerium.

[3] Sulfanilic acid has been used as a qualitative reagent for quadrivalent cerium by E. Montignie, *Bull. soc. chim.*, **6**, 889 (1939). A red color develops slowly in acid solution, reaches a maximum intensity and then fades. The sensitivity is less than with brucine. Arsanilic acid also gives an unstable red color (J. F. Miller, *Ind. Eng. Chem., Anal. Ed.*, **9**, 181 (1937)).

[4] R. G. Harry and E. A. Rudge, *J. Soc. Chem. Ind.*, **51**, 64T (1932).

[5] Very small quantities of cerium (IV) can probably be determined by the use of ferrous *o*-phenanthroline complex (diminution of the orange-red color).

[6] F. M. Shemyakin and V. A. Volkova, *J. Gen. Chem. U. S. S. R.*, **9**, 698 (1939).

[7] A solution of ceric sulfate containing 28 p.p.m. of Ce treated as described in the procedure showed the following extinctions after various times of standing: 5 minutes, 0.096; 10 minutes, 0.098; 20 minutes, 0.098; 1 hour, 0.092; 3 hours, 0.091. A solution containing 14 p.p.m. Ce showed practically the same reading after 1 hour as after 5 minutes.

Permanganate produces a yellow color, paler than that given by an equivalent amount of ceric ion. Chromate oxidizes brucine very slowly in acid solution, yielding a brown color. Ferric iron gives no appreciable coloration in small amounts. Persulfate slowly produces a yellow-brown color.

§ Procedure

The solution may contain a few tenths of a milligram of cerium in a volume of about 10 ml., and should be approximately 1 *N* in sulfuric acid. Oxidize cerous cerium with ammonium persulfate as described on p. 252, except boil for 10 minutes, adding water if necessary, to be certain that all persulfate is destroyed. Cool the solution to room temperature, add 0.25 ml. of 0.1 per cent brucine in 1 *N* sulfuric acid, and dilute to volume (10 ml. if possible). Determine the transmittancy of the solution after 10 minutes, using a blue filter. It is advisable to read the solution again after another 10 minutes to be certain that the transmittancy is not changing as the result of the presence of undecomposed persulfate.

C. 8-Hydroxyquinoline Method

Determination of cerium based on chloroform extraction of cerium 8-hydroxyquinolate has been described with special reference to cerium in cast iron.[8] Cerium can be completely extracted in the *p*H range 9.9–10.5 from a citrate-ammonia solution. Cerium is said to be extracted in the cerous state. The chloroform solution has a red-brown color (maximum absorption at 505 mμ). The colored solution obeys Beer's law. Addition of acetone to the chloroform aids the extraction of the cerium compound. The interference of iron is overcome by converting it into ferrocyanide by the use of cyanide and dithionite. The following elements, in the amount stated (per cent on a 1 g. sample, according to procedure below), do not give appreciable color: Al (6), Sb (1.5), As (0.4), Bi (*ca.* 0.1), Cr (7), Co (2), Cu (6), Pb (0.5), Hg^{II} (2), Mo (2), Ni (5), Se (0.6), Te (*ca.* 0.25), Sn (*ca.* 0.25), Ti (*ca.* 1), W (*ca.* 1), Zr (2), Since the procedure described is intended for relatively large amounts of cerium—*ca.* 0.02 to 0.2 per cent—interference by some of the elements listed might become significant for smaller amounts of cerium.

Phosphorus in amounts up to 2 per cent of the sample is without effect, but fluoride must be absent. Vanadium imparts a color to the chloroform and must not exceed 0.2–0.3 per cent when a 1 g. sample is taken. Manganese gives a coloration unless removed as ferrocyanide. The precipitation of small amounts of manganese is assured by addition of a little

[8] W. Westwood and A. Mayer, *Analyst*, **73**, 275 (1948).

sulfuric acid after the dithionite reduction. It is stated that other rare earth metals present in *Mischmetall* produce no color.

The error in the determination does not exceed ±0.003 per cent for 0.02–0.2 per cent cerium in cast iron.

Special Solutions

Citric acid, 500 g. in 1 liter of solution.

Potassium cyanide, 400 g., together with 15 g. sodium hydroxide, in 1 liter.

Sodium dithionite, 2.5 g. in 25 ml. of water containing 5 drops of ammonium hydroxide.

8-Hydroxyquinoline. Dissolve 6 g. in 200 ml. of dry, acid-free chloroform and add 20 ml. of acetone; prepare fresh daily. (Obtain the chloroform by shaking with one-half its volume of 1:20 ammonia solution containing 25 g. ammonium chloride per liter, drying with potassium carbonate for 1 hour, and filtering.)

§ Procedure

Dissolve 1 g. of cast iron in 30 ml. of 1:1 hydrochloric acid, filter, collect the filtrate in a 200 ml. volumetric flask, wash with 1:20 hydrochloric acid, and dilute filtrate and washings to the mark. Transfer a 20 ml. aliquot to a beaker, add 2 ml. of citric acid solution, and then concentrated ammonium hydroxide dropwise until alkaline (a drop in excess changes the color from yellow to light green). Add 5 or 6 drops of ammonia in excess and then 4.0 ml. of potassium cyanide. Heat to boiling, add 1.0 ml. of sodium dithionite solution, and then 3 drops of 1:4 sulfuric acid. Boil for 15 seconds and wash down the sides of the beaker with water. Cool to room temperature and add 2 or 3 drops of phenolphthalein solution. Now add citric acid dropwise (hood!) until the pink color is discharged, followed by ammonia to give a faint pink coloration. Add exactly 5 ml. of concentrated ammonia (density 0.88), transfer the solution to a separatory funnel and dilute to 50 ml. with water.

Add 11 ml. of 8-hydroxyquinoline-chloroform solution, shake vigorously for 3 minutes, allow to settle, and draw off the chloroform into a small flask containing 1 g. of anhydrous sodium sulfate. Filter the dried chloroform through a coarse paper and obtain the transmittancy of the solution at 505 mμ versus the chloroform reagent solution in the comparison cell. The transmittancy should be read immediately if any vanadium is present in the sample.

If alloy cast irons, or iron containing more than about 1 per cent of manganese, are to be analyzed, remove alloying elements by electrolysis with a mercury cathode. For details, see the original.

D. The Carbonate-Peroxide Method

A dilute solution of a cerous salt gives a white precipitate of the carbonate when treated with potassium carbonate, which dissolves in an excess of the

latter. On standing, the solution becomes yellow owing to the formation of perceric carbonate by air-oxidation. This reaction has been made the basis of a colorimetric method.[9] The yellow color appears at once if hydrogen peroxide is added. Uranium gives a yellow or yellow-orange color under the same conditions.

E. By Fluorescence

Cerous salts fluoresce in aqueous solution and possibly a method for the determination of cerium may be based on this behavior (p. 508).

[9] J. Plank, *Z. anal. Chem.*, **116**, 312 (1939). Benzidine and tannin have been used for the detection of cerium by E. Herzfeld, *Z. anal. Chem.*, **115**, 421 (1938). Various other reagents have been proposed for the same purpose.

CHAPTER XIV

CHROMIUM

I. Separations

A. Precipitation Methods

The most useful method for the separation of chromium involves oxidation in basic medium, whereby chromate is formed and remains in solution while a great many metals such as iron, titanium, manganese, nickel and cobalt are precipitated. The elements remaining in solution with chromium are partly innocuous so far as the succeeding colorimetric determination is concerned (aluminum, arsenic, phosphorus), and partly disturbing (uranium in the chromate comparison method, vanadium and much molybdenum in the diphenylcarbazide method). The oxidation can be effected in hot solution with sodium peroxide, with hydrogen peroxide and sodium hydroxide, or with bromine and sodium hydroxide. The oxidation can also be carried out by fusion with sodium peroxide, with a 10:1 mixture of sodium carbonate and potassium nitrate, or even sodium carbonate alone for some samples such as silicate rocks. Manganese is oxidized to manganate in the fusion but this can be reduced to hydrated manganese dioxide by adding alcohol to the hot solution of the melt. Chromium shows little tendency to be retained in the insoluble material remaining after leaching the sodium carbonate melt of a silicate, and a refusion is ordinarily not required.[1] A flux containing too much nitrate or too high a temperature in the fusion should be avoided as possibly leading to attack of the platinum crucible and introduction of a little platinum into the solution.

The slight solubility of chromic hydroxide enables chromium to be separated from most of the metals accompanying chromium in the above chromate separation; the chromate is reduced to the trivalent state and the boiling solution is treated with an excess of sodium hydroxide. If carbonate is also added, uranium will remain in solution. Perhaps a very small amount of ferric iron can be added as collector; its amount should not ex-

[1] In this connection it may be mentioned that when iron and aluminum hydroxides are precipitated by ammonia from a solution containing chromate, some of the latter is carried down in the precipitate. In the presence of much phosphate the coprecipitation of chromate is greatly decreased as shown by K. K. Järvinen, *Z. anal. Chem.*, **75**, 1 (1928).

ceed a few tenths of a milligram if chromium is to be determined by the diphenyl carbazide method which permits the presence of very little iron.

B. Extraction Methods

Perchromic acid can be extracted by ethyl acetate and other immiscible organic solvents. When the extraction is made from weakly acidic solutions (in which perchromic acid is more stable than in strongly acid medium) quantitative recovery of milligram quantities (0.5–5 mg.) can be obtained.[2] The ethyl acetate phase is shaken with a sodium hydroxide solution to bring chromium into the aqueous phase as chromate. This is a separation from vanadium. See p. 606 for directions.

Vanadate can be separated from chromium (VI) by adding 8-hydroxyquinoline to the solution and extracting at a *p*H of about 4 with chloroform. Chromium is left in solution (p. 266).

Vanadium as well as iron can be precipitated in acid solution with cupferron and thus separated from chromium (III). The insoluble cupferrates can be extracted by chloroform.

Ether extraction of a hydrochloric acid solution separates most of the ferric iron as well as molybdenum (if iron is present in excess) from chromium.

II. Methods of Determination

The diphenylcarbazide method for chromium is at least five times as sensitive as the chromate method,[3] and possesses the further advantage of giving a color not to be mistaken for that of any other substance. On the other hand the chromate method serves well when the quantity of chromium is not too small. It can be carried out very simply and is not affected by the presence of vanadium.

A. The Chromate Method

This method is generally applied after oxidation of chromium in basic medium or by alkaline fusion, which effects a simple separation from most of the cations giving colored solutions. Procedures for the oxidation have already been mentioned. So far as color intensity is concerned the determination could also be carried out in acid medium (oxidation with per-

[2] M. D. Foster, *U. S. Geol. Survey Bull.*, **950**, 15 (1946).

[3] The respective spectrophotometric sensitivities correspond to 0.01 (366 mμ) and 0.002 (540 mμ) γ Cr per cm.^{2} If the absorption of the chromate solution is measured at longer wave lengths the advantage of the carbazide method becomes relatively greater.

sulfate in the presence of silver as catalyst)[4] but then iron and other metals may interfere (p. 268), particularly with small amounts of chromium.

At low concentrations chromate solutions obey Beer's law closely (p. 77). Chromate ion absorbs strongly below 480 mμ, with maximum absorption at about 370 mμ. When a filter photometer is used in measuring the transmittancies of chromate solutions, the optical density may not be proportional to the chromium concentration because of the difficulty in obtaining a sufficiently selective filter, with the result that the measurement is made at the edge of the absorption band.

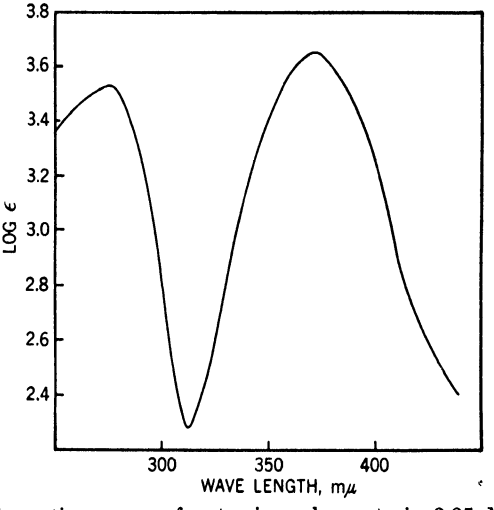


Fig. 30. Absorption curve of potassium chromate in 0.05 *N* potassium hydroxide. (After G. Rössler.)

There is usually less deviation from linearity when chromium is present as dichromate. The extinction coefficient of chromate ion has been reported not to change by more than about 1 per cent in 10 per cent solutions of various salts.[5] On the other hand, ferric ion has been found to increase the color intensity of dichromate (p. 269).

The most serious interference in the chromate method results from uranium and cerium which can pass into the filtrate, imparting a yellow color to it. Copper also may be found in the filtrate in small amounts giving rise to a faint blue color. Iron will at times be found in the filtrate in colloidal form. The yellow coloration thus resulting may be compara-

[4] For transmission curves of chromate and dichromate solutions see C. T. Kasline and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **8**, 463 (1936); R. E. Kitson and M. G. Mellon, *ibid.*, **16**, 42 (1944).

[5] S. Christow, *Z. anal. Chem.*, **125**, 278 (1943).

tively strong when the sample contains both much iron and silica. Alkaline solutions may extract from filter paper substances imparting a faint yellowish color to the filtrate.

§ General Procedure

Convert chromium in the sample to the sexivalent state by a suitable method (*cf.* p. 265), reduce any manganate by heating with alcohol, and dilute the clear alkaline solution to such volume that the chromium concentration is 5–100 p.p.m. Obtain the transmittancy of the solution with the aid of a filter having maximum transmission in the violet portion of the spectrum (370 mμ is the best wavelength). The standard solutions for the construction of the reference curve should have the same alkalinity as the sample solution and should preferably have the same concentration of foreign salts such as sodium carbonate. Standards may be prepared from potassium chromate $\left(\frac{K_2CrO_4}{Cr} = 3.73, \frac{2\ K_2CrO_4}{Cr_2O_3} = 2.55\right)$.

If a Duboscq colorimeter is used, the chromium concentration of the solution may be in the neighborhood of 10 p.p.m. In the standard series method of comparison, solutions as dilute as 1 p.p.m. may be used in 1.8 × 15 cm. tubes. The colorimetric titration technique may also be conveniently applied.

B. The Diphenylcarbazide Method

In acid solution diphenylcarbazide gives a soluble red-violet product with sexivalent chromium.[6] The formula of the colored substance is not known. The reaction is extraordinarily sensitive, the molar extinction coefficient of the colored compound, calculated on the basis of the molarity of the dichromate solution, being 31,400[7] at 540 mμ, the wavelength of maximum absorption.

This reaction is the basis of the best method for the determination of the most minute amounts of chromium.[8] The method is nearly specific for chromium in the sense that the only element giving a similar violet color in mineral acid solution is molybdenum (VI), which however reacts much less sensitively. Mercury (I and II) gives a blue or violet-blue color, but except at low acidities the reaction is not sensitive especially if chloride is

[6] A. Cazeneuve, *Bull. soc. chim.*, [3] **23**, 701 (1900); **25**, 761 (1901). The chromium-diphenylcarbazide compound can be extracted from aqueous solution by *n*-hexanol and cyclohexanol as shown by H. A. Bernhardt et al., U. S. Atomic Energy Commission Document MDDC-1541 (1947).

[7] G. P. Rowland, Jr., *Ind. Eng. Chem., Anal. Ed.*, 11, 442 (1939).

[8] First used by A. Moulin, *Bull. soc. chim.*, **31**, 295 (1904).

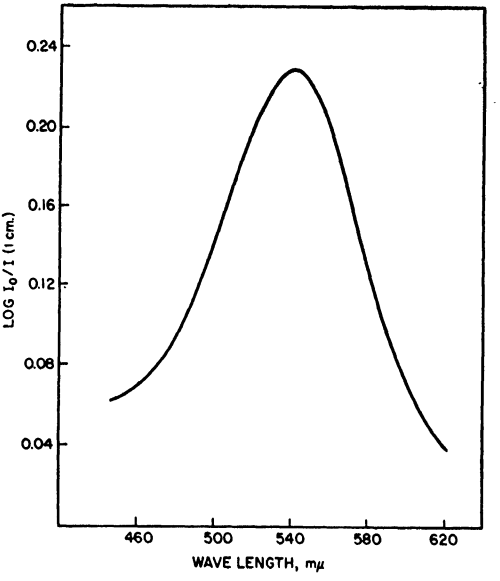


Fig. 31. Extinction curve of chromium (VI)—diphenylcarbazide compound. (According to H. A. J. Pieters, W. J. Hanssen, and J. J. Geurts, *Anal. Chim. Acta*, 2, 383 (1948).)

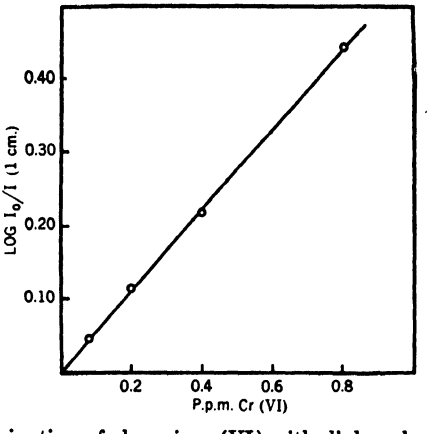


Fig. 32. Determination of chromium (VI) with diphenylcarbazide (green filter, Cenco No. 2).

present. Iron (III) and vanadium (V) are disturbing elements, for they yield yellow or yellow-brown compounds with the reagent.

A suitable acidity for the chromium-diphenylcarbazide reaction is 0.2 *N*. At low acidities the color does not develop immediately, but in 0.2 *N* min-

TABLE 39

DETERMINATION OF CHROMIUM BY THE DIPHENYLCARBAZIDE METHOD

The sample solution was 0.2 *N* in sulfuric acid and contained 1 ml. of 0.25 per cent diphenylcarbazide solution (in 50 per cent acetone) per 25 ml. A filter photometer was used with a green filter (Cenco No. 2).

Addition	Cr taken p.p.m.	Cr found p.p.m.	Remarks
	0.800	(Standard)	
	0.800	0.800	2 ml. diphenylcarbazide
	0.405	0.409	
	0.405	0.410	0.5 *N* H_2SO_4
	0.405	0.413	2 minutes after mixing
		0.410	10 minutes after mixing
		0.403	20 minutes after mixing
		0.388	2 hours after mixing
	0.405	0.392	2 minutes after mixing
		0.392	10 minutes after mixing
		0.388	30 minutes after mixing
	0.20	0.21	
	0.080	0.084	
	0.080	0.078	2 minutes after mixing
		0.078	15 minutes after mixing
Mo^{VI}, 200 p.p.m.	0.405	0.409	2 minutes after mixing
		0.402	10 minutes after mixing
Hg^{II}, 200 p.p.m. (as $HgCl_2$)	0.405	0.405	
Fe^{III} (as $FeCl_3$), 200 p.p.m.	0.405	0.51	2 minutes after mixing
		0.46	5 minutes after mixing
		0.445	10 minutes after mixing
Fe^{III} (as $FeCl_3$), 100 p.p.m.	0.405	0.47	2 minutes after mixing
		0.46	5 minutes after mixing
		0.44	10 minutes after mixing
Fe^{III} (as ferric alum), 200 p.p.m.	0.405	0.413	2 minutes after mixing
		0.385	5 minutes after mixing
		0.37	10 minutes after mixing
Fe^{III} (as ferric alum), 200 p.p.m.	0.200	0.24	2 minutes after mixing
Fe^{III} (as ferric alum), 200 p.p.m. (solution contained 1 ml. of 1:5 H_3PO_4 in addition to sulfuric acid).	0.405	0.409	2 minutes after mixing
		0.425	5 minutes after mixing
		0.45	15 minutes after mixing
Fe^{III} (as ferric alum), 200 p.p.m. (solution contained 1 ml. of 1:5 H_3PO_4 in addition to sulfuric acid).	0.080	0.089	3 minutes after mixing
		0.11	7 minutes after mixing
V^{V}, 4 p.p.m.	0.405	0.44	2 minutes after mixing
		0.425	5 minutes after mixing
V^{V}, 4 p.p.m. (solution contained 1 ml. 1:5 H_3PO_4 in addition to sulfuric acid).	0.080	0.104	2 minutes after mixing
		0.088	20 minutes after mixing

eral acid solution maximum color intensity is attained within a few seconds. Sulfuric acid is to be preferred for acidification because iron gives less color in the presence of this acid than in the presence of hydrochloric acid. Solutions having an acidity much greater than 0.2 *N* are not desirable because the color is less stable in these. In 0.2 *N* sulfuric acid the chromium-diphenylcarbazide compound is quite stable[9] (see Table 39). Beer's law is closely followed, as several workers have found (Fig. 32). Reasonable amounts of neutral salts are without effect on the color; a solution 5 per cent in sodium sulfate showed the same color intensity as a salt-free solution.

The determination of chromium may be carried out in the presence of a limited amount of iron. As already mentioned, iron yields a yellow or brown color with diphenylcarbazide. Such a solution absorbs very little light above a wavelength of 460 mμ, and it has been stated[7] that the interference of iron can be eliminated by the use of a suitable green filter. If a sufficiently selective green filter is not used the error may be considerable (Table 39), especially if chloride is present. In sulfuric acid solution, with chloride absent, the yellow color developed by iron is not strong and good results can be obtained if the transmittancy of the solution is measured immediately after the addition of reagent. On standing the transmittancy of the solution increases. In the presence of phosphoric acid the transmittancy decreases on standing, but approximately correct results are obtained on immediate reading. Practically, the presence of iron in the sample is a matter of little concern since it is usually separated in the oxidation of the chromium.

The interference of vanadium is a more serious possibility because it gives a stronger yellow color than does iron and it is not separated in the preparation of the sample for analysis. If the ratio of vanadium to chromium does not exceed 10:1, nearly correct results for chromium can be obtained by allowing the solution to stand for about 10 minutes after the addition of the reagent. The vanadium-diphenylcarbazide color fades fairly rapidly so that the nearly pure red-violet chromium color is obtained after 10–15 minutes if the vanadium is not too greatly preponderant. When the ratio is unfavorable, vanadium must be separated. This may be done conveniently by adding 8-hydroxyquinoline to the solution and extracting the compound $V_2O_3(C_9H_6ON)_4$ at a *p*H of about 4 with chloroform.[10] The

[9] Rowland, *loc. cit.*, found the color to fade less rapidly than indicated by our figures. Thus a solution containing 0.375 p.p.m. Cr in ca. 0.1 *M* sulfuric acid gave the following values for I/I_0: 59.8 immediately after mixing, 60.1 after one-half hour, and 63.0 after 15 hours. Rowland used 1 ml. of alcohol saturated with the reagent for each 100 ml. of dichromate solution.

[10] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 336 (1936).

excess of the 8-hydroxyquinoline is simultaneously extracted by the chloroform, and chromate is left in the aqueous phase unchanged.[11]

Under the conditions recommended there is no interference from small amounts of mercury and molybdenum (Table 39).

Reagents

Diphenylcarbazide, 0.25 per cent in a 1:1 mixture of acetone and water. The solution becomes brown on standing (probably due to diphenylcarbazone formation) and is preferably prepared fresh daily.[12]

Sulfuric acid, 6 *N*, free from reducing substances. Add dilute potassium permanganate solution to the hot acid until a very faint pink color appears.

§ Procedure

The sample solution may contain from 0.02 to 0.5 p.p.m. of Cr (VI).[13] To 10–20 ml. of solution add sufficient sulfuric acid to make its concentration approximately 0.2 *N* when diluted to 25 ml., mix, add 1 ml. of diphenylcarbazide solution, and make up to 25 ml. with water. Determine the transmittancy of the solution soon after the addition of the reagent unless vanadium is present in appreciable amounts (the solution then is red or brownish instead of red-violet) in which case read after 10 to 15 minutes to obtain more nearly correct results. Use a green filter having the transmission maximum at 540 mμ. To eliminate any error due to a coloration in the reagent, measure the transmittancy against a blank solution.

When a Duboscq colorimeter is used, a suitable chromium concentration is 0.5 p.p.m.

C. Other Methods

Disodium-1,8-dihydroxynaphthalene-3,6-disulfonate (chromotropic salt) reacts with chromium (VI) in acid solution to give a soluble compound of red color.[14] The reagent has been used for determining chromium in steel[15] and in plant ash.[14] The reaction is sensitive. Ferric iron gives a green color (not formed in the presence of sufficient phosphoric acid), vana-

[11] By applying the procedure described on p. 266, two solutions of 20 ml. containing 1.00 and 2.50 γ of Cr in the presence of 300 and 200 γ of V respectively yielded the values 1.03 and 2.52 γ of Cr. A filter photometer was used.

[12] A reagent solution which discolors less rapidly than the above can be prepared by dissolving 0.25 g. diphenylcarbazide and 4 g. phthalic anhydride in 100 ml. of 95 per cent alcohol (J. F. Ege, Jr., and L. Silverman, *Anal. Chem.*, **19**, 693 (1947)). Probably this solution can be used in place of the acetone solution in the above procedure.

[13] For procedures for the oxidation of chromium see p. 258. Permanganate formed by persulfate oxidation in acid solution can be reduced by boiling with a regulated amount of hydrochloric acid or, if iron is absent, by addition of a little sodium azide to the cold solution.

[14] P. Koenig, *Chem. Ztg.*, **35**, 277 (1911).

[15] F. Garrat, *J. Ind. Eng. Chem.*, **5**, 298 (1913).

dium (V) a brown color, and titanium a red or red-brown color, all in acid solution.

Serichrome Blue R also has been used for the colorimetric determination of chromium by "after chroming" of wool dyed by it.[16]

III. Applications of the Chromate and Diphenylcarbazide Methods

A. Silicate Rocks

The chromate method may be used for samples containing fair amounts of chromium, say more than 0.01 per cent Cr_2O_3. The accurate determination of smaller amounts of chromium requires the use of the diphenylcarbazide method.[17]

§ Procedure for Chromate Method

Fuse 1 or 2 g. of very finely ground rock powder with five times its weight of a 10:1 mixture of sodium carbonate and sodium nitrate until complete decomposition has been effected. Leach the melt with 25–50 ml. of water. The cake should be transferred to a small beaker and disintegrated with a glass rod flattened at one end. Add a few drops of alcohol and heat near the boiling point until all manganate has been reduced. Filter through paper previously washed with a little hot sodium carbonate solution, and wash the precipitate with hot water containing a little sodium carbonate. Collect the filtrate in a suitable color comparison tube (or volumetric flask if the color is strong) and compare against a standard chromate solution containing sodium carbonate. If the color is very faint it may not be due to chromium (p. 260) and the diphenylcarbazide method should be applied as described below.

§ Procedure for Diphenylcarbazide Method

The exact procedure to be followed depends upon the vanadium content of the rock sample. If vanadium does not greatly preponderate over chromium (V < 10 Cr), the latter can usually be determined directly, but with unfavorable vanadium-chromium ratios a separation of vanadium by 8-hydroxyquinoline is required.

1. Direct Determination of Chromium. Mix 0.25 to 0.5 g. of finely ground sample (0.0001 to 0.1 per cent Cr) with five times its weight of sodium carbonate,[18] and fuse in a platinum crucible for 15 or 20 minutes

[16] G. C. Spencer, *Ind. Eng. Chem., Anal. Ed.*, **4**, 245 (1932).

[17] See C. F. J. van der Walt and A. J. van der Merwe, *Analyst*, **63**, 809 (1938), for a diphenylcarbazide method for chromium in rocks, soil, and plant ash.

[18] Sodium carbonate will not completely decompose chromite, and if this mineral is likely to be present sodium carbonate-nitrate or sodium peroxide must be used. The

(*footnote continued on next page*)

in the usual case but longer if magnetite, ilmenite, etc. are present in appreciable amounts. (If the amount of vanadium in the sample is unknown it is advisable to fuse a larger sample so that an aliquot can be treated for the removal of vanadium if this is found to interfere in the direct determination of chromium.) Leach the melt with hot water, preferably by transferring the cake to a small beaker and triturating with a glass rod flattened at one end. Restrict the volume of water to about 5 ml. if the solution is finally to be made up to 25 ml. Add a few drops of alcohol and heat near the boiling point until all manganate has been reduced.

Filter through a very small filter paper into a 25 or 50 ml. volumetric flask. Wash with hot water containing a little sodium carbonate. Cool the combined filtrate and washings and carefully add dilute sulfuric acid to neutralize the sodium carbonate and make the acidity approximately 0.2 *N* when the solution has been diluted to volume (1.0 g. Na_2CO_3 requires 3.2 ml. of 6 *N* sulfuric acid for neutralization). Swirl the solution carefully to liberate carbon dioxide in supersaturated solution, add 1 or 2 ml. of 0.25 per cent diphenylcarbazide solution, and make up to 25 or 50 ml. with water. Mix and obtain the transmittancy of the solution, or compare against a standard solution in a Duboscq colorimeter (p. 264). If the sample solution is red or red-brown, vanadium exceeds chromium in amount. In such a case better results are obtained if the transmittancy is determined after 10–15 minutes, when the vanadium color will have been considerably reduced through fading.

2. Determination of Chromium after Separation of Vanadium with 8-Hydroxyquinoline. Fuse the sample and leach the melt as described under (1). Dilute the filtrate and washings to volume and transfer an aliquot representing 0.1 to 0.25 g. of sample to a small separatory funnel. From a buret add exactly the volume of 2 *N* sulfuric acid required to neutralize the solution, as found by adding methyl orange to another aliquot and titrating with the acid until the color of the indicator just deviates from a pure yellow.[19] Swirl the solution to liberate excess carbon dioxide. Add 0.1 ml. of 2.5 per cent 8-hydroxyquinoline solution in 2 *N* acetic acid (sufficient for 0.2–0.3 mg. V) and extract with two 3 ml. portions of pure chloroform, shaking $^1/_2$–1 minute each time. Discard the chloroform. Add another 0.1 ml. portion of 8-hydroxyquinoline solution and shake with

diphenylcarbazide method, however, is not likely to be applied when chromite is present, for this will generally mean a sample relatively high in chromium. If nitrate or peroxide is used in the fusion, the acidified filtrate must be treated with persulfate (p. 267) to reoxidize chromium.

[19] Methyl orange may be added to the solution used in the analysis if the latter is boiled with ammonium persulfate-silver nitrate after the removal of vanadium, the indicator then being destroyed.

TABLE 40
DETERMINATION OF CHROMIUM IN VARIOUS MATERIALS BY THE DIPHENYLCARBAZIDE METHOD

Sample	Cr present[a] %	Cr found %	Remarks
1. Silicate rock	0.0018	0.0017	
2. Silicate rock (0.10% V_2O_3)	0.0048	0.0044	Vanadium separated with 8-hydroxyquinoline
3. Silicate rock (0.10% V_2O_3)	0.035	0.034	Vanadium separated with 8-hydroxyquinoline
4. Peat ash	0.0075	0.0071	

[a] Most of chromium present was added; samples originally contained following percentages of Cr: (1) 0.0004 (2) 0.0014 (3) 0.0014 (4) 0.0025.

two more 3 ml. portions of chloroform. The last chloroform extract should be virtually colorless. To remove chloroform droplets from the solution, filter through a very small filter paper previously washed with water and catch the filtrate in a 25 or 50 ml. volumetric flask. Wash the separatory funnel and filter with a few small portions of water. Make the filtrate and washings about 0.2 *N* in sulfuric acid and add 1 ml. of 0.25 per cent diphenylcarbazide solution. Dilute the solution to volume and obtain the transmittancy.

Note. With pure reagents there is no reduction of sexivalent chromium in the above procedure, but if desired the solution may be oxidized with persulfate to assure the presence of all the chromium as chromate. After the extraction of vanadium, make the solution about 0.5 *N* in sulfuric acid, add 1.0 ml. of 1 per cent silver nitrate and 0.5 g. of ammonium persulfate for each 25 ml. of solution, and boil for 10 minutes. Cool, filter to remove any precipitate of silver chloride, add 1 or 2 ml. of diphenylcarbazide solution, and make up to 25 or 50 ml.

B. IRON ORE

§ Procedure

Mix 0.5 g. of sample with 5 g. of sodium peroxide in a nickel or iron crucible, free from chromium, and heat carefully until the mixture is completely fused. Leach the melt with water, transfer the solution and insoluble matter to a volumetric flask (50 to 250 ml. depending on the amount of chromate), make up to the mark, and mix. Filter through dry asbestos. If the color of the filtrate is sufficiently strong, compare against a standard potassium chromate solution. Otherwise, take a suitable aliquot of the filtrate (say 25 or 50 ml.), and boil the solution for a few minutes to decompose most of the peroxide. Add sufficient sulfuric acid to make its concentration about 0.5 *N*, 0.5 ml. of 1 per cent silver nitrate solution, and 0.5–1.0 g. of ammonium persulfate. Boil the solution for 10 minutes, cool to room

temperature, filter if turbid, add 2 ml. of 0.25 per cent diphenylcarbazide solution (for a final volume of 50–100 ml.), make up to the mark, and compare against a suitable standard solution or obtain the transmittancy of the solution with a photometer.

If the ore contains relatively much vanadium the procedure given under "Silicate rocks" (p. 266) must be followed if the diphenylcarbazide method is used. In this case the filtrate from the peroxide fusion must be boiled for one-half hour to destroy all peroxide before acidification, or better, chromium should be reoxidized with persulfate after the solution is made acid.

C. Iron and Steel

Ammonium persulfate, perchloric acid,[20] potassium permanganate,[21] and potassium bromate[22] have been used as oxidizing agents for chromium in acid solution in its determination in steel. In most procedures the color of sexivalent chromium is measured or compared in acid medium and good results can be obtained if the amount of chromium in the sample is not too small (Method II below). When the chromium content is less than 0.005–0.01 per cent the residual color of iron and of alloying elements such as nickel and cobalt introduces uncertainties and it is then best to separate the chromium from the bulk of the iron, as by precipitation with sodium bicarbonate. Most of the iron, present in the ferrous state after solution of the sample, remains in the solution. The precipitate may then be fused with sodium peroxide, and chromium determined in the filtrate, which will be free from all but traces of such elements as iron, nickel, and cobalt.[23] This is Method I below. Diphenylcarbazide can be used in the final determination if required by acidifying the solution and reoxidizing any reduced chromium with persulfate.[24]

[20] L. Singer and W. A. Chambers, Jr., *Ind. Eng. Chem., Anal. Ed.*, 16, 507 (1944).

[21] B. S. Evans, *Analyst*, 46, 38 (1921).

[22] M. Z. De Lippa, *Analyst*, 71, 34 (1946).

[23] In a variant procedure, Evans (*loc. cit.*) adds much ammonium phosphate to the acidic solution containing ferric iron and sexivalent chromium and pours the solution into hot sodium hydroxide solution. Only a little chromate is lost by coprecipitation under these conditions, whereas in the absence of phosphate considerable chromate is dragged down. This procedure has been used successfully by Evans preparatory to determination of less than 0.002 per cent of chromium by diphenylcarbazide (*Analyst*, 46, 285 (1921).

[24] W. J. Agnew, *Analyst*, 56, 24 (1931), applied the diphenylcarbazide method after permanganate oxidation of the solution of the steel and removal of iron by sodium carbonate precipitation. H. A. J. Pieters, W. J. Hanssen, and J. J. Geurts, *Anal. Chim. Acta*, 2, 382 (1948), determine chromium in steel by the use of diphenylcarbazide without removing iron. Phosphoric acid is added to minimize the effect of iron.

Method I

§ Procedure[25]

Dissolve 1 g. (for 0.05 per cent Cr) to 5 g. or more (for 0.01 to 0.001 per cent Cr) of sample in 10 per cent sulfuric acid by volume, allowing 10 ml. of acid for each gram of sample together with an excess of 10 ml. Boil the solution until the sample has dissolved, dilute to 100 ml. with boiling water, and from a buret add an 8 per cent solution of sodium bicarbonate until a permanent precipitate appears. Then add 4 ml. of bicarbonate solution in excess, boil for one minute, allow the precipitate to settle, and filter through a rapid paper. Wash the flask and precipitate two or three times with hot water. Ignite the precipitate in a nickel crucible (chromium-free) and fuse the residue with about ten times its volume of sodium peroxide. Dissolve the cold melt in water, boil the solution for 5 minutes, and filter through asbestos, or less preferably, through paper. Wash with cold 2 per cent sodium hydroxide solution containing 1 per cent sodium sulfate. Transfer the solution to a suitable color comparison tube, or make up to volume and take a suitable aliquot for color comparison in any convenient way. The comparison solution should have an alkalinity comparable to that of the sample solution.

If the chromate color is very weak, the diphenylcarbazide method should be applied. In this case the solution is acidified with sulfuric acid and oxidized with persulfate as described under "Iron ore," p. 267, vanadium being separated if necessary.

Method II

Chromic ion is oxidized with perchloric acid. The transmittany of the acid solution is determined before and after the addition of a little ferrous salt to reduce dichromate; the difference represents chromium.[20] The iron present in the solution greatly intensifies the dichromate color and its concentration must be kept constant within a few per cent. The method is suitable for the determination of 0.01 to 1 per cent chromium in steel. According to the authors, satisfactory results are obtained with steels containing respectively 3 per cent copper, 3 per cent nickel, 1 per cent cobalt, 1 per cent vanadium, and 1.5 per cent molybdenum and titanium. If more than 1 per cent silicon is present, a special standard curve must be established.

§ Procedure

Dissolve 1.000 g. of steel (for amounts of chromium up to 0.1 per cent) in 10 ml. of 1:1 nitric acid and 20 ml. of 70 per cent perchloric acid. Evap-

[25] G. E. F. Lundell, J. I. Hoffman, and H. A. Bright. *Chemical Analysis of Iron and Steel.* Wiley, New York, 1931, p. 300.

orate to dense fumes of perchloric acid and boil for 5 minutes to oxidize chromium. Cool the beaker and its contents rapidly in water. Dissolve the soluble salts in 20 ml. of water, transfer to a 50 ml. volumetric flask, cool to room temperature, and dilute to the mark.

Transfer a portion of the solution to a 1 cm. absorption cell, add 10–20 mg. of ferrous ammonium sulfate to reduce dichromate, and adjust the photometer to give a transmittancy reading of 100 with a filter transmitting between 410 and 480 mμ. Refill the cell with the oxidized solution and obtain the transmittancy. (In the absence of appreciable amounts of colored ions such as copper and nickel, find the transmittancy of the oxidized solution, add ferrous salt to the solution in the cell and then find the transmittancy of the reduced solution.) Any silica present in the solution must be allowed to settle before a reading is made.

Establish the standard curve by adding known amounts of chromium to a steel of low known chromium content and treating as above. U. S. Bureau of Standards sample 22b is suitable for the purpose. The transmittancy of the sample and standard solutions should be found at the same temperature.

TABLE 41

DETERMINATION OF CHROMIUM IN STEEL BY PERCHLORIC ACID METHOD[a]

Alloying element, %	Cr present, %	Cr found, %
	0.007	0.007, 0.008
	0.008	0.009, 0.009
	0.023	0.023, 0.023
3 Cu	0.022	0.022
3 Ni	0.022	0.020
1 Co	0.023	0.021

[a] Singer and Chambers; values selected from lower Cr range.

D. BIO MATERIALS

§ Procedure

Ash the sample by ignition at about 500° C. (see p. 410 for details). Take a suitable weight of the ash (not more than 1–2 γ of chromium need be present), fuse with sodium carbonate in a platinum crucible and determine chromium with diphenylcarbazide according to the directions given under Silicate Rocks, p. 265.

Note. Organic matter may also be destroyed with a mixture of nitric, sulfuric, and perchloric acids. The diluted digest is boiled with silver nitrate and persulfate to oxidize chromium, permanganate is destroyed by the addition of a little hydrochloric acid, and chromium then determined with diphenylcarbazide.

CHAPTER XV

COBALT

The importance of cobalt in animal nutrition has led to the development of procedures for the determination of minute amounts of the element in soils, plants, and animal tissues. Most investigators have used the nitroso-R salt method (IIA) because of its high sensitivity. The thiocyanate method (IIC) is less sensitive, but very satisfactory for some classes of material.

I. Separations

Separation of cobalt from much iron is frequently required in trace analysis; sometimes separation from copper is necessary, and occasionally from other elements such as nickel and chromium. Extraction methods are of special importance in the isolation of cobalt.

A. Dithizone Extraction

Copper can be separated from cobalt by extraction of the former with dithizone from a fairly acidic medium (p. 296). The separation has not been studied systematically, but it has been applied with good results. It seems likely that even at a *p*H as high as 2 no significant amount of cobalt would be extracted by a carbon tetrachloride solution of dithizone, whereas copper is readily extracted at this *p*H if the carbon tetrachloride is free from inhibiting impurities (p. 303). Marston and Dewey[1] use a strong (0.2 per cent) solution of dithizone in chloroform for removal of copper from a citrate solution at *p*H 3 to 4 without coextraction of any cobalt. It should be noted that at a given *p*H, copper is extracted more easily by a carbon tetrachloride than by a chloroform solution of dithizone. The use of dithizone for the removal of copper and other metals reacting in acidic solution presupposes the presence of these metals in comparatively small amounts so that inordinately large volumes of dithizone will not be required.

Extraction of cobalt as dithizonate from basic citrate medium is a good method of separation from ferric iron, titanium, chromium, vanadium, and other metals not forming dithizonates. Marston and Dewey[1] found that cobalt begins to be extracted from an acetate buffer (0.02 *M*) at *p*H 3 and

[1] H. R. Marston and D. W. Dewey, *Australian J. Exptl. Biol. Med. Sci.*, **18**, 343 (1940).

that the extraction is complete at *p*H 6. From a citrate buffer (0.02 *M*) a *p*H of at least 8 is needed for complete extraction; the extraction of cobalt becomes more difficult as the citrate concentration is increased. In these experiments the volumes of the aqueous and carbon tetrachloride phases were equal, and the dithizone concentration in the carbon tetrachloride was 0.05 per cent. With a chloroform solution of dithizone of the same concentration, a *p*H approximately 2 units higher was required for the same percentage extraction as when carbon tetrachloride was used. The rate of extraction is said to be somewhat slow; an increase in temperature aids the extraction. Nickel accompanies cobalt in the dithizone separation.

Directions for carrying out the dithizone extraction are given later.

B. Extraction of Cobalt Thiocyanate Complex

A means of separating cobalt from iron and nickel is provided by the extractability of the thiocyanate complex of cobalt with amyl alcohol or its mixture with ether. Iron can be kept in the aqueous phase by reduction to the ferrous state or by complexing. Bayliss and Pickering[2] extract the cobalt complex from a citrate-buffered solution. Such amounts of iron as are encountered in bio material are not extracted. The following directions are given.

To the sample solution add 5 ml. in excess of 1:1 hydrochloric acid and 20 ml. of 60 per cent ammonium thiocyanate solution (420 g. of salt in 280 ml. of water). Now add ammonium citrate solution (210 g. of citric acid neutralized to phenolphthalein with ammonia and diluted to 1 liter) until the red color of the ferric thiocyanate complex just disappears. Dilute with water to 50 ml. and add 4 ml. of ethyl ether to saturate the solution. Extract with three successive 20-ml. portions of a mixture of 35 ml. of amyl alcohol and 65 ml. of ether. Return the cobalt to the aqueous phase by shaking the organic solvent extract with two 20 ml. portions of 2 *M* ammonium hydroxide. Evaporate the aqueous solution to dryness and destroy thiocyanate by adding 20 ml. of 6 *M* nitric acid and evaporating to dryness. Neutralize the resulting ammonium hydrogen sulfate with ammonia and again evaporate to dryness. Cobalt can then be determined in the residue by any of the usual methods.

Under the above conditions, 86 per cent of the cobalt is removed in a single extraction, the partition coefficient being about 15. The addition of citrate to the disappearance of the red iron thiocyanate color adjusts the *p*H to about 3.5, which is said to be close to the optimum.

Possibly the procedure described on p. 281 can be applied for the separation of cobalt from iron, nickel, and copper.

[2] N. S. Bayliss and R. W. Pickering, *Ind. Eng. Chem., Anal. Ed.*, **18**, 446 (1946).

C. Extraction of Cobalt Diethyldithiocarbamate

Cobalt diethyldithiocarbamate can be extracted from a citrate-containing solution at *p*H 6.5 by carbon tetrachloride and similar solvents. Many other metals are also extracted (p. 305), but a separation from small amounts of iron is possible in this way (p. 290). It is claimed that this method of separation is superior to the dithizone procedure when much calcium and phosphorus is present, since these are less likely to give a precipitate at the lower *p*H of the carbamate extraction.

D. Other Separations

The nitroso-naphthol complexes of cobalt can be extracted from aqueous medium by chloroform and carbon tetrachloride. These compounds are extremely slightly soluble in water, so that there should not be much doubt about the complete extraction of cobalt at a suitable *p*H. The solubilty of cobalt α-nitroso-β-naphtholate has been reported as 1.5 mg. per liter of water at room temperature. A *p*H of 3–4 has been recommended for the extraction of this complex by the use of chloroform.[3] Little is known about the separations that can be made.

Cobalt β-nitroso-α-naphtholate is soluble to the extent of only 0.2 mg. per liter of water. It can be extracted by carbon tetrachloride. By shaking the extract with strong hydrochloric acid, copper, iron, and other metals can be brought into the aqueous phase, while cobalt remains in the carbon tetrachloride.[4] It seems possible that conditions can be found which will allow direct extraction of cobalt, with iron and copper being left in the aqueous solution.

Much iron can be separated from cobalt by ether extraction of ferric chloride from 1:1 hydrochloric acid solution.[5] Iron can be precipitated as phosphate at a *p*H of about 3.5 without coprecipitation of appreciable amounts of cobalt.[6]

Copper has been removed by hydrogen sulfide precipitation from acid medium, but the dithizone separation is to be preferred. If much copper must be removed, resort can be made to electrolytic deposition.

Sodium peroxide oxidation in hot solution has been used to separate cobalt from chromium. The solubility of cobaltic hydroxide has been reported as 0.006 mg. per liter. The presence of iron aids the precipitation of minute amounts of cobalt.

[3] R. Paulais, *Ann. pharm. franç.*, **4**, 101 (1946). Phosphoric acid is used to complex iron.

[4] E. Boyland, *Analyst*, **71**, 230 (1946).

[5] For continuous extraction of ferric chloride by ether, see K. J. McNaught, *Analyst*, **62**, 467 (1937). The separation is applied in the determination of cobalt in limonite.

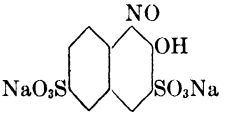
[6] V. North and R. C. Wells, *Ind. Eng. Chem., Anal. Ed.*, **14**, 859 (1942).

Cobalt has been isolated from plant materials and soil extracts by precipitation with 8-hydroxyquinoline at *p*H 5.1–5.2.[7] Ferric or aluminum hydroxyquinolate serves as a collector.

II. Methods of Determination

A. The Nitroso-R Salt Method

Cobalt reacts with nitroso-R salt



(yellow in aqueous solution) to give a soluble red complex salt, which is stable in dilute acid solution. Three moles of reagent combine with one of cobalt. This reaction furnishes a most sensitive method for the determination of traces of cobalt such as occur in soils, plants, and animal organs.

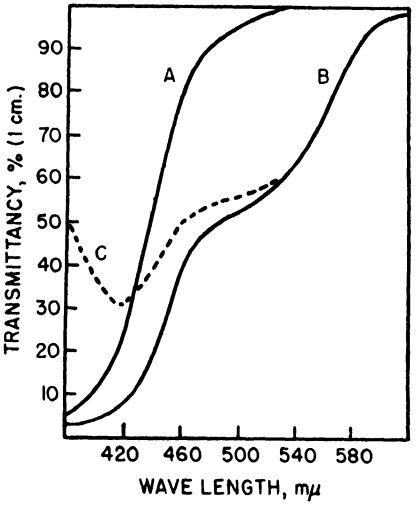


Fig. 33. Transmittancy curves of: (A) Nitroso-R salt blank (0.02 per cent final concentration of reagent) versus water, (B) 1 p.p.m. Co + nitroso-R salt versus water, (C) 1 p.p.m. Co + nitroso-R salt versus nitroso-R salt blank. (Data of Claassen and Westerveld.)

The cobalt complex is usually formed in a hot acetate medium (procedure of McNaught[8]) or citrate-phosphate-borate buffer (Marston and

[7] R. O. Scott and R. L. Mitchell, *J. Soc. Chem. Ind.*, **62**, 5 (1943).
[8] K. J. McNaught, *Analyst*, **67**, 97 (1942).

Dewey), not far from neutrality, and mineral acid is then added to decompose the complexes of most of the other heavy metals that may be present. Even the copper (greenish) and nickel (brownish) complexes are decomposed in hot 1 *N* nitric acid. The excess reagent can be converted into the lighter colored nitro acid by boiling with dilute (2 *N*) nitric acid. In one procedure (Marston and Dewey) the excess of reagent is destroyed by bromination, but such removal of reagent is not necessary when a photometer is used.

The nitroso-R salt method has been studied in some detail by Marston and Dewey.[1] They found that the cobalt complex was not formed below a *p*H of 2.5. At a *p*H of 6 the reaction is complete in 5 minutes at room temperature in various buffer media. In acetate medium the reaction is complete in 3 minutes at the boiling temperature at a *p*H slightly greater than 5; under the same conditions a *p*H of about 5.5 is needed when a citrate-phosphate buffer is used. The safe upper *p*H limit is approximately 8 with various buffers. The presence of citrate is of advantage in basic medium since it prevents the precipitation of cobalt hydroxide as well as of other metal hydroxides. Ammonium salts are objectionable in basic medium because they weaken the color as the result of ammine formation. High concentrations of alkali and alkaline earth metals, chloride, sulfate, nitrate, acetate, and citrate do not affect the reaction. Beer's law is obeyed.

According to Marston and Dewey, the following metals in concentrations ten times that of cobalt do not interfere even when the excess of reagent is very small: ferric iron, manganese, zinc, cadmium, lead, and tin. Palladium gives a red color, particularly in acid solution, fading on boiling. When the excess of reagent is limited, copper and especially nickel give rise to low results by combining with the reagent and preventing the formation of the cobalt complex. The error is diminished, or avoided altogether with small amounts of these metals, by the use of a basic citrate medium (*p*H 8) instead of an acetate buffer, boiling for 2 minutes, and the addition of a sufficiently large excess of reagent. With 8 mg. of nitroso-R salt, correct results could be obtained in the presence of 6 mg. of nickel. Although ferric iron does not interfere directly, appreciable amounts should not be present because of its yellow-brown color in citrate medium. It may be removed by ether extraction from hydrochloric acid solution. However, it is usually better to isolate cobalt by dithizone extraction from basic medium after copper has been removed (if necessary) by dithizone extraction from acidic solution. Nickel will at least partly accompany cobalt in the dithizone extraction, but ordinarily it will not be present in sufficient amount in the sample to interfere.

The procedures of McNaught and of Marston and Dewey have been

tested photometrically by Olson,[9] some of whose results are shown in Fig. 34 and Tables 42 and 43. The procedure of Marston and Dewey was modified by decreasing the concentration of nitroso-R salt and not destroying

TABLE 42

EFFECT OF LIGHT ON COLOR INTENSITY OF COBALT NITROSO-R SALT COMPLEX (PROCEDURE B)[a]

	Extinction (420 mμ filter) on standing			
	0 min.	30 min.	60 min.	90 min.
Blank in diffuse daylight	0.196	0.192	0.192	0.192
Blank in darkness	0.200	0.198	0.198	0.198
5 γ Co, in diffuse daylight	0.384	0.384	0.380	0.370
5 γ Co, in darkness	0.388	0.388	0.388	0.386

[a] Data of P. B. Olson.

TABLE 43

DETERMINATION OF COBALT WITH NITROSO-R SALT

(Procedures as in text; final volume 10 ml. Filter used had maximum transmission at 420 mμ except where otherwise indicated)

Foreign metal present, mg.		Co taken, γ	Co found, γ	
			Proc. A	Proc. B
5	Fe (III)	2.0	2.6[a], 1.8[b]	2.2
5	Fe (III)	10.0	10.9[a], 10.2[b]	10.2
10	Fe (III)	2.0	3.2[a], 1.9[b]	2.2
10	Fe (III)	10.0	11.7[a], 10.0[b]	10.2
1	Cu	2.0	1.9	2.0
1	Cu	10.0	10.5	10.2
5	Cu	2.0	—[c]	1.8
5	Cu	10.0	—[c]	10.1
10	Cu	2.0	—	1.8
0.1	Ni	2.0	2.0	2.0
0.1	Ni	10.0	10.2	10.2
0.2	Ni	2.0	—	2.3

[a] Filter with maximum transmission at approximately 420 mμ.
[b] Filter with maximum transmission at approximately 500 mμ.
[c] Very little color produced.

the excess of reagent. The modified procedure of Marston and Dewey (Procedure B) is seen to be superior to that of McNaught (Procedure A) in the presence of comparatively much iron and especially copper. Procedure A is somewhat simpler and is sometimes suitable.[10]

[9] Paul Olson, University of Minnesota, 1948.

[10] From data given by R. S. Young, E. T. Pinkney, and R. Dick, *Ind. Eng. Chem., Anal. Ed.*, **18**, 474 (1946), it may be inferred that 5 mg. of aluminum, zinc, magnesium, and calcium will not interfere under the conditions of this procedure; up to 2.5 mg. of manganese and 0.5 mg. of chromium may be present. Cyanide, peroxide, persulfate, and reducing agents must be absent.

Various other nitroso-R salt procedures have been described.[11]

Special Solutions

Nitroso-R salt, 0.2 per cent aqueous solution. The solution undergoes no change for months if kept in the dark.

Standard cobalt solution, 0.0100 per cent cobalt. This solution can be prepared accurately enough for most purposes by dissolving 0.0404 g. of $CoCl_2 \cdot 6H_2O$ in water, adding 1 ml. of concentrated hydrochloric acid, and diluting to 100 ml. From this solution prepare a more dilute one (*e.g.*, 10 γ of cobalt per ml.).

Citric acid (for Procedure B), 0.20 *M*. 4.2 g. in 100 ml.

Buffer solution (for Procedure B), 6.2 g. of boric acid, 35.6 g. of disodium phosphate dihydrate, and 500 ml. of 1.00 *N* sodium hydroxide in a total volume of 1 liter.

§ Procedure A (Acetate Medium)

Evaporate the solution (1–10 γ of cobalt) almost to dryness, add 1 ml. of concentrated nitric acid, and continue the evaporation just to dryness. Take up the residue in 5 ml. of water, 0.25 ml. of 1:1 hydrochloric acid, and 0.25 ml. of 1:10 nitric acid. Boil for a few minutes if necessary to dissolve all solid material. Add exactly 0.5 ml. of nitroso-R salt solution and 1.0 g. of hydrated sodium acetate. The *p*H of the solution should be close to 5.5 at this point; the acidity may be checked by removing a small drop of the solution and testing with bromcresol green indicator. Boil for 1 minute, add 1.0 ml. of concentrated nitric acid, and boil again for 1 minute. Cool to room temperature in the dark, dilute to 10 ml. in a volumetric flask, and obtain the transmittancy of the solution at 420 mμ or higher (see Note). In the presence of 5 mg. or more of iron make the measurement at 500–550 mμ to reduce the error resulting from absorption of light by the yellow solution.

§ Procedure B (Citrate-Phosphate-Borate Medium)

The sample solution (1–10 γ of cobalt) should be almost neutral, with a volume not greater than 5 ml. Mineral acids if present can be removed by evaporation to dryness. Add 1.0 ml. of citric acid solution and 1.2 ml. of phosphate-boric acid buffer. The *p*H of the solution should now be close to 8.0; it may be checked by withdrawing a small drop and testing with cresol red. Add exactly 0.5 ml. of nitroso-R salt solution while stirring. Boil for 1 minute, add 1.0 ml. of concentrated nitric acid, and again boil for

[11] E. B. Kidson and H. O. Askew, *New Zealand J. Sci. Tech.*, **21B**, 178 (1940); H. T. Macpherson and J. Stewart, *Biochem. J.*, **32**, 763 (1938). Also see footnote 20.

1 minute.[12] Cool the solution in the dark and make up to 10 ml. Obtain the transmittancy of the solution at approximately 420 mμ or higher (see Note).

Note. There is considerable contradiction in the literature concerning the best wave length for the measurement of the optical density of the cobalt complex. The question has lately been considered by Claassen and Westerveld.[13] In agreement with others they find that the transmission minimum lies at *ca.* 415 mμ (Fig. 33). However, they recommend measuring at 550 mμ, since at this wave length the reagent absorbs

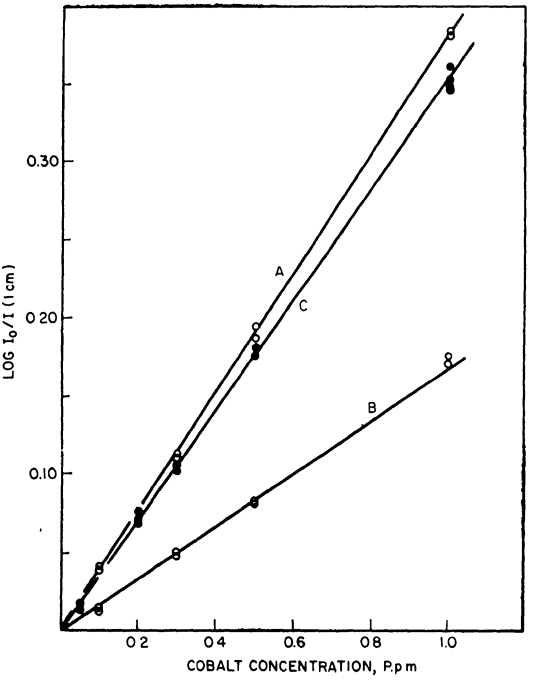


Fig. 34. Determination of cobalt with nitroso-R salt by Marston and Dewey's method (without destruction of excess reagent) with 420 mμ filter (A) and 500 mμ filter (B), and by McNaught's method with 420 mμ filter (C). Extinction of blank subtracted in each case. (Data of Paul Olson.)

[12] If it is desired to destroy the excess of reagent (as would be necessary if the color is to be compared in a Duboscq colorimeter), add 0.5 ml. of 0.2 *M* bromine water at this point and allow the solution to stand for 5 minutes. Then boil for 1 minute to expel bromine.

[13] A. Claassen and W. Westerveld, *Rec. trav. chim.*, **67**, 720 (1948). These authors report that oxides of nitrogen are very detrimental in the presence of small amounts of copper, which alone would not give low results for cobalt. The following elements are stated not to interfere in the acetate procedure (twice as much nitroso-R salt used as in the above procedure) when 20 mg. are present in 100 ml. of solution: silver, tungsten, molybdenum, lead, cadmium, boron, and fluoride (200 mg.).

hardly at all and any slight variation in the color intensity of the blank will then not be a source of error. The loss in sensitivity at the higher wave length is made up by the use of a thicker stratum of solution. In the procedure of these authors twice as much reagent is used as in the above procedure, and if measurement of the transmittancy is made at or near 420 mμ for maximum sensitivity, it is best made against a blank solution, not water, since with relatively much cobalt readings below 10 per cent will be obtained against water, and such values cannot be determined precisely (p. 64).

Another reason for preferring the higher wave length for the measurement is the absorption by ferric iron in the blue region.

B. The Nitrosocresol Method[14]

o-Nitrosophenol (p. 122) and *o*-nitrosocresol are sensitive cobalt reagents, the latter being more satisfactory. The nitrosocresol method may perhaps be regarded as a somewhat special one for cobalt, in the sense that it has advantages over the nitroso-R salt method when the amount of cobalt to be determined is very small, say less than 0.1 γ. The reagent is not obtainable in solid form, its solution must be prepared by the analyst, it is not very stable, and special precautions must be taken to prevent the interference of traces of iron in the procedure. The cobalt complex of *o*-nitrosocresol absorbs mostly in the ultraviolet (maximum absorption at 360 mμ). The nitrosocresol method involves extraction of the cobalt complex with ligroin, and, in the words of the authors, the sensitivity is increased, compared to the nitroso-R salt method:

"...because the final volume can be kept smaller and an absorption tube of smaller diameter can be used. It is only with difficulty that the 10 cm. tube, which is 5 mm. in diameter, can be filled and emptied using aqueous solutions. Tubes of even smaller diameter can readily be emptied and filled when a liquid such as ligroin is used; 10 cm. absorption tubes 3 mm. in diameter have been successfully used."

The method is especially intended for bio material, and the procedure is therefore given later (p. 288).

C. The Thiocyanate Method

In a medium containing a sufficient concentration of ethyl alcohol or acetone, an alkali metal thiocyanate produces a blue color with cobalt, which is due to the formation of a complex cobalt thiocyanate (possibly $Co(CNS)_4^=$ is formed). In water solution the complex is dissociated and no color is obtained unless a very large excess of thiocyanate is present. Acetone is usually preferred to ethyl alcohol, but there is not much difference between the two solvents.[15] According to Tomula[16] the color in-

[14] G. H. Ellis and J. F. Thompson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 254 (1945).

[15] For a procedure with ethyl alcohol see N. Uri, *Analyst*, **72**, 478 (1947). In 50 per cent alcoholic medium the color intensity becomes constant at about 15 per cent (*w/v*) ammonium thiocyanate concentration.

[16] E. S. Tomula, *Z. anal. Chem.*, **83**, 6 (1931).

tensity reaches a practically constant maximum value in a medium containing 50 per cent by volume of acetone (final concentration of ammonium thiocyanate 5 per cent). The color intensity also depends upon the thiocyanate concentration, the increase in intensity being very rapid up to an ammonium thiocyanate concentration of 2 per cent, more gradual thereafter, but still not quite constant at 10 or 12 per cent (50 per cent acetone solution). However, the change in intensity with thiocyanate concentration at 5 or 6 per cent is so slight that one can work without difficulty at this concentration if the same amount of thiocyanate is added to unknown and standards.

The difference in cobalt concentration between the unknown and standard should not exceed 100 per cent, if a Duboscq colorimeter is used.

Among interfering elements may be mentioned iron (III), copper, uranium, bismuth, and nickel, as well as those metals forming slightly soluble thiocyanates or complex thiocyanates consuming the reagent. The color given by ferric iron and cupric copper can be destroyed, if not too large amounts of these metals are present, by the addition of stannous chloride to a slightly acid solution. Because of air oxidation it is difficult to make more than a few tenths of a milligram of iron (in 5–10 ml.) harmless in this way. Molybdenum will give an amber color in acidic solution, particularly if stannous chloride is added. Small amounts of iron can also be made harmless with phosphate.

Nickel interferes only to the extent that its green color disturbs the color comparison. If the amount of nickel is not too large, satisfactory determinations of cobalt can be obtained by using a yellow filter (see Table 44). At very low nickel concentrations the ratio of nickel to cobalt may be as large as 10 without sensible interference from the nickel. Thus 10 γ cobalt in 5 ml. of solution can be determined accurately in the presence of 100 γ of nickel even without the use of a filter, 1 $\times$ 8 cm. tubes being used for the comparison.

Instead of adding a miscible organic solvent such as acetone to develop the color of the cobalt complex, it is possible to extract it from aqueous medium with amyl alcohol or amyl alcohol mixed with ethyl ether. This procedure is useful when nickel and iron preponderate greatly, and is used advantageously in other cases as well. The directions given below are those of Young and Hall,[17] who use a 3:1 volume mixture of amyl alcohol and ethyl ether to extract the blue cobalt complex. This ratio is stated to give the maximum color intensity. Sodium thiosulfate (as reducing agent) and phosphate are employed to prevent coloration by ferric iron and copper. Vanadium does not interfere if ammonium acetate and tartaric acid

[17] R. S. Young and A. J. Hall, *Ind. Eng. Chem., Anal. Ed.*, 18, 265 (1946).

are also added; otherwise it produces a blue color. Most other metals do not interfere. The regulation of the acidity is of great importance in this procedure, especially so far as the suppression of the interference of iron is concerned.

Special Solutions

Ammonium thiocyanate, 50 g. in 100 ml. of aqueous solution.

Stannous chloride, 20 g. of the dihydrate in 100 ml. of 2 *N* hydrochloric acid.

Thiosulfate-phosphate (for extraction procedure), 125 g. of sodium thiosulfate pentahydrate and 31 g. of trisodium phosphate dodecahydrate in 1 liter of water.

Amyl alcohol-ethyl ether mixture (for extraction procedure), 3 volumes of the alcohol to 1 volume of ether. Use analytical quality reagents.

§ Procedure

Acetone Method. Take a convenient volume of neutral or slightly acid sample and add sufficient ammonium thiocyanate solution and C. P. acetone to make their respective concentrations not less than 5 per cent and 50 per cent (by volume) when the mixture is made up to volume. After mixing, compare the solution against a standard containing identical concentrations of thiocyanate and acetone and a comparable amount of cobalt ($\pm 50\%$) as the unknown. If the photometric technique is applied, use a filter giving maximum transmission at 600–620 mμ.

If small amounts of ferric iron and copper are present, add enough hydrochloric acid to the sample solution to make the acidity about 2 *N* and then 3 ml. of stannous chloride for each 10 ml. of sample. Add ammonium thiocyanate and acetone as before and compare against a standard containing the same amounts of acid and stannous chloride as the unknown. When small amounts of nickel are present (*cf.* Table 44) use a yellow or yellow-green filter.

When a Duboscq type of colorimeter is used the cobalt concentration of the final solution must be greater than 2 p.p.m. By using narrow tubes (1 × 8 cm.), quantities of cobalt of the order of a few micrograms can be determined.

Extraction Method. Add exactly 0.5 ml. of 1:1 hydrochloric acid to the almost neutral sample solution and dilute to 25 ml. in a volumetric flask. While stirring add a 5 ml. aliquot of this solution (Co < 20 γ, Fe < 9 mg.) to 8 ml. of thiosulfate-phosphate solution and 10 ml. of ammonium thiocyanate solution. The *p*H of this mixture should be 3.5–4.0. Shake in a separatory funnel for 1 minute with 10.0 ml. of amyl alcohol–ethyl ether mixture, which has previously been shaken with a little of the phosphate-thiosulfate solution. Run the organic solvent layer into a 1 cm. absorption cell and obtain the extinction with the aid of a red filter.

If more than 9 mg. of iron is present in the 5 ml. aliquot of the sample,

proceed as above except add also 2 ml. of ammonium acetate (700 g. in 1 liter of water) and 3 drops of tartaric acid (50 g. in 100 ml. of water) before extraction. Up to 35 mg. of iron may be present in the 5 ml. aliquot in this modification of the procedure.

See p. 285 for another extraction procedure with amyl alcohol.

TABLE 44

DETERMINATION OF COBALT BY THE THIOCYANATE METHOD IN ACETONE MEDIUM AND BY THE AMYL ALCOHOL EXTRACTION METHOD

No.[a]	Procedure	Foreign metals	Co taken γ	Co found γ
1	Acetone		34	35
2	Acetone		70	70
3	Acetone		340	350
4	Acetone		3.0	2.5
5	Acetone		12.0	12.0
6	Acetone	35 γ Ni	35	33
7	Acetone	117 γ Ni	35	39
8	Acetone	210 γ Ni	70	93
9	Acetone	350 γ Ni	350	330
10	Acetone	125 γ Ni	12.0	11.3
11	Acetone	50 γ Cu	12.0	12.0
12	Amyl alcohol	200 γ Ni	5	5
13	Amyl alcohol	500 γ Ni, 100 γ Cu	6	6

[a] Determinations 1-3, 6-10 by Tomula, *loc. cit.*; 4, 5, 11, 12, 13 by Sandell and Perlich, *loc. cit.* Duboscq colorimeter with greenish yellow filter used in Nos. 6-10, and 1 × 8 cm. tubes in Nos. 4, 5, 11, 12, 13 (no filter).

D. OTHER METHODS

See Table 45 for a summary of other colorimetric methods for cobalt. Some of these are sufficiently sensitive to qualify as trace methods.

III. Special Applications

A. SILICATE ROCKS[18]

The method involves decomposition of the sample with hydrofluoric-perchloric acid and extraction of the cobalt from the ammoniacal citrate solution of the residue with dithizone in carbon tetrachloride. Copper, zinc, lead, and more or less of the nickel present accompany cobalt in the dithizone separation, but ordinarily there is no interference from these metals. The carbon tetrachloride solution of the dithizonates is evaporated to dryness, organic matter is destroyed by perchloric acid oxidation, and cobalt is then determined by the thiocyanate-acetone method. The lower limit of this method is about 0.001 per cent cobalt. For more accu-

[18] E. B. Sandell and R. W. Perlich, *Ind. Eng. Chem., Anal. Ed.*, 11, 309 (1939).

TABLE 45.–ADDITIONAL METHODS FOR COBALT

Reagent	Method	Reference
Potassium ferricyanide + ammonia	Red color is produced. Add 10 ml. 1:1 NH_4OH and 5 ml. 0.1 per cent $K_3Fe(CN)_6$ to 10 ml. slightly acid or neutral test solution. Comparison can be made by colorimetric titration. Many metals interfere.	W. J. Agnew, *Analyst*, **53**, 31 (1928). R. J. DeGray and E. P. Rittershausen, *Ind. Eng. Chem., Anal. Ed.*, **14**, 858 (1942).
Ammonia + peroxide	Pink color (cobalt ammine). Add 2 ml. 20 per cent NH_4Cl and a slight excess of NH_4OH to sample, followed by 0.6 g. Na_2O_2 (or H_2O_2). Mix and compare against similar standard.	B. S. Evans, *Analyst*, **50**, 389 (1925); W. Heins, *Z. anal. Chem.*, **78**, 432 (1929).
Hydrochloric acid	Solid sample dissolved in concentrated hydrochloric acid and transmittancy determined at 625 mμ. At this wave length the color of iron (III) is $^1/_{100}$, of nickel $^1/_{127}$, and of copper (II) $^1/_{100}$ as strong as that of cobalt. Cr and V interfere. A maximum of 1 ml. of water may be present in 25 ml. without altering the color intensity.	P. Giesecke, *Am. Inst. Mining Metall. Engrs., Tech. Public.* No. **1740** (1944).
Dimethylglyoxime	Brown color (cobalt dimethylglyoxime) in nearly neutral solution.	S A. Braley and F. B. Hobart, *J. Am. Chem. Soc.*, **43**, 482 (1921).
Dimethylglyoxime + benzidine	Orange-red color in neutral solution.	A. Chiarottino, *Industria chimica*, **8**, 32 (1933); *Chem. Abstracts*, **27**, 2396 (1933).
Hydrogen peroxide + bicarbonate	Green color, possibly due to $[Co(KCO_3)_2]_2O$. Add 0.5 ml. 3 per cent H_2O_2 to 10 ml. neutral solution and dilute to 50 ml. with saturated $KHCO_3$ or ammonium bicarbonate solution. As little as 4 p.p.m. of Co can be determined.	A. Blanchetière and J. M. Pirlot, *Compt. rend. soc. biol.*, **101** 858 (1929).
Sodium α-nitroso-β-naphtholate	Orange-red color in ammoniacal citrate solution. Procedure described under sodium β-nitroso-α-naphtholate may be used.	F W. Atack, *J. Soc. Chem. Ind.*, **34**, 641 (1915); E. G. Jones, *Analyst*, **43**, 317 (1918). For determination of cobalt in the presence of much manganese by precipitation with α-nitroso-β-naphthol and solution of the cobalt naphtholate in chloroform see L. Waldbauer and N. M. Ward, *Ind. Eng. Chem., Anal. Ed.*, **14**, 727 (1942).
Sodium β-nitroso-α-naphtholate	Add 5 ml of ammonium citrate solution (60 g. per 100 ml.) to *ca.* 10 ml. of neutral cobalt solution containing up to 10 p.p.m. of Co, then 5.0 ml. of 3 *M* ammonia, 70 ml. of water and 3.0 ml. of 0.05 per cent reagent (0.1 g. β-nitroso-α-naphthol, 1 ml. 1 *M* sodium hydroxide, 200 ml. water). Dilute to 100 ml. and determine transmittancy with 550 mμ filter. Copper interferes especially, nickel, chromium, and ferric iron to a lesser extent; manganese should be absent.	J. H. Yoe and C. J. Barton, *Ind. Eng. Chem., Anal. Ed.*, **12**, 405 (1940). For a method in which the cobalt complex is extracted by benzene see C. E. Cardini, W. Jung, and M. Fuksman, *Anales asoc. quim. argentina*, **31**, 191 (1943).
o-Nitrosophenol	See p. 122.	
Arsenophosphotungstic acid	Indirect; reagent reduced by cobalt in basic cyanide medium (blue color).	A. Lieberson, *J. Am. Chem. Soc.*, **52**, 464 (1930).
Oxalate + lead dioxide	Oxidation in acetic acid-acetate medium gives green $Co(C_2O_4)_3^{=}$. Not sensitive.	G. H. Cartledge and P. M. Nichols, *Ind. Eng. Chem., Anal. Ed.*, **13**, 20 (1941).
2,2′,2″-Terpyridyl	Add 5 ml. of 0.1% terpyridyl hydrochloride solution to 25 ml. sample solution of *p*H 2–10; use blue-green filter. Copper, iron, and nickel interfere badly. Sensitive method.	M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **15**, 74 (1943).

rate determination of cobalt in silicic rocks, in which the cobalt content is very low, the nitroso-R salt method should be applied. Cobalt can be isolated by dithizone as described below. Since the amounts of copper and nickel present will almost always be small, they need usually not be separated before the final determination is made (p. 276).

Special Reagents

Sodium citrate, 10 per cent. Usually the solution need not be shaken with dithizone (see p. 313) to remove heavy metals; the cobalt content of sodium citrate is generally insignificant.

Dithizone, 0.01 per cent (*w/v*) in carbon tetrachloride.

§ Procedure

Weigh 0.25 gram of finely powdered basic rock or 0.5–1.0 g. of acidic rock into a platinum dish, add a few milliliters of water, 0.5 ml. of 70 per cent perchloric acid, and 2.5 ml. of hydrofluoric acid (for a sample greater than 0.25 g. these amounts should be correspondingly increased). Evaporate the mixture to dryness, take up the residue in 0.5 ml. of perchloric acid and 2 or 3 ml. of water, and again evaporate to dryness. To the residue add 0.5 to 1 ml. of concentrated hydrochloric acid and 5 ml. of water. Heat to bring all soluble material into solution, add 5 ml. of sodium citrate solution, neutralize the cold solution with concentrated ammonium hydroxide using litmus paper, and add a few drops in excess. If there is an appreciable amount of precipitate or residue in the solution at this point, filter through a small paper, wash with small portions of water, and ignite the paper and its contents. Fuse the residue with approximately 0.1 gram of sodium carbonate, add an excess of dilute hydrochloric acid to the cooled melt, and heat to effect as complete solution as possible. Add 2 or 3 ml. of 10 per cent sodium citrate solution, make slightly ammoniacal, and reserve the solution.

To the main solution (filtrate from any insoluble material after the hydrofluoric acid decomposition), containing 5 ml. of 10 per cent sodium citrate and at least 0.2 to 0.25 ml. of concentrated ammonium hydroxide in excess (these quantities are for a 0.25-gram sample), add 5 ml. of dithizone. Shake vigorously for one-half minute and draw off the carbon tetrachloride extract. Add 2 or 3 ml. of dithizone to the solution, shake as before, and continue in this manner until the last portion of dithizone does not become red after shaking for 1 minute. In like manner extract the ammoniacal citrate solution of the sodium carbonate melt with a milliliter or two of dithizone. Wash the combined carbon tetrachloride extracts with 5 ml. of water, and run the carbon tetrachloride layer into a small (25 ml. if possible) Erlenmeyer flask. Evaporate the carbon tetrachloride and add 0.25

ml. of concentrated sulfuric acid and 0.25–0.5 ml. of 60–70 percent perchloric acid. Heat at 200–250° C. until the liquid is entirely colorless. Then fume off the sulfuric acid. Add 0.5 ml. of water and 3 or 4 drops of stannous chloride solution (20 grams of $SnCl_2 \cdot 2H_2O$ in 100 ml. of 2 *N* hydrochloric acid). Transfer the solution to a small glass-stoppered flat-bottomed tube (1 × 8 cm.) or a small vial. Rinse the flask with 0.5 ml. of ammonium thiocyanate (50 grams in 100 ml. of water), then with 2 ml. of reagent-quality acetone, and transfer these washings to the tube. The concentration of acetone in the final solution must be at least 50 per cent by volume. After mixing, make the color comparison against a series of standards containing the same amounts of stannous chloride, ammonium

TABLE 46

DETERMINATION OF COBALT IN SILICATE ROCKS BY THE THIOCYANATE METHOD
Acetone used in Nos. 1–6, amyl alcohol in Nos. 7–9

No.	Co present %	Co found %
1	0.0004	0.0004
2	0.0009	0.0008
3	0.0100	0.0100
4	0.0250	0.0235
5[a]	0.0048	0.0045
6[b]	0.0048	0.0048
7	0.0003	0.0002
8	0.00075	0.0007
9[c]	0.0006	0.0006

[a] 0.05% Ni.
[b] 0.02% Cu.
[c] 0.05% Ni, 0.01% Cu.

thiocyanate, and acetone as the unknown. The percentage of cobalt in a basic rock such as a gabbro or diabase is likely to be less than 0.01 and the standards can be prepared accordingly. In acidic rocks the percentage is likely to be less than 0.001. The color of the sample solution should be pure blue, differing little if at all in hue from the standards. A greenish hue may be due to incomplete destruction of organic matter, insufficient stannous chloride to reduce copper, or the presence of much nickel.

Alternatively the cobalt determination can be made by the amyl alcohol extraction method. This method should be used when much nickel is present in the sample, and it is also recommended for acidic rocks. Transfer the cobalt solution, treated with stannous chloride as before, to a 1 × 8 cm. glass-stoppered tube, and add 1.5 ml. of ammonium thiocyanate solu-

tion (50 grams in 100 ml. of water) and 0.50 ml. of amyl alcohol. Treat the standards similarly. Shake vigorously for 10 to 15 seconds and compare the colors of the amyl alcohol layers by viewing the tubes transversely against a white background.

Run a blank on the reagents and apply a correction if required.

B. Soils

Since the cobalt content of soils may run below 1 p.p.m., a sensitive reagent such as nitroso-R salt or nitrosocresol must be used for its determination. When the total cobalt content of the sample is to be determined, hydrofluoric acid decomposition is advisable, but perchloric acid can be used in many cases.[19] The amount of copper in soils is usually not high enough to lead to interference in the nitroso-R salt method outlined below. Dithizone can be used to remove copper when necessary.

If hydrofluoric-perchloric acid decomposition is to be applied, take a 0.5 g. sample and follow the directions on p. 284. Otherwise digest 1 g. of finely powdered sample for 1 hour at the boiling temperature with 5 ml. of 60 per cent perchloric acid in a small covered beaker. Then fume off practically all of the perchloric acid. Add 20 ml. of 1 *N* hydrochloric acid and digest (covered) near the boiling point for 15 minutes. Filter through a small loose-textured paper, wash with 10 ml. of hot 0.1 *N* hydrochloric acid and then with water. Collect the filtrate and washings in a 50 ml. volumetric flask and dilute to volume.

Transfer 20 or 25 ml. of the mixed solution to a separatory funnel, add 10 ml. of 10 per cent sodium or ammonium citrate, and then ammonium hydroxide to give a *p*H of 8 to 9. If a precipitate should form, add more citrate. Shake the solution with 5 ml. portions of 0.01 per cent dithizone in carbon tetrachloride until the last portion still shows a green color after shaking for 1 minute. Wash the combined carbon tetrachloride extracts with a few milliliters of water containing a drop of 1:1 ammonia. Transfer the carbon tetrachloride solution of cobalt and other metal dithizonates to a small Erlenmeyer flask, evaporate to dryness, add 0.25 ml. of concentrated sulfuric acid and 0.25 ml. (or more if necessary) of 60–70 per cent perchloric acid, and heat at 200–250° C. until the solution is entirely colorless. Increase the temperature to fume off sulfuric acid and determine cobalt by Procedure B on p. 277.

[19] R. S. Holmes, *Soil Sci.*, **59**, 81 (1945), states that perchloric acid can be used for the decomposition of most soil samples; those high in unweathered minerals may not yield all their cobalt by this treatment. See this paper for the use of *o*-nitrosocresol as cobalt reagent.

C. Steel

Cobalt has been determined in steel by the nitroso-R salt method[20] and by the use of thiocyanate-acetone.[21] In the latter method, iron is removed by the use of zinc oxide. These procedures are primarily intended for relatively large quantities of cobalt and directions will therefore not be given here.

D. Bio Material

Most workers destroy organic matter by wet oxidation. Cobalt is best isolated by dithizone extraction from basic citrate medium. Ordinarily other separations are not needed; if the amount of copper present is large enough to affect the determination of cobalt by the nitroso-R salt method, it can be removed by extracting the acidic solution with dithizone before cobalt is isolated from the basic solution.

Directions are given below for the determination of cobalt by the use of nitroso-R salt and of *o*-nitrosocresol. The latter reagent provides the more sensitive determination because a small volume of immiscible solvent is used to extract the cobalt complex. As little as 0.03 γ of cobalt can be determined within approximately ± 5 per cent. On the other hand, the nitroso-R salt method is simpler (*cf.* p. 279).

1. Nitroso-R Salt as Reagent

§ Procedure[22]

Take 5 g. of sample (or more or less as may be required to give at least 0.2 γ of cobalt) and destroy organic matter with perchloric and nitric acids as described on p. 411. If it is desired to avoid the use of perchloric acid, decompose with sulfuric and nitric acids (p. 320). (For dry ashing, see p. 319.) When a colorless digest has been obtained, fume off all, or almost all, of the perchloric or sulfuric acid. Add 10 or 15 ml. of 1:2 hydrochloric acid and heat at the boiling point with stirring until practically all the residue has been brought into solution. If calcium sulfate remains undissolved,

[20] F. W. Haywood and A. A. R. Wood, *J. Soc. Chem. Ind.*, 62, 37 (1943), dissolve the sample in sulfuric and phosphoric acids (the latter decolorizes ferric iron), oxidize with nitric acid, and apply McNaught's method. See R. S. Young, E. T. Pinkney, and R. Dick, *Ind. Eng. Chem., Anal. Ed.*, 18, 474 (1946) for a similar procedure applied to metallurgical products.

[21] H. M. Putsché and W. F. Malooly, *Anal. Chem.*, 19, 236 (1947).

[22] These directions are similar to those of R. Q. Parks, S. L. Hood, C. Hurwitz, and G. H. Ellis, *Ind. Eng. Chem., Anal. Ed.*, 15, 527 (1943), which in turn are based on those of Marston and Dewey.[1] Among other recent procedures, see McNaught[8]; E. B. Kidson and H. O. Askew[11]; H. T. Macpherson and J. Stewart[11]; N. D. Sylvester and L. H. Lampitt, *J. Soc. Chem. Ind.*, 59, 57 (1940); D. J. Hiscox, *Sci. Agr.*, 27, 136 (1947).

add more acid and continue the digestion. Filter off any silica that may be present and, if the amount is comparatively large, treat with hydrofluoric acid in the usual way (p. 289) to recover any cobalt that may be present.

Add 10 ml. of 10 per cent sodium citrate to the hydrochloric acid solution and dilute to about 50 ml. Now add 1:1 ammonium hydroxide to give a *p*H of approximately 8.5 (*m*-cresol purple may be used as indicator). If a precipitate forms during the neutralization, add more citrate. Shake the solution for a minute with 10 ml. of a 0.02 per cent solution of dithizone in carbon tetrachloride, and transfer the carbon tetrachloride phase to another separatory funnel. Repeat the extraction with 10 ml. portions of dithizone until the color of the last extract is practically the same as that of pure dithizone.

Wash the combined carbon tetrachloride extracts with 5 ml. of water, and run the carbon tetrachloride into a small covered beaker. Evaporate the carbon tetrachloride at a low temperature and add 0.5 ml. of sulfuric acid and 0.5 to 1 ml. of 60 per cent perchloric acid. Evaporate to fumes of sulfuric acid, adding more perchloric acid if necessary to give a colorless solution. Finally evaporate off the sulfuric acid, avoiding overheating of the residue (which must dissolve in the citric acid solution subsequently added). Then determine cobalt according to the directions in Procedure B, p. 277.

2. Nitrosocresol as Reagent

The following method[14] has given recoveries of from 90 to 107 per cent, with an average of 97 per cent, of 0.2 γ of cobalt added to corn grain, turnip leaves, milk, and liver.

Special Reagents

Stock cupric o-nitrosocresol solution. To 900 ml. of water containing 6 g. of hydroxylamine hydrochloride and 15 g. of cupric chloride add 5 ml. of *m*-cresol. Then add 15 ml. of 30 per cent hydrogen peroxide with stirring. After standing 2 hours at room temperature, add 25 ml. of concentrated hydrochloric acid, and shake with successive portions of petroleum ether until all the reagent has been extracted. Wash the combined extracts several times with water and then shake with 50 or 100 ml. portions of 1 per cent aqueous cupric acetate solution until the petroleum ether becomes colorless (*ca.* 400 ml. of dark red solution of the copper complex will be obtained). Filter and store the reagent in a refrigerator. It is stable for some months.

Sodium nitrosocresol solution. Add 10 ml. of concentrated hydrochloric acid to 75 ml. of the cupric nitrosocresol solution and shake with 300 to 500 ml. of petroleum ether. Shake the petroleum ether phase with two 100 ml. portions of 0.01 *N* hydrochloric acid and then with two portions of redistilled water, 100 ml. each. Next shake the petroleum ether with 25 ml. portions of a solution obtained by adding 20 ml. of 1 *N* sodium hydroxide to 1 liter of sodium borate buffer (see below) until most of the color has left the petroleum ether. The resulting aqueous solution of the reagent can be kept for about a month with refrigeration.

Sodium borate buffer. 20 g. boric acid and 22.8 ml. 1.0 *N* sodium hydroxide in 1 liter redistilled water (*p*H 7.7–7.8).

Sodium diethyldithiocarbamate, 0.1 per cent aqueous solution. Shake with carbon tetrachloride to remove copper and any cobalt present.

Dithizone. 0.5 g. in 1 liter analytical-reagent carbon tetrachloride. Preserve the solution in a cold dark place.

Hydroxylamine-acetate buffer. 10 g. hydroxylamine hydrochloride and 9.5 g. anhydrous sodium acetate in 500 ml. redistilled water (*p*H 5.0–5.2).

Potassium nitrate, 5 per cent in water. It may be purified if thought necessary by adding sodium diethyldithiocarbamate and shaking with carbon tetrachloride.

Ammonium citrate. 400 g. in 1 liter of solution. Remove heavy metals by adding ammonia to give a *p*H of 8.5 and extracting with 25 ml. portions of dithizone solution until the aqueous phase remains orange. Remove the dithizone by extracting with carbon tetrachloride.

Ligroin. Eastman's, b.p. 70 to 90°. Distil over dilute, alkaline potassium permanganate and shake three times with water.

§ Procedure

Destruction of organic matter. This may be done by digestion with acids (p. 320) or by ignition. For the latter, heat the sample in a silica dish (only slightly etched) in a muffle furnace at 500–600° overnight. If ashing is not complete, add 5 or 10 ml. of 1:1 nitric acid and 1 ml. of potassium nitrate solution, evaporate to dryness, heat at 600°, and repeat the treatment with acid if required. When samples are high in silica, or for greater security in any case, ash in a platinum dish, and evaporate the residue to dryness with 3 or 4 ml. of hydrofluoric acid and 1 ml. of perchloric acid. Dissolve the ash by heating with 1:1 hydrochloric acid in appropriate amount. If any appreciable residue remains, continue the heating for an hour.

Separation of cobalt from iron. Transfer the acid solution to a small separatory funnel and add 1 ml. of ammonium citrate solution for each gram of original sample. Adjust the *p*H to 8.5 with ammonium hydroxide (phenolphthalein as indicator). If a precipitate forms add more citrate. Add 5 or 10 ml. of dithizone and shake vigorously for one-half minute. Draw off the carbon tetrachloride layer and repeat the extraction until the last portion of dithizone remains an unchanged green.

Evaporate the combined carbon tetrachloride extracts in a small beaker and add 2 ml. of perchloric acid (60 or 72 per cent). Cover the beaker with a watch glass and heat on a hot plate until the liquid is colorless. Then remove the cover glass and evaporate off the perchloric acid. Dissolve the residue in 5 ml. of 0.01 *N* hydrochloric acid and transfer to a separatory funnel.

Determination of cobalt. To the cobalt solution add 5 ml. of borate buffer and then sodium nitrosocresol solution dropwise until all copper has re-

acted as shown by the appearance of an orange color which is distinct from the pink of the copper complex. Finally add 1 ml. of reagent in excess. Now add a measured volume of ligroin, usually 4 or 5 ml., and shake for 5 minutes. Remove the aqueous phase and shake the ligroin with 5 ml. of 1 per cent copper acetate solution for 1 minute. Separate the water layer and wash the ligroin with a little water and then with 5 ml. of hydroxylamine-sodium acetate to reduce any ferric iron that may be present. Unless relatively much cobalt is present the ligroin solution will appear colorless. Transfer the ligroin to a 5 or 10 cm. absorption tube and obtain the transmittancy at 360 mμ (Corning filters Nos. 5860 and 4308 can be used in combination).

Run a blank through the procedure. As the reagent starts to decompose high blank values are obtained. With a final ligroin volume of 4 ml. and a 10 cm. tube the blank transmittancy should not be less than 95 per cent, compared to pure ligroin.

Note. Instead of dithizone, sodium diethyldithiocarbamate can be used to separate cobalt from iron if too much of the latter is not present. The use of the carbamate is advantageous with samples such as milk which contain much calcium and phosphorus and tend to give a precipitate at the *p*H required for the extraction of cobalt with dithizone. Cobalt carbamate can be extracted at the lower *p*H of 6.5, at which a precipitate is less likely to be obtained with such samples. To prevent the reaction of relatively much iron with carbamate, more citrate may have to be added and volumes are thus inconveniently increased. On the other hand, ferric iron does not react at all with dithizone and a sharper separation from cobalt can be effected with this reagent. If it is desired to use the carbamate separation, adjust the pH to 6.5 (bromthymol blue) after addition of citrate, add 5 ml. of sodium diethyldithiocarbamate, and shake with 10 or 20 ml. of carbon tetrachloride for 10 minutes. Then evaporate the carbon tetrachloride solution and destroy organic material in the residue with perchloric acid as described above.

CHAPTER XVI

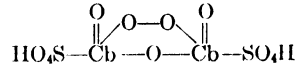
COLUMBIUM AND TANTALUM

These elements are lacking in sensitive characteristic color reactions and their determination in minute amounts is rendered still more difficult by the lack of good methods for the isolation of traces. The tannin method of Schoeller[1] and his coworkers for the separation of these elements from each other and from other elements is intended mostly for use on samples in which columbium and tantalum make up a considerable fraction of the whole.

Phenylarsonic acid has been used for preliminary concentration of columbium and tantalum in silicate analysis.[2] Rankama[3] has employed salicylic acid[4] for enrichment of columbium and tantalum in the phenylarsonic acid precipitate containing titanium and zirconium.

Columbium

Columbium is more amenable than tantalum to colorimetric determination. A characteristic reaction of columbium is that with hydrogen peroxide, which in a strong sulfuric acid solution produces a yellow color.[5] The peroxy compound is thought to have the following composition in sulfuric acid medium (Schaeppi and Treadwell):



Unfortunately this reaction is not very sensitive. The color given by titanium under these conditions is greatly weakened by the addition of

[1] W. R. Schoeller, *The Analytical Chemistry of Tantalum and Niobium.* Chapman and Hall, London, 1937. For the determination of small amounts (tenths of a per cent) of tantalum in columbium oxide see p. 131 of that book, and for the converse p. 132. An application of the tannin method to the determination of small amounts of columbium and tantalum in wolframite is described by J. A. Tschernichow and M. P. Karsajewskaja, *Z. anal. Chem.*, **98**, 97 (1934).

[2] I. P. Alimarin and B. I. Frid, *Mikrochemie*, **23**, 17 (1937).

[3] K. Rankama, *Bull. comm. geol. Finlande*, No. 133 (1944).

[4] J. H. Müller, *J. Am. Chem. Soc.*, **33**, 1506 (1911).

[5] G. Thanheiser, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, **22**, 255 (1940); P. Klinger and W. Koch, *Arch. Eisenhüttenw.*, **13**, 127 (1939).

concentrated phosphoric acid (enough to make its concentration 40–50 per cent by volume), whereas the color given by columbium persists. Tantalum yields no color, even in the absence of phosphoric acid. The smallest amount of columbium that can be detected visually when 0.5 ml. of sample solution (as of a potassium hydroxide fusion) is treated with 0.25 ml. of 3 per cent hydrogen peroxide and 5 ml. of concentrated sulfuric acid amounts to about 0.02 mg. (examination in a 1.8 × 15 cm. color comparison tube). The very faint yellow color remains when 5 ml. of phosphoric acid is added. Under the same conditions (phosphoric acid present), 0.5 mg. of titanium yields a very faint color equivalent to 0.02–0.04 mg. of columbium. However, even larger amounts of titanium may be present if its effect is compensated by the addition of a like amount to the comparison solution. The quantity of titanium in the sample can be determined with hydrogen peroxide in dilute acid solution in which columbium gives no color.

Columbium, unlike tantalum, can be reduced to the trivalent state by various metals such as zinc and tin in acid solution. In this way a brown color is obtained which can be made the basis of a colorimetric method. Thus, Meimberg treats the sample solution in concentrated hydrochloric acid with zinc and compares with a series of similar standards.[6]

Thiocyanate reacts with trivalent columbium in acid solution to give a yellow-orange product of strong color and it is possible to base a quantitative method on this behavior.[7] The following directions are given by Alimarin and Podval'naya. The mineral or ore is fused with potassium pyrosulfate, and columbium and tantalum are isolated with pyrogallol and phenylarsonic acid (*cf.* Alimarin and Frid[8]). The oxides are fused with pyrosulfate, the melt is taken up in 10 to 20 ml. of hot 15 per cent tartaric

[6] E. Meimberg, *Z. angew. Chem.*, **26**, 83 (1913). This method was applied in determining columbium in tantalite. The latter was dissolved in hydrofluoric and hydrochloric acids and the bulk of the tantalum separated as potassium fluotantalate. For reduction of columbium in phosphoric acid solution with zinc see Giles, *Chem. News*, **95**, 37 (1907).

[7] M. E. Pennington, *J. Am. Chem. Soc.*, **18**, 51 (1896); J. Moir, *Chem. News*, **113**, 256 (1916) (both qualitative). Gentry and Sherrington, *Analyst*, **73**, 65 (1948), obtained a strong color when adding thiocyanate to a hydrochloric acid solution of columbium which had been reduced with tin amalgam. The color intensity is reported to depend critically upon the acid concentration. I. P. Alimarin and R. L. Podval'naya, *Zhur. Anal. Khim.*, **1**, 30 (1946), worked out a quantitative method with stannous chloride as reducing agent.

acid and diluted with water to 25 or 100 ml. depending upon the size of sample. An aliquot containing 0.008 to 0.2 mg. of columbium oxide is mixed with 5 ml. of 20 per cent potassium thiocyanate, 3 ml. of 15 per cent stannous chloride, and 5 ml. of concentrated hydrochloric acid. (The concentration of potassium thiocyanate in the final mixture should be 7–15 per cent and that of hydrochloric acid 30–50 per cent.) Extract the yellow columbium thiocyanate complex with 10 ml. of ether and evaluate the color intensity in any convenient way. The maximum color intensity is attained 30–40 minutes after mixing the reagents. Interfering elements are molybdenum, tungsten, uranium, vanadium, iron, chromium, cobalt, copper, gold, and platinum. The color is bleached by fluoride, sulfate, phosphate, arsenate, and, especially, by oxalate.

Among other reagents for columbium may be mentioned pyrogallol,[8] thymol,[9] and quinalizarin. In concentrated sulfuric acid solution the latter reagent gives a red color with small amounts of columbium and also tantalum; quinalizarin alone has a violet color in sulfuric acid. This reaction is a little more sensitive than the hydrogen peroxide test. If 0.25 ml. of 0.01 per cent quinalizarin solution in acetone is added to 5 ml. sulfuric acid (> 90 per cent) containing 0.01 mg. of columbium, a reddish violet color is produced which is slightly different from that of a blank. The effect of other metals has not been studied. Minute amounts of boric and germanic acids give a blue color under these conditions.

Columbium (but not tantalum) compounds fused with sodium fluoride on a platinum wire give a bead which fluoresces in the near ultraviolet. Uranium gives a much stronger fluorescence under the same conditions (p. 597).

Tantalum

It has been reported that tantalum can be separated from columbium with sodium hypophosphite.[10] In the presence of ammonium oxalate, only tantalum is precipitated; the sensitivity is 1:1,000,000. The oxides

[8] N. F. Krivoshlykov, *Trudy LKKhTI*, 1939, No. 7, 103; *Chem. Abstracts*, **34**, 2729. The oxides are fused with sodium bisulfate, the solution of the melt treated with ammonium oxalate acidified with sulfuric acid and an equal volume of 5 per cent pyragallol solution saturated with sodium sulfite added. A yellow color (not sensitive) is obtained in the presence of columbium. Titanium gives a similar color. It is said that tantalum does not interfere in alkaline solution. See further M. S. Platonov and N. F. Krivoshlykov, *Trudy Vsesoyuz. Konferentsii Anal. Khim.*, **2**, 359 (1943); *Chem. Abst.*, **39**, 3492. I. P. Alimarin and B. I. Frid, *ibid.*, **2**, 333 (1943); *Chem. Abst.*, **39**, 3751.

[9] J. Moir, *loc. cit.*

[10] I. P. Alimarin and T. A. Burova, *J. Appl. Chem.* (U. S. S. R.), **18**, 289 (1945); *Chem. Abst.*, **40**, 3362.

are first fused with potassium pyrosulfate and the melt is dissolved in ammonium oxalate solution.

Pyrogallol gives an insensitive color test with tantalum in *acid* solution.[11] Columbium and titanium are said to be without effect. A number of qualitative reactions for tantalum have been described, involving the use of rhodamine B, "brilliant green," gentian violet, and methylene blue.[12] Many metals interfere.

[11] Krivoshlykov, *loc. cit.* The limit of the reaction is stated to be 0.05–0.07 mg. Ta_2O_5 per milliter. See also Platonov and Krivoshlykov, *loc. cit.*; Alimarin and Frid, *loc. cit.*; Thanheiser, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, **22**, 255 (1940).

[12] M. Y. Shapiro, *J. Applied Chem. U. S. S. R.*, **11**, 1028 (1938); *Chem. Abstracts*, **33**, 1624 (1939).

CHAPTER XVII

COPPER

Copper is an important trace element, and a great deal of work has been done on methods for its determination in minute amounts. The methods now available are in the main very satisfactory and leave little to be desired.

I. Separations

A. Sulfide Precipitation

Copper must frequently be separated from other constituents of the sample before it can be determined by the methods described in II. Precipitation of copper in dilute acid solution with hydrogen sulfide immediately suggests itself as a method of separation from iron, nickel, cobalt, manganese, etc., and, perhaps less successfully, from zinc. No critical study of the separation of micro quantities of copper with hydrogen sulfide has been made. Although some workers have reported incomplete recovery of copper by this method, others have used it with apparently good results.[1] The isolation of copper by precipitation as sulfide in weakly acidic solution has been investigated by Greenleaf,[2] who found lead to be a better collector than cadmium or tin (Table 47). The time elapsing between precipitation and filtration of the precipitate has a considerable effect on the completeness of the copper recovery. Thus Greenleaf found that in precipitating 5 γ quantities of copper with hydrogen sulfide in the presence of 5 mg. of lead, the amounts recovered varied as follows depending upon the treatment after precipitation: 4.57 and 4.54 γ when the mixture was shaken 30 minutes after hydrogen sulfide treatment; 5.41 and 4.85 γ when the mixture stood overnight; and 4.93, 4.74, 4.57, and 4.51 γ when it was allowed to stand 3 days. The recommended procedure for isolation of copper from solutions of decomposed foods calls for precipitation of copper sulfide from a medium having a *p*H of 2 and containing *ca.* 4 per cent of ammonium citrate and 5 mg. of lead as nitrate (volume 40–50 ml.). The stoppered flask is shaken for 1 hour after passage of hydrogen sulfide for a few minutes, or allowed to stand overnight. The precipitate is washed

[1] *E.g.*, S. Ansbacher, R. E. Remington, and F. B. Culp, *Ind. Eng. Chem., Anal. Ed.*, **3**, 314 (1931); E. J. Coulson, *J. Assoc. Official Agr. Chem.*, **19**, 219 (1936).

[2] C. A. Greenleaf, *J. Assoc. Official Agr. Chem.*, **24**, 337 (1941).

TABLE 47

PRECIPITATION OF COPPER AS SULFIDE WITH VARIOUS COLLECTORS

The solution, having a volume of 50 ml., was adjusted to *p*H 2, hydrogen sulfide was passed in, and the precipitate filtered off immediately.

Collector	Cu taken γ	Cu found γ
Paper pulp	5.0	0.4
	10.0	9.1
	50.0	43.3
Cadmium, 5 mg.	5.0	0.5
	10.0	5.7
	50.0	46
Lead, 5 mg.	5.0	4.2, 3.5
	10.0	8.3, 11.3
	15.0	13.8
	20.0	17.8
	50.0	51.7
Tin, 10 mg.	5.0	3.2
	10.0	6.5
	15.0	8.4
	20.0	16.5

with a 0.1 *N* hydrochloric acid solution containing 3 per cent sodium sulfate and saturated with hydrogen sulfide.

High concentrations of chloride prevent the complete precipitation of copper sulfide, even in neutral solution. The following figures show the magnitude of the effect:[3]

Percentage NaCl	Cu in 800 ml. of solution, mg.	
	Taken	Found
20	0.2	0.05
20	0.5	0.35
20	1.0	0.77
10	0.20	0.16, 0.18
5	0.20	0.20, 0.20
2.5	0.20	0.20, 0.20

B. DITHIZONE EXTRACTION

The extraction of copper by dithizone from acid solution is a good method of separation from many metals. The equilibrium constant for keto cupric dithizonate has not been exactly determined but a somewhat rough determination has yielded the value 1×10^{10} for:

[3] W. Biltz and E. Marcus, *Z. anorg. Chem.*, 64, 236 (1909).

$$K = \frac{[CuDz_2']_{CCl_4}}{[Cu^{++}]_{H_2O}} \times \frac{[H^+]^2_{H_2O}}{[Dz]^2_{CCl_4}}.$$

The determination was made in approximately 1 *N* hydrochloric acid, and concentrations instead of activities were substituted into the preceding expression.

This tentative value of *K* may be used to calculate the approximate completeness of extraction of copper from a 1 *N* hydrochloric acid solution. Suppose 50 ml. of 1 *N* hydrochloric acid containing 10 γ of copper are shaken with 10 ml. of 0.01 per cent dithizone in carbon tetrachloride. How much copper will be left in the aqueous phase when equilibrium is attained? The ratio of concentrations of copper in the carbon tetrachloride and aqueous phase is given by:[4]

$$\frac{[CuDz_2']_{CCl_4}}{[Cu^{++}]_{H_2O}} = K \times \frac{[Dz]^2_{CCl_4}}{[H^+]^2_{H_2O}} = 10^{10}(4 \times 10^{-4} - 3.2 \times 10^{-5})^2$$

$$= 1.35 \times 10^3.$$

$$\therefore [Cu^{++}]_{H_2O} = \frac{[CuDz_2']_{CCl_4}}{1350} = \frac{1.6 \times 10^{-5}}{1350} = 1.2 \times 10^{-8}.$$

This concentration corresponds to about 0.04 γ of copper in 50 ml. of aqueous solution. Even making allowance for the uncertainty in the value of *K*, it may be concluded that copper can be practically completely extracted from 1 *N* hydrochloric acid solution under these conditions, especially if a double extraction is made. In practical work the acidity is generally 0.1–0.2 *N* instead of 1 *N* so that the factor of safety is further increased.[5] The extraction is more rapid in less acidic solutions and it is inadvisable to use higher acidities unless the separations require it. Electrolytes are said to hinder the extraction of copper even at a *p*H of 2 and in the presence of much of these, extraction at *p*H 3 has been recommended.[6] It is important to use carbon tetrachloride free from inhibiting impurities (p. 303).

The question of the extent to which certain other heavy metals such as bismuth, zinc, nickel, cobalt and lead are extracted by dithizone in acid solution cannot be answered exactly until the equilibrium constants of these dithizonates have been determined. It may be expected that sharp sepa-

[4] For simplicity in calculation, it is assumed that all of the copper enters the carbon tetrachloride phase. The final result shows that this approximation is justified.

[5] C. H. Schonk, *Chem. Weekblad*, **42**, 295 (1946), claims that chromic ion acts as a catalyst in speeding up the reaction between dithizone and copper, so that in its presence copper can be determined by extractive titration at a *p*H of 2.8. He also states that the reaction takes place more rapidly in the presence of foreign substances in general (except electrolytes at high concentration), and that commercial dithizone provides a faster reaction than the purified product.

[6] C. A. Greenleaf, *J. Assoc. Official Agr. Chem.*, **28**, 269 (1945).

rations can be made from manganese, nickel, cobalt (*cf.* p. 271), lead, and perhaps from moderate amounts of zinc (see p. 617). There is some evidence that nickel and cobalt in low concentrations are not extracted to an appreciable extent even at as high a *p*H as 3. Ferric iron does not form a dithizonate (*cf.* p. 106), but it slightly oxidizes dithizone. However, moderate amounts of iron do not interfere (see p. 316).

The other metals reacting with dithizone in mineral acid solution (0.1–1 *N*) are palladium, gold, silver, mercury, and bismuth, the latter incompletely when only a moderate excess of dithizone is used in the extraction as is usually the case. So far as silver, mercury, and bismuth are concerned, the use of alkali halides or halogen acids as precipitants and complex formers permits the separation of copper from these metals, but the possibilities have not been fully explored. Although the point does not seem to have been tested, it seems likely that much silver can be separated from cupric copper by precipitation as the chloride. The minute amount of silver remaining in solution probably will react very incompletely in acid chloride solution with dithizone, and still less so if a little iodide is added. Mercury (II) does not react with dithizone in a bromide solution at *p*H 1 in consequence of the formation of slightly dissociated $HgBr_4^=$. The separation of copper from small amounts of mercury on the basis of this behavior has been carried out by shaking the chloroform solution of the dithizonates of the two metals (20 ml.) with 5 ml. of 40 per cent potassium bromide solution and 50 ml. of 0.25 *N* hydrochloric acid.[7] Copper remains in the chloroform layer, mercury goes into the aqueous phase.

Any bismuth which has been coextracted with copper from acid solution may be removed from the organic solvent layer by shaking the latter with an equal volume of 2 per cent potassium iodide solution in 0.01 *N* hydrochloric acid.[8] The aqueous phase is then shaken with 5 or 10 ml. of 0.001 per cent dithizone to recover any small amount of copper which may have gone into it. The following results were obtained by Greenleaf[8] in applying this method (*cf.* p. 301):

Cu taken, γ	Bi taken, γ	Cu found, γ
25	0	24 6
25	500	24.5
0	500	0.0

In another method for separating copper from bismuth, the aqueous solution of *p*H 3 is treated with potassium iodide and copper is extracted with a carbon tetrachloride solution of dithizone. Traces of coextracted bismith can be removed by washing the carbon tetrachloride extract with an iodide solution of *p*H 2.

[7] E. P. Laug and K. W. Nelson, *J. Assoc. Official Agr. Chem.*, **25**, 399 (1942).

[8] C. A. Greenleaf, *J. Assoc. Official Agr. Chem.*, **25**, 385 (1942).

Attempts to separate copper from mercury (II) by extracting the former from an aqueous iodide solution with a chloroform dithizone solution have not been successful.[9]

The destruction of cupric dithizonate and excess dithizone in the extracts, which must precede the determination of the separated copper, may be effected by evaporating the organic solvent and heating the residue with a mixture of sulfuric and perchloric acids[10] until an entirely colorless solution is obtained.

Another possible method of destroying the dithizonate and returning copper to the aqueous solution involves shaking the carbon tetrachloride solution with an acid permanganate solution and removing the excess of the latter together with manganese dioxide by treatment with a suitable reducing agent. This method has not been investigated for copper, but it gives good results in the case of mercury.

C. Miscellaneous Separations

Copper has been separated from small amounts of lead, zinc, and iron (II) by extracting its diethyammonium diethyldithiocarbamate complex with chloroform from 2 *N* hydrochloric acid solution.[11] Arsenic (III), bismuth, and mercury accompany copper.

An ion-exchange resin (Amberlite IR-100) has been used to isolate copper from milk and milk products.[12] The protein is precipitated and copper brought into ionic form by acidifying to a *p*H of 1 with perchloric acid. The *p*H of the filtrate is adjusted to approximately 5 and the solution is passed through a column of the resin. The adsorbed copper is liberated by running 2 *N* hydrochloric through the column. Virtually complete recovery is obtained.

Copper has been isolated from very dilute solutions by passing the latter through cotton that has been saturated with an alcoholic solution of sodium stearate and dried.[13] The adsorbed copper is eluted with hydrochloric acid.

Electrolytic deposition of copper is of some value in the isolation of traces.[14]

[9] R. F. Milton and J. L. Hoskins, *Analyst*, **72**, 7 (1947).

[10] N. D. Sylvester and L. H. Lampitt, *Analyst*, **60**, 377 (1935).

N. Strafford, P. F. Wyatt, and F. G. Kershaw, *Analyst*, **70**, 232 (1945).

[12] H. A. Cranston and J. B. Thompson, *Ind. Eng. Chem., Anal. Ed.*, **18**, 323 (1946).

[13] L. Seekles, E. Havinga, and R. Bijkerk, *Rec. trav. chim.*, **64**, 296 (1945). The method is applied in the determination of copper in bio material.

[14] See, for example, F. Grendel, *Pharm. Weekblad*, **67**, 913, 1050, 1345 (1930), and also p. 30 of this book.

II. Methods of Determination

There are innumerable organic compounds that give sensitive color reactions with copper, and many colorimetric methods have been described. The two most important colorimetric reagents are dithizone and sodium diethyldithiocarbamate.[15] Dithizone is the more sensitive reagent, but mercury and silver, as well as much iron, interfere in its direct use, and special measures must be taken when these are present. The diethyldithiocarbamate method may be applied in the presence of restricted amounts of iron as well as mercury and perhaps silver. On the other hand, manganese, nickel, and cobalt interfere in the carbamate method but not in the dithizone procedure. Bismuth interferes in both procedures but less so in the dithizone method than in the carbamate. The smaller amounts of copper determinable with dithizone will frequently make it the preferred reagent in trace analysis. The dithizone method has the further advantage of being carried out in acid solution, and complications due to precipitation of calcium, and other phosphates, which may occur in the carbamate method, are avoided. A disadvantage of dithizone is the relatively poor stability of its solutions.

A. The Dithizone Method

Copper reacts with dithizone (carbon tetrachloride solution) in dilute (0.1 *N*) mineral acid medium to form the keto complex (red-violet). Palladium, gold,[16] silver, and mercury (I and II) react under the same conditions, as already mentioned, and must be absent. Bismuth also reacts in acid solution, although less readily than copper, and leads to error if present in more than small amounts. Ferric iron oxidizes dithizone to a certain extent and may not be present in appreciable amounts; phosphate may be expected to reduce the interference of much iron. On the other hand metals such as lead, zinc,[17] cadmium, nickel,[18] etc., which do not react appreciably with dithizone in 0.1 *N* hydrochloric acid, are without effect unless present in high concentrations (*cf.* p. 97). The most generally

[15] Various derivatives of diethyldithiocarbamic acid also find use as sensitive copper reagents. Among these may be mentioned dihydroxyethyldithiocarbamic acid (p. 309) and diethylammonium diethyldithiocarbamate.[11]

[16] H. Fischer, *Angew. Chem.*, **50**, 919 (1937), states that cyanide in acid medium prevents the reaction of gold, and thiocyanate that of palladium. Schonk (*loc. cit.*) could not verify the effect of thiocyanate on palladium at *p*H 2.8.

[17] Schonk (*loc. cit.*) found that zinc begins to interfere at a concentration of 5 p.p.m. in a medium of *p*H 2.8 when the extractive technique is used in the determination of copper.

[18] Brown (footnote 21, p. 302) was able to determine 0 to 8 γ of copper with an error not exceeding 0.2 γ in the presence of 78 mg. of nickel; the solution was 0.1 *N* in hydrochloric acid.

applicable procedure for the determination of copper involves its isolation from an acidic aqueous solution by a preliminary extraction with a carbon tetrachloride solution of dithizone, if need be in the presence of bromide or iodide as complex formers, as described on p. 321 *et seq.* Such preliminary isolation of copper is a prerequisite to the general use of the directions given below. Sometimes when the amount of silver, mercury, and bismuth is small, a shorter total procedure can be used, in which a preliminary extraction of copper is not made.[19]

TABLE 48

DETERMINATION OF COPPER WITH DITHIZONE BY THE MIXED COLOR METHOD
(EFFECT OF SOME FOREIGN IONS AND HIGH ACIDITIES)

10 ml. aqueous solution (0.1 *N* in HCl) + 5 ml. *ca.* 0.001 per cent dithizone in CCl_4

Addition	Cu taken γ	Cu found γ
(0.5 *N* HCl)	3.0	2.85
(1.0 *N* HCl)	3.0	2.35
10 mg. Fe^{III}	0.0	1.5
1 mg. Zn	2.0	2.0
0.5 mg. Bi	2.0	2.5

The mono-color method (p. 100), cannot readily be applied in the determination of copper, because on washing the carbon tetrachloride solution of keto copper dithizonate with dilute ammonia or other alkaline solution to remove excess dithizone, slight transformation into the enol complex (brown) occurs.[20] The mixed-color method gives good results. It is very rapid and simple. Either a green or a red filter may be used in obtaining the transmittancy of the copper dithizonate-dithizone solution (compare Figure 35 and page 102). A green filter (or better monochromatic

[19] Thus G. H. Bendix and D. Grabenstetter, *Ind. Eng. Chem., Anal. Ed.*, **15**, 649 (1943), extract the slightly acidic solution (*p*H *ca.* 2, phosphate–citric acid buffer) with a measured volume of 0.0015 per cent dithizone in carbon tetrachloride, and then shake the extract with a 0.01 *N* hydrochloric acid solution of 2 per cent potassium iodide to decompose the dithizonates of silver, mercury, and bismuth. Copper is thus left alone in the carbon tetrachloride layer, in which it is photometrically determined. This method has been modified by S. L. Morrison and H. L. Paige, *Ind. Eng. Chem., Anal. Ed.*, **18**, 211 (1946), who make the final determination by the mixed color technique (see p. 320). Satisfactory results were obtained in determining 5 γ of copper in the presence of small amounts (0.2 to 1 mg.) of iron, tin, lead, zinc, cadmium, nickel, cobalt, manganese, and bismuth. Mercury and silver were found to interfere except in very small amounts.

[20] Various authors, however, have described monocolor methods. Where the highest accuracy is not sought such methods may be more or less satisfactory. See, for example, J. Schwaibold, B. Bleyer, and G. Nagel, *Biochem. Z.*, **297**, 324 (1938).

light of wave length 510 mμ) is to be preferred because a slight change in the dithizone solution after establishment of the standard curve has very little effect on the results.

It is also possible to measure the extinction of the cupric dithizonate-dithizone mixture at two suitable wave lengths (p. 104), the advantage being that the exact strength of the dithizone solution need not be known. More preliminary work is required in this method, but this may be justified

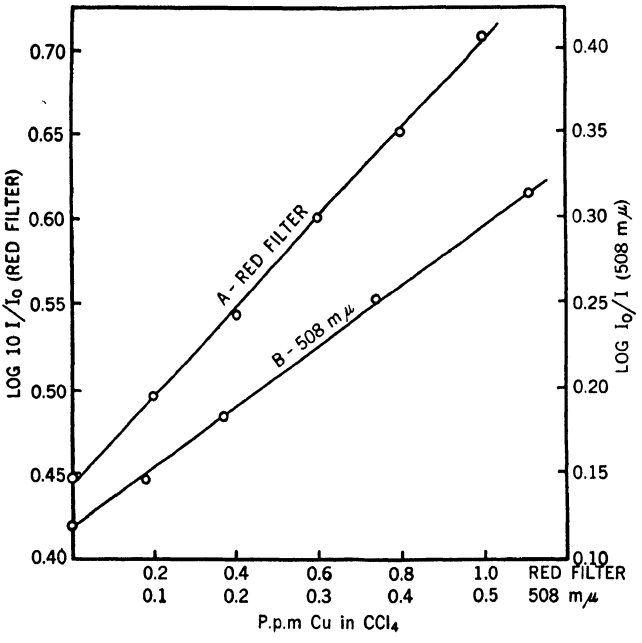


Fig. 35. Determination of copper with dithizone. *A*. Transmittancy obtained with a red filter (data of S. Anonsen). *B*. Transmittancy determined at 508 mμ. (From data of Liebhafsky and Winslow, *J. Am. Chem. Soc.*, **59**, 1969 (1937).) Stratum thickness 1 cm. in each case.

if many determinations are to be made over a period of time. A nomographic procedure based on this principle has been described, in which 525 and 650 mμ filters are used for the transmittancy measurements.[21]

Under the conditions recommended in the procedure, the relation between extinction and copper concentration is linear up to 1 p.p.m. of copper in the organic solvent. The aqueous solution may be 0.05–0.1 *N* in hydrochloric acid but not much stronger, especially if the excess of dithizone in the mixture is only slight. The use of this relatively high acidity is of ad-

[21] E. A. Brown, *Ind. Eng. Chem., Anal. Ed.*, **18**, 493 (1946). A similar procedure has been described by C. A. Greenleaf, *J. Assoc. Official Agr. Chem.*, **30**, 144 (1947).

vantage in diminishing interference from bismuth, zinc, and other metals that react at lower acidities. When such elements are absent, or if their concentration is low, the acidity can be reduced, for example to 0.01 *N*. It is very important that the carbon tetrachloride used be pure. A product of inferior quality may contain a substance which inhibits the reaction between copper and dithizone in acid solution, so that even after shaking for 5 minutes the reaction is incomplete.

Reagents

Dithizone, 0.001–0.0012 per cent (weight/volume) in carbon tetrachloride. The latter must be reagent-quality, free from any substances inhibiting the reaction with copper in acid solution. The solid dithizone need not be specially purified. As purchased, the solid generally contains 85–90 per cent dithizone. The 0.001 per cent solution is advantageously prepared daily by accurate dilution of a 0.01 per cent solution, which is quite stable if kept cold and in the dark (p. 108).

Water. This must be copper-free. Since distilled water frequently contains copper, redistil in an all-Pyrex apparatus.

Hydrochloric acid. The analytical reagent generally is nearly copper-free, although it may contain traces of mercury. Preferably the reagent-quality acid should be redistilled, especially if minimal amounts of copper are to be determined.

Standard copper solution, 0.01 per cent. Dissolve 0.1964 g. of clear uneffloresced crystals of $CuSO_4 \cdot 5H_2O$ in water, add enough hydrochloric (or sulfuric) acid to make the final acidity about 0.1 *N* and dilute to 500 ml. From this solution prepare a weaker one (conveniently 0.002 per cent) by dilution with 0.1 *N* hydrochloric acid. Alternatively the standard copper solution may be prepared by dissolving pure metallic copper in a slight excess of 1:1 nitric acid, diluting with water, boiling to remove all oxides of nitrogen, and diluting to volume.

§ Procedure

The sample solution may conveniently have a volume of about 10 ml. and should contain not more than 5 γ of copper if 5 ml. of dithizone are to be used. Make the solution 0.05–0.1 *N* (or 0.01 *N* if foreign metals that might react at this acidity are absent) in hydrochloric (or sulfuric) acid and shake for 2 minutes in a small separatory funnel with 5.0 ml. of 0.001 per cent dithizone (delivered from a covered buret or a pipet). If the color of the carbon tetrachloride is a red-violet, an excess of dithizone may not be present; in such a case add another 5 ml. portion (or less) of dithizone and shake again. The color of the final solution should deviate from that of a pure copper dithizonate solution.

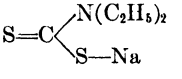
Allow a few drops of carbon tetrachloride to flow out of the funnel to displace any aqueous solution in the bore of the stopcock and dry the stem of the funnel with filter paper rolled around a thin glass rod. Deliver the carbon tetrachloride into a suitable cell and cover the latter to prevent evaporation. The solution should be entirely clear (filtration of the carbon tetrachloride through a small plug of glass wool to remove water droplets is

rarely necessary). Obtain the transmittancy either at 510 mμ (or in the range 500–550 mμ) or 625 mμ (or in the range 600–650 mμ). In constructing the reference curve use copper solutions having approximately the same volume and acidity as the sample solution. Establish a separate curve for volumes of dithizone other than 5 ml. The possibility of a change in the concentration of the dilute dithizone solution on standing must be borne in mind (slow decomposition, especially on exposure to light, and in warm weather, and possible evaporation of carbon tetrachloride). Once the calibration curve has been established, one or two points suffice for checking.

The standard series method may also be used in the determination of copper, in which case 1.8 × 15 cm. glass stoppered flat-bottomed tubes are employed. One to 4 γ of copper will give a suitable mixed color with 5 ml. of 0.001 per cent dithizone, although a smaller volume of dithizone will give more accurate results in the lower part of this range. By using 1 ml. of dithizone, a few tenths of a microgram of copper can be determined with considerable accuracy. If the approximate amount of copper present is not known, add only 0.5–1 ml. of dithizone, shake, and then if necessary add more until a suitable mixed color is obtained.

B. The Carbamate Method

The addition of an aqueous solution of sodium diethyldithiocarbamate to a slightly acid or ammoniacal solution of a cupric salt produces a brown



precipitate of the very slightly soluble copper carbamate. In very dilute solutions a colloidal suspension is obtained which is suitable for colorimetric comparison,[22] especially if it is stabilized by gum arabic[23] or similar substances. The copper carbamate is soluble in such organic solvents as amyl alcohol, amyl acetate, bromobenzene, and carbon tetrachloride. Generally one of these is used to extract the copper compound and the resulting yellow-brown solution is compared against a similar solution, or its light absorption is measured. In this way any difficulties associated with the use of a colloidal suspension are avoided, the interference of certain colored substances such as iron is prevented under proper conditions, and the sensitivity can be increased.

Many of the heavy metals give slightly soluble products with diethyldithiocarbamate, most of which are soluble to a greater or less extent in the

[22] T. Callan and J. A. R. Henderson, *Analyst*, **54**, 650 (1929).
[23] T. P. Hoar, *Analyst*, **62**, 657 (1937).

organic solvents mentioned. Some of these are white (colorless) or nearly so (zinc, indium, cadmium, mercury (II), silver, lead, tin) while others are strongly colored. Titanium and the rare earth metals do not give a coloration. Iron (III), yields a brown-black precipitate in acid or neutral medium, but does not react in ammoniacal citrate solution if the *p*H is 9 or above provided its amount is not too large.[24] The chief interfering metals in the copper determination are nickel, cobalt, and bismuth,[25] which in ammoniacal citrate solution give greenish yellow, dull green, and yellow precipitates respectively and impart similar colors to the organic solvent used in the extraction. The color intensities imparted by these salts, however, are much weaker (1/20–1/30)[25] than that given by the copper compound. The interference of nickel and cobalt can be prevented by adding 1 ml. of 0.5 per cent dimethylglyoxime solution to the sample solution before the addition of ammonia.[26] The nickel dimethylglyoxime precipitate is best separated by centrifugation. Cobalt remains in the aqueous layer, to which it imparts an orange color not extracted by carbon tetrachloride. Uranium yields a strong yellow-brown color with carbamate in neutral medium but not in a citrate solution containing ammonia. Manganese interferes to a considerable extent in the extraction procedure by imparting a pinkish color to the organic solvent layer. The formation of this color is associated with the air-oxidation of manganese in the basic solution, because no color is obtained if hydroxylamine hydrochloride is added. Fortunately this color is unstable, and the solution soon becomes virtually colorless if only small amounts of manganese are present; also, pyrophosphate reduces the coloration due to manganese.[27] The effect of manganese is smaller the higher the *p*H and the greater the citrate concentration. Small amounts of platinum, such as may be introduced when platinum dishes are used in the preparation of the sample, do not interfere.

When much iron and manganese is present, and they impart a color to the carbon tetrachloride layer, error can be avoided by washing the separated carbon tetrachloride with an equal volume of 0.5 *M* ammonium hydroxide.[28] The copper carbamate remains unchanged, whereas the ferric iron and manganese complexes are decomposed with formation of the hydroxides, which separate as a film on the glass if the concentration is sufficiently great.

[24] L. A. Haddock and N. Evers, *Analyst*, **57**, 495 (1932).

[25] The coloration given by bismuth is not destroyed by cyanide while that of copper is, and D. L. Drabkin, *J. Assoc. Official Agr. Chem.*, **22**, 320 (1939), has recommended that the interference of bismuth be avoided by obtaining the transmittancies of two sample solutions, one with cyanide, the other without, thus finding copper by difference.

[26] L. I. Butler and H. O. Allen, *J. Assoc. Official Agr. Chem.*, **25**, 567 (1942).

[27] E. J. Coulson, *J. Assoc. Official Agr. Chem.*, **20**, 178 (1937).

[28] F. Nydahl, *Z. anal. Chem.*, **116**, 315 (1939).

The *p*H of the solution has but a slight effect on the color intensity of the copper carbamate in the organic solvent in the range 5.7–9.2.[27]

The extraction procedure given below is applicable in the presence of small amounts of iron and manganese, as well as minor quantities of zinc, lead, tin (IV), arsenic, antimony, and other metals not giving colored diethyldithiocarbamates. The interference of small amounts of iron is prevented as already mentioned by carrying out the reaction in an ammoniacal solution having a *p*H of 9.0–9.2. It must be pointed out that the amount of iron which may be present is limited. Some procedures described in the literature must be applied with caution because they are more subject to interference from iron than is indicated. The procedure described here allows the presence of 5 mg. of ferric iron, but not much more, in 25–30 ml. of solution containing 1 g. of ammonium citrate.[29] Pyrophosphate probably would be more effective than citrate in preventing the interference of iron, but its use leads to difficulties in the presence of calcium which gives a precipitate in ammoniacal solution. In the presence of citrate (*p*H 9.0) small amounts of calcium phosphate yield no precipitate but larger amounts give a turbid solution, and results for copper then tend to be low. As much as 0.5 mg. of manganese may be present if the transmittancy of the carbon tetrachloride extract is determined after 20 minutes with the aid of a blue filter. It appears that appreciable amounts of zinc tend to give low results, presumably by combining with the reagent. Unfortunately the amount of diethyldithiocarbamate cannot be increased without increasing the error due to iron.

Carbon tetrachloride, chloroform, bromobenzene, amyl alcohol, and iso-amyl acetate have been used as extractants, the first being the most popular. Chloroform has the advantage of dissolving more of the copper carbamate than does carbon tetrachloride, so that practically all of the colored product can be removed in one extraction.[30] It has the disadvantage of being more soluble in water. Solvents lighter than water are inconvenient to use.

The relation between the copper concentration and the extinction of the organic solvent solution is linear, or very nearly so, if monochromatic light is used. With a green filter the relation was found to be practically linear up to a concentration of 5 p.p.m. of copper in carbon tetrachloride, and with a blue filter up to 2.5 p.p.m. or even higher, depending on the characteristics of the filter. The use of a blue filter permits more accurate determination of small amounts of copper than does a green filter, and moreover the former is better when iron and manganese are present.

[29] For a procedure permitting the presence of as much as 200 mg. of iron, see P. Karsten, S. C. Rademaker, and J. J. Walraven, *Anal. Chim. Acta*, **2**, 705 (1948).

[30] H. Barnes, *Analyst*, **71**, 578 (1946).

One portion of carbon tetrachloride does not extract all of the copper diethyldithiocarbamate,[31] but this is immaterial if the sample solution and the copper solutions for the establishment of the standard curve have approximately the same volume (±5 per cent) and the shaking is sufficiently long and vigorous to assure attainment of equilibrium. If preferred, two extractions can be made, in which case the length of shaking becomes less critical.

Solutions of copper diethyldithiocarbamate in carbon tetrachloride or iso-amyl acetate are rather stable in the dark, no appreciable change in

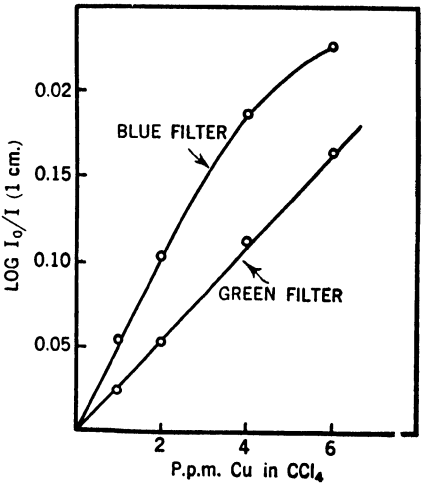


Fig. 36. Determination of copper with sodium diethyldithiocarbamate after extraction with carbon tetrachloride (30 ml. aqueous phase, 5 ml. carbon tetrachloride).

color intensity occurring in a period of several hours. Exposure to light causes fading (Table 49). It is stated that a carbon tetrachloride solution containing the equivalent of 27.5 γ of copper in 25 ml. showed only 2.5 γ after standing for 3 hours in diffuse daylight; there was no change after a few hours' exposure to artificial light.[32]

[31] From 90 to 95 per cent of the total copper is found in the carbon tetrachloride phase when 10 ml. of the latter solvent are shaken with 35 ml. of aqueous solution containing 1 g. of ammonium citrate and 1 ml. of 0.1 per cent sodium diethyldithiocarbamate and having a *p*H of 9 (data of R. W. Geiger). The addition of 1 g. of ammonium sulfate does not change the amount of copper extracted. The fraction of the copper going into the carbon tetrachloride phase depends upon the carbamate concentration. Nydahl[33] found practically all of the copper to be extracted with one portion of carbon tetrachloride when 10 ml. of 0.1 per cent carbamate reagent was present in 60 ml. of sample solution, or about 5 times as much as in the preceding experiments.

[32] J. F. Reith, J. T. L. B. Rameau, E. G. Mulder, L. Seekles, L. C. E. Kniphorst, and W. B. Deijs, *Chem. Weekblad*, **43**, 106 (1947).

TABLE 49

FADING OF COLOR OF COPPER DIETHYLDITHIOCARBAMATE IN CARBON TETRACHLORIDE ON EXPOSURE TO LIGHT[a]

(Solution kept in separatory funnel; 1.5 p.p.m. of Cu in CCl_4.)

Conditions	Extinction (blue filter, 1 cm.)		
	10 min.	45 min.	90 min.
Darkness	0.217	0.217	0.219
Near window, cloudy day	0.210	0.128	0.099
Near window, sunny day (not in direct rays of sun)	0.205	0.122	0.077
Desk top, 12 feet from window	0.209		

[a] Data obtained by R. W. Geiger, University of Minnesota, 1947.

TABLE 50

DETERMINATION OF COPPER WITH SODIUM DIETHYLDITHIOCARBAMATE AFTER EXTRACTION WITH CARBON TETRACHLORIDE

20.0 γ Cu taken in each determination. Aqueous phase (30 ml.) contained 1 g. ammonium citrate and had *p*H 9.0–9.2. 1.0 ml. 0.1% sodium diethyldithiocarbamate; 5 ml. CCl_4 for extraction.

Foreign substances	Cu found	
	Green filter γ	Blue filter γ
5 mg. Fe^{III}	19.8	20.0
10 mg. Fe^{III}	21.5	
0.5 mg. Mn		
Immediate reading	26	22.5
Reading after 10 min.		20.8
Reading after 20–25 min.	21.0	19.8
0.5 mg. Mn + 5 mg. Fe^{III}		
Immediate reading	31	23
Reading after 15 min.	23	21.0
0.5 mg. Ni	>50	
2 mg. Zn	17	16
0.5 mg. Bi	18	24
2 mg. Hg		21.0
20 mg. Ca + 250 mg. $(NH_4)_2HPO_4$ (turbid solution)	18.5	18.0

Reagents

Ammonium citrate, 20 g. in 100 ml. of solution.

Sodium diethyldithiocarbamate, 0.1 per cent aqueous solution. Preserve in a brown bottle; the solution is stable for some weeks.

Standard copper solution. See p. 303.

Carbon tetrachloride, analytical reagent. Products whose purity is not certain should be shaken with strong sulfuric acid, washed with water, dried with sodium hydroxide, and distilled.

§ Procedure

The sample solution may conveniently have a volume of 10–20 ml. and may contain up to 40 γ of copper.[33] Not more than 5 mg. of iron or 0.5 mg. of manganese should be present. Iron must be in the ferric state. Add 5 ml. of ammonium citrate solution and adjust the *p*H to 9–9.2 by the addition of ammonium hydroxide. This may be done by adding 2–3 drops of thymol blue to the solution and using a buffer solution of *p*H 9.0–9.2 for comparing the color. If much iron is present, transfer a drop of the sample to a spot plate when the approximate desired *p*H has been reached, add a very small drop of indicator, and compare against a drop of buffer solution. Cool the solution to room temperature if necessary and dilute to 25 or 30 ml. ($\pm$1 ml. if only one extraction is to be made).

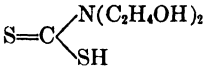
Add 1.0 ml. of carbamate solution and shake for 2.0 minutes in a separatory funnel with exactly 5 ml. of carbon tetrachloride. (Alternatively, extract with a 5 and a 4 ml. portion of carbon tetrachloride, shaking 1 minute each time, and make up to 10 ml. with about 1 ml. of carbon tetrachloride which has been used to rinse the separatory funnel after the second extraction.) Allow the carbon tetrachloride layer to settle and when it is free from water droplets run it directly into a suitable cell, after drying the stem of the funnel with a piece of filter paper rolled around a thin glass rod. If necessary, the carbon tetrachloride can be filtered through a small plug of glass wool. Use a blue or green filter or preferably monochromatic light of 440 mμ wave length in obtaining the transmittancy of the carbon tetrachloride solution (see above) and keep the cell covered to prevent evaporation. If the presence of appreciable manganese in the sample solution is known or suspected, allow the carbon tetrachloride to stand for 20 minutes before determining the transmittancy. These operations should be carried out in artificial light, or in subdued daylight with as little exposure to illumination as practicable (Table 49).

In constructing the reference curve employ copper solutions which have been treated exactly like the sample solution, and whose final volume is the same as that of the latter.

Dihydroxyethyldithiocarbamic acid as copper reagent. Geiger and Müller were the first to advocate the use of this compound for the colorimetric determination of copper.[34] It forms a yellow-brown soluble copper (II)

[33] More copper may be present if the volume of carbon tetrachloride used in the subsequent extraction is increased above 5 ml.

[34] E. Geiger and H. G. Müller, *Helv. Chim. Acta*, 26, 996 (1943)



complex salt, which cannot be extracted by carbon tetrachloride. The color intensity with copper is constant in the *p*H range 1.4 to 9 if the readings are made soon after addition of the reagent; after 1 hour the intensity is constant in the range 4.7 to 9, and after 16 hours in the range 6 to 8.4. The decrease in color strength on standing is due to decomposition of the reagent; on addition of more reagent the color is restored to its original value. The alkali metals, aluminum, arsenic, barium, calcium, cadmium, chromium, mercury, manganese, lead, strontium, titanium, zinc, and tin, do not change the transmittancy of the copper carbamate solution (1 p.p.m. of copper with 10 p.p.m. of the foreign metal) according to the authors. Silver, iron (III), nickel, and cobalt yield colored solutions. Small amounts of these metals can be prevented from interfering by addition of thiosulfate (for silver), sodium hexametaphosphate (for iron), and cyanide (for nickel and cobalt).

The reagent is prepared by treating 10 g. of diethanolamine in 85 ml. of methyl alcohol with 1.0 g. of carbon disulfide and diluting to 100 ml. with methyl alcohol. The solution is indefinitely stable in a closed container.

Geiger and Müller give the following directions for the determination. Add 5 ml. of 0.5 *M* sodium bicarbonate solution to the copper solution (*p*H then 7 to 8). In the presence of nickel and cobalt in amounts approximately equal to that of copper, add potassium cyanide and adjust the *p*H to 4 with hydrochloric acid and sodium citrate. If iron is present (as much as 10 p.p.m in the final solution), add 0.5 g. of sodium hexametaphosphate (Calgon). Add 3 to 10 drops of the reagent solution, dilute to volume (*e.g.*, 100 ml.), and obtain the transmittancy at 432 mμ.

This procedure has been modified by Woelfel,[35] who gives the following directions for the determination in the absence of much iron and other metals that give precipitates with pyrophosphate which is added as complex former. The solution should contain 2 to 10 milliequivalents of mineral acid and not more than 0.2 mg. of copper and 10 mg. of ferric iron. Dilute to 50 ml., add 1 ml. of 3 per cent sodium pyrophosphate solution for every 2 mg. of iron present, and adjust the *p*H to 5 or 6 with sodium acetate. If no turbidity develops in 5 minutes add 1 ml. of carbamate reagent, dilute to 100 ml. and determine the transmittancy at 430–440 mμ. Beer's law holds up to 4 p.p.m. at least of copper.

In the foregoing procedure low concentrations of aluminum, barium, calcium (400 p.p.m.), cadmium, lead manganese, tin (IV), and zinc cause

[35] W. C. Woelfel, *Anal. Chem.*, **20**, 722 (1948).

trouble by producing turbidities. Bismuth, cobalt, nickel, silver, and uranium give colored products with the reagent. Mercury (I and II) and tin (II) hinder development of the copper color.

Consult the paper of Geiger and Müller for the use of other substituted amides of dithiocarbonic acid as copper reagents.

C. Other Methods

No useful purpose would be served in listing here all the other colorimetric methods that have been proposed for the determination of copper.[36] Many of these methods are of slight importance from the practical standpoint. However, a few methods, of greater or less utility, may be mentioned.

The blue color given by ammonia with cupric salts is not sufficiently strong to be of much value in trace analysis.[37] More sensitive is the reaction with strong hydrochloric acid (yellow color) or hydrobromic acid (red-violet color),[38] but iron gives even a stronger color. However, it is possible to distinguish between copper and ferric iron in strong hydrochloric acid by spectrophotometric measurement. In this medium iron absorbs strongly in the ultraviolet but very little above 550 mμ, whereas copper absorbs strongly in the red and infrared. At the wave length of maximum absorption by copper, 970 mμ, the sensitivity of the nickel reaction is $^1/_{170}$ that of copper, and the sensitivities for iron and cobalt are still smaller.[39]

Potassium ferrocyanide gives a moderately sensitive reaction with cupric ions; the colloidal red-brown precipitate may be stabilized with gelatin.[40]

Potassium ethyl xanthate gives a reaction with copper that is similar to the one produced by diethyldithiocarbamate but less satisfactory.

Rubeanic acid (dithiooxamide) has been used to some extent in the determination of copper.[41] In an acetic acid-acetate medium it yields a very slightly soluble green-black cupric salt, which can be kept in colloidal dispersion by the use of gum arabic or other protective colloid. Among interfering elements may be mentioned iron, nickel, cobalt, silver, mercury, platinum, and palladium. Procedures have been given for the determina-

[36] For a comparative study of many colorimetric methods for copper see R. H. Müller and A. T. Burtsell, *Mikrochemie ver. Mikrochim. Acta*, **28**, 209 (1940); *Chem. Abstracts*, **34**, 7776 (1940).

[37] Various amines have been recommended as more satisfactory than ammonia. One of these is tetraethylenepentamine, which according to T. B. Crumpler, *Anal. Chem.*, **19**, 325 (1947), is 3.5 times as sensitive as ammonia for copper.

[38] G. Denigès and E. Simonot, *J. pharm. chim.*, **11**, 186 (1915).

[39] P. Giesecke, *Am. Inst. Mining Metall. Engrs., Tech. Publ.* No. **1740**, p. 13 (1944).

[40] H. Hahn, R. Juza, and R. Langheim, *Z. anal. Chem.*, **110**, 270 (1937).

[41] E. J. Center and R. M. MacIntosh, *Ind. Eng. Chem., Anal. Ed.*, **17**, 239 (1945); N. L. Allport and G. H. Skrimshire, *Quart. J. Pharm. Pharmacol.*, **5**, 461 (1932).

tion of relatively small amounts of copper in bearing metal and similar alloys,[42] ores,[43] and steel.[44]

Cuprous copper in ammoniacal solution (reduction with hydroxylamine hydrochloride) gives an orange color with *o*-phenanthroline in the presence of a miscible organic solvent.[45]

A method which has been much used in the past involves the extraction of copper pyridine thiocyanate, $[Cu(C_5H_5N)_2](CNS)_2$, with chloroform or other solvent, to which a green color is imparted.[46]

For the use of other reagents such as salicylic acid, and *m*-benzaminosemicarbazide see the book of Snell and Snell.[47] The dye Benzo Fast Yellow 5 GL (C.I. 546, diphenylurea-*p,p'*-disazo-bis-salicylic acid) has been shown to be a very sensitive reagent for copper (0.1 p.p.m. can be detected spectrophotometrically), but it is not specific.[48]

III. Applications of the Dithizone and Carbamate Methods

A. Silicate Rocks

The following procedure for copper is based on one[49] developed for the simultaneous determination of copper, zinc, and lead in silicate rocks. The method involves separation of these and other reacting heavy metals by extraction of the basic solution of the decomposed sample with dithizone. The carbon tetrachloride solution of the dithizonates is then shaken with dilute (0.01–0.02 *N*) hydrochloric acid which decomposes lead and zinc dithizonates, transferring these metals to the aqueous phase, and leaving copper dithizonate with more or less of the nickel and cobalt in the carbon tetrachloride.

If only copper is to be determined it would be more convenient to extract it directly from the acid (0.2–0.3 *N*) solution of the decomposed sample with dithizone. There are no data available to show the reliability of this method, but it may be expected that it will be successful. A disturbing factor is the possibility of serious oxidation of dithizone by ferric iron. It is known that ferric iron does not interfere with the separation of copper from a sulfuric acid solution (p. 316), but it remains to be seen whether the same is true for a hydrochloric acid solution such as the one that is

[42] A. Ringbom and F. Sundman, *Finska Kemistsamfundets Medd.*, **51**, 42 (1943).
[43] A. Ringbom, *Metall u. Erz*, **40**, 228 (1943).
[44] K. Quandel, *Arch. Eisenhüttenw.*, **14**, 601 (1940/41).
[45] M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **15**, 116 (1943)
[46] R. Biazzo, *Ann. Chim. applicata*, **16**, 96 (1926).
[47] F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Vol. I. Van Nostrand, New York, 1936, p. 143.
[48] E. I. Stearns, *Ind. Eng. Chem., Anal. Ed.*, **14**, 568 (1942).
[49] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **9**, 464 (1937).

obtained after decomposition of a silicate rock by the procedure given below.

TABLE 51

DETERMINATION OF COPPER IN SILICIC AND SUB-SILICIC SILICATE ROCKS BY THE MIXED-COLOR DITHIZONE METHOD

Cu present or added, %.....	0 003	0.0080	0.012	0.014	0.026
Cu found, %.....	0.0025	0.0085	0.011	0.015	0.024

Special Solutions

Dithizone, 0.01 and 0.001 per cent in carbon tetrachloride. See p. 303.

Hydrochloric acid, 6 *N*. Redistilled acid is preferable.

Hydrochloric acid, 0.02 *N*. Copper-free water should be used for dilution.

Ammonia, sp. gr. 0.9. Distil concentrated ammonia or absorb the tank gas in water. Keep in a waxed bottle.

Sodium citrate, 10 per cent. Dissolve 10 g. of trisodium citrate in 100 ml. of water, add 0.5 ml. of ammonia, and shake with small portions of 0.01 per cent dithizone until the carbon tetrachloride is colored only faintly pink. Store the solution in a wax-lined bottle.

§ Procedure

Weigh 0.25 g. of 100-mesh rock powder into a platinum dish and add 0.5 ml. of 70 per cent perchloric acid, 3 ml. of water, and 2–3 ml. of hydrofluoric acid. Heat on a low temperature hot plate, stirring occasionally with a platinum wire if caking occurs, until the solution has evaporated to dryness and the excess perchloric acid has been expelled. Repeat the evaporation with 2 ml. of hydrofluoric acid. Add 0.5 ml. of perchloric acid together with a milliliter or two of water, again evaporate to dryness, and expel the excess of acid. To the residue add 2 ml. of 6 *N* hydrochloric acid and 5 ml. of water, and warm, if necessary, to bring all soluble material into solution. Next add 5 ml. of sodium citrate solution, cool to room temperature, and add ammonia dropwise until the solution is basic to litmus paper, and finally an excess of 0.25 ml. If the solution becomes turbid on the addition of ammonia, it is advisable to let it stand 10 minutes before beginning the filtration as described in the next paragraph.

Filter the solution through a small paper of medium texture, transfer any residue in the dish to the paper and wash with three or four 1 ml. portions of water containing a drop of ammonia and sodium citrate solution. If the filtrate becomes turbid on standing, refilter it. Reserve the filtered solution (solution 1). Ignite the paper and its contents in a platinum crucible, avoiding an unnecessarily high temperature. Mix the residue with 0.15 g. of sodium carbonate and fuse. Add 2–3 ml. of water to the melt and warm to hasten disintegration. Filter through a small paper

filter, keeping most of the residue in the crucible, and wash with 8–10 ml. of water. Reserve the filtrate (solution 2), transfer the paper to the crucible previously used, ignite, and add 0.5–1 ml. of hydrofluoric acid and 2 drops of perchloric acid to the residue. Evaporate to dryness, expel the excess of perchloric acid, add a few drops of water and one of perchloric acid to the residue, and evaporate as before. To the residue add 0.5–1 ml. of 6 *N* hydrochloric acid and a few milliliters of water and warm. (If there is a residue at this point and lead is also to be determined, filter it off and fuse it with sodium carbonate.) Add 0.5 ml. of sodium citrate and make basic with a few drops of ammonia in excess (solution 3).

Transfer the main solution (solution 1) to a separatory funnel and shake for one-half minute with 5 ml. of 0.01 per cent dithizone solution; if the carbon tetrachloride is green at the end of this time shake for an additional half minute. Draw off the carbon tetrachloride into another separatory funnel, leaving a few drops in the first funnel to prevent loss of aqueous phase. Unless the separated carbon tetrachloride is distinctly green, add another 5 ml. portion of dithizone and shake well for 0.5–0.75 minute. Draw off the carbon tetrachloride and continue to extract until the last portion of dithizone remains distinctly green. Next extract the solution of the leached sodium carbonate melt (solution 3), using 2 ml. portions of dithizone, and combine these extracts with the others. Finally, as a precautionary measure, extract the filtrate from the sodium carbonate leach (solution 2), after adding 0.5 ml. of sodium citrate and hydrochloric acid to give a greenish color with a drop of thymol blue.

Shake the combined carbon tetrachloride extracts for a few seconds with about 3 ml. of water to which has been added a small drop of ammonia (to remove any droplets of iron-containing solution which would otherwise interfere if lead is also to be determined), and run the carbon tetrachloride into a clean separatory funnel. Shake the extract vigorously for 1 minute with 10 ml. of 0.02 *N* hydrochloric acid. If the carbon tetrachloride remains red on shaking and does not become greenish or purple, add sufficient dithizone to impart a purplish color to the mixture and shake again for 1 minute. Draw off the carbon tetrachloride into another separatory funnel and shake for 2 minutes with a fresh 10 ml. portion of 0.02 *N* hydrochloric acid. Combine the acid extracts, add a few drops of carbon tetrachloride to rinse out any droplets of colored carbon tetrachloride, and reserve this solution for the determination of zinc (p. 629) and lead (p. 406).

Evaporate the carbon tetrachloride containing copper dithizonate to dryness in a 50 or 100 ml. Pyrex Erlenmeyer flask, add 0.5 ml. of concentrated sulfuric acid and 0.2 ml. of 70 per cent perchloric acid to the residue, and heat at 200–250° C. until the solution is entirely colorless. Cool, dilute with 10 ml. of water, neutralize with 1:1 ammonia, using methyl

orange as indicator, add a drop of 6 *N* sulfuric acid in excess, and after cooling dilute to 25 ml. in a volumetric flask.

Determine copper according to the general procedure given on p. 303. For copper contents in the range 0.001 to 0.01 per cent, a 5 ml. aliquot is suitable when 5 ml. 0.001 per cent dithizone is used (photoelectric photometer); for higher percentages the size of the aliquot must be reduced or a larger volume of dithizone used.

B. Soils

Directions for the determination of copper in soils by the use of dithizone have been given by Holmes.[50] The 100-mesh sample is digested with perchloric acid, the excess of the latter is evaporated, and the residue is taken up in hydrochloric acid. Ammonium citrate is added, the *p*H is adjusted to 3.5 with ammonium hydroxide, and copper is extracted with a carbon tetrachloride solution of dithizone.

After copper has been isolated in this manner, it is best to evaporate off the carbon tetrachloride and destroy organic matter in the residue by heating with sulfuric and perchloric acids. Copper can then be determined with dithizone or sodium diethyldithiocarbamate as described elsewhere in this chapter (pp. 303–309). No account need be taken of silver, mercury, and bismuth, since these metals will not be present in detectable amounts.

C. Steel

Copper may be separated by precipitation with hydrogen sulfide in acid solution[51] or by extraction with dithizone. The latter procedure is a convenient one and is described below. The separated copper may be determined either with dithizone or sodium diethyldithiocarbamate as preferred; the former reagent is used in the following procedure.

§ Procedure

Dissolve 0.2–0.25 g. of steel (0.01–0.1 per cent copper) in a mixture of 4 ml. 6 *N* sulfuric acid and 10 ml. of water, heating gently. When action has ceased add 0.5 ml. of concentrated nitric acid and boil for 1–2 minutes to expel oxides of nitrogen. Cool and dilute the solution to 100 ml. in a volumetric flask. Transfer 20 ml. of the solution to a small separatory funnel and shake for 1 minute with 5 ml. of 0.01–0.015 per cent dithizone

[50] R. S. Holmes, *Soil Sci.*, **59**, 77 (1945).

[51] G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, *Chemical Analysis of Iron and Steel.* Wiley, New York, 1931, p. 267. Also see O. I. Milner, *Ind. Eng. Chem., Anal. Ed.*, **18**, 94 (1946), who determines copper in large samples of steel by the ammonia method after sulfide precipitation.

in carbon tetrachloride. The color of the extract gives an indication of the amount of copper present. Draw off the extract into another separatory funnel, and extract the solution with another 5 ml. portion of dithizone. The second extract should show practically the same color as the original dithizone; if it does not, extract a third time with another 5 ml. portion to insure the complete recovery of copper.

TABLE 52

DETERMINATION OF COPPER IN STEEL WITH DITHIZONE

Bureau of Standards sample No.	Copper present %	Copper found %
9c	0.020	0.020
10d	0.010	0.010
111	0.122	0.126
33b	0.114	0.116
Synthetic sample (56% Fe, 33% Ni, 11% Co)	0.0055	0.0050

Shake the combined extracts for a few seconds with 5 ml. of water to which 1–2 drops of 6 *N* sulfuric acid has been added, and run the carbon tetrachloride into a 50 or 100 ml. Pyrex Erlenmeyer flask; rinse the funnel with a few milliliters of carbon tetrachloride to displace any remaining dithizone solution. Evaporate the carbon tetrachloride solution to dryness, and add 0.75 ml. of concentrated sulfuric acid and 0.25 ml. of perchloric acid to the residue. Heat at about 250° C. until the acid is entirely colorless (approximately 15 minutes' heating is required). Cool, dilute with 10 ml. of water, add a drop of methyl orange, and approximately neutralize with pure ammonium hydroxide (1:1). Finally add a drop of 6 *N* sulfuric acid in excess. After cooling dilute to 25 ml. in a volumetric flask.

Depending upon the probable copper content of the sample, transfer 10 ml. (0.01 per cent copper) or 1–2 ml. (0.1 per cent copper) of solution to a small separatory funnel, add 0.20 ml. of 6 *N* sulfuric acid, and if necessary dilute to about 10 ml. with water. From a covered buret run in 5.0 ml. of 0.001–0.0012 per cent dithizone in carbon tetrachloride and shake for 2.0 minutes. If the carbon tetrachloride solution assumes the full red-violet color of cupric dithizonate run in another 5.0 ml. (or 10 ml.) of dithizone so that after shaking for 2 minutes a mixed color is obtained. Dry the stem of the funnel and deliver the carbon tetrachloride into a suitable cell. Determine the transmittancy of the solution (p. 304). Run a blank through the procedure.

D. Water

The carbamate method is usually directly applicable to the determination of copper in natural waters because interfering substances are not likely to be present. Colored waters can usually be decolorized by adding ammonium persulfate and boiling.

§ Procedure

Acidify 50 ml. of water (Cu > 0.1 p.p.m.) with hydrochloric acid (methyl orange as indicator) to insure the presence of copper in the ionic form.[52] Add 5 ml. of 20 per cent ammonium citrate solution and an excess of 2 ml. of concentrated ammonia. Shake with 5 ml. of carbon tetrachloride after the addition of 1 ml. of 0.1 per cent sodium diethyldithiocarbamate solution, and determine the transmittancy of the extract (see p. 309).

If the standard series method is to be applied, use 1.8 × 15 cm. glass-stoppered flat-bottomed tubes with 10–15 ml. of water treated with proportionate amounts of the reagents mentioned above and shake with 1.0 to 2.0 ml. of carbon tetrachloride. The volume of the standards must be the same as that of the sample.

E. Bio Materials

Organic matter may be destroyed in the dry or wet way but preferably by the latter. In the former method, nitric acid, sulfuric acid, or magnesium nitrate is frequently added after carbonization to aid the oxidation. The temperature of ignition should not in general exceed 500° C. and a lower maximum temperature is sometimes advisable. Failure to recover all the copper after dry-ashing is probably not due to volatilization[53] but rather to partial conversion of the copper into acid-insoluble forms by reaction with the material of the vessel in which the ignition is made or with other constituents of the ash. Comrie[54] found that when organic samples were ashed with sulfuric acid in old etched silica dishes, appreciable amounts of copper were lost, especially when the amount of ash was small. He

[52] If it is necessary to determine copper in concentrations below 0.1 p.p.m., concentrate the sample by evaporation after acidification and destroy organic matter if required. For the determination of the most minute traces of the metal, concentrate in a silica dish, and separate and determine copper by the dithizone method, patterning the procedure after the directions on p. 313. See E. Abrahamczik, *Mikrochemie ver. Mikrochim. Acta*, **25**, 228 (1938), for the determination of very low concentrations of copper and other heavy metals in natural waters. He reports the limit of detectability as 0.05 γ of copper per liter (evidently with a 10 liter sample).

[53] There may be some exceptions. J. G. Maltby, *Nature*, **160**, 468 (1947), has suggested that low values for copper in such materials as vinegar, prepared for analysis by dry ashing, may be due to the formation of volatile copper compounds.

[54] A. A. D. Comrie, *Analyst*, **60**, 377 (1935).

recommends the addition of magnesium nitrate to the sample to furnish a bulkier ash and the transfer of the latter to a Pyrex flask before dissolving in acid. High[55] has shown that metallic copper may be formed in dry-ashing, especially if the temperature exceeds 500° C. The metal will remain largely unaffected if hydrochloric acid is used to treat the ash, as is usually the case. If the ash is extracted with a mixture of hydrochloric and nitric acids, all the copper is brought into solution and the results are identical with those obtained in wet-oxidation, even if the ignition is made at 600–850° C. Any silica remaining after the acid treatment of the ignition residue must be hydrofluorized, for copper has a marked tendency to be retained by silica. It is usually preferable to apply wet-oxidation for bio samples high in silica.

In wet ashing, perchloric acid is frequently used in conjunction with sulfuric or nitric acid or both,[56] but the two latter alone will usually be satisfactory. The recovery of all the copper of the sample is more certain in the wet digestion method than in dry ashing. On the other hand the blank is likely to be larger when acids are used, although if reagents of good quality are employed very little copper should be introduced. Some C. P. concentrated sulfuric acid may contain as much as 1 to 2 p.p.m. of copper. Redistilled acids should be used if possible. Sulfuric acid should be avoided if the sample contains much calcium, for any calcium sulfate not finally brought into solution is likely to retain copper.

The analyst has a choice of a number of methods for the determination of copper in the solution of the decomposed sample:

(*a*) Direct determination with dithizone.

(*b*) Direct determination with sodium diethyldithiocarbamate.

(*c*) Isolation of copper with dithizone, destruction of the latter, and determination of copper with dithizone or diethyldithiocarbamate.

It appears that in many cases the simple direct methods (*a*) or (*b*) give satisfactory results. The substances that can interfere have already been mentioned in the earlier parts of this chapter. There is something to be said in favor of both of these reagents. Diethyldithiocarbamate is more

[55] J. H. High, *Analyst*, **72**, 60 (1947).

[56] Regarding the use of perchloric acid in the destruction of organic matter see E. Kahane, *L'Action de l'Acide Perchlorique sur les Matières Organiques. I. Généralitiés* (48 *pp.*), *II. Applications* (124 pp.), Hermann et Cie, Paris, 1934, and the brochure of G. F. Smith, *Mixed Perchloric, Sulfuric and Phosphoric Acids and Their Applications in Analysis*, G. F. Smith Chemical Co., Columbus, Ohio, and further G. F. Smith, *Ind. Eng. Chem., Anal. Ed.*, **18**, 257 (1946). Decomposition with sulfuric-nitric-perchloric acid is recommended by Nydahl[28] and Piper, *Soil and Plant Analysis*, Interscience, New York, 1947, p. 331. The latter author also describes a procedure in which purified sodium perchlorate is used in place of perchloric acid when this contains too much copper for accurate work.

stable and is simpler to use than dithizone. On the other hand, the direct carbamate procedure is subject to interference from bismuth, nickel and cobalt, which in small amounts do not cause trouble in the dithizone procedure; the nickel content of plant material may sometimes be high enough to affect the figure for copper. The amount of iron and manganese present in bio samples is not likely to be sufficiently great to cause any difficulty in the carbamate method; rarely, much calcium and phosphate may give rise to difficulty through formation of a precipitate in the basic citrate medium.

The most universally applicable and reliable procedure involves preliminary isolation of copper with dithizone, and its final determination with either this reagent or diethyldithiocarbamate.

We will give a number of procedures for the determination of copper in bio materials and allow the analyst to make a choice depending upon the nature of the sample and the accuracy and time requirements.

§ Procedure

Destruction of Organic Matter. The size of sample taken should preferably be such that at least 1 γ of copper is present in it, or in an aliquot, if the final determination is made with dithizone, or at least 5 γ is present if the determination is made with sodium diethyldithiocarbamate. Follow (*a*) or (*b*) in the decomposition, but preferably (*b*) unless it is known that the sample is of such nature that all of the copper can be recovered by dry ashing.

(*a*) *Dry oxidation*: The exact procedure in ashing will depend upon the nature of the sample.[57] In general, transfer the sample to a silica dish[58] and dry or evaporate the material on a steam bath or equivalent heat source (in the case of milk add a few drops of 6 *N* sulfuric acid). Then heat carefully over a burner or on a hot plate to char the material. At this point it is frequently advantageous to moisten the residue with nitric acid or a 20 per cent solution of magnesium nitrate; the latter is especially valuable with materials difficult to ash or those furnishing only small amounts of ash. Place the dish in a muffle furnace after evaporating on a hot plate, slowly raise the temperature to 500° C. and continue to heat until all carbonaceous material has been destroyed. If difficulty is experienced in obtaining a white ash, moisten the residue with nitric acid or

[57] For directions for ashing various organic materials consult *Methods of Analysis*, Association of Official Agricultural Chemists.

[58] A platinum or porcelain dish (or casserole) may also be used. Either should be digested with hot 1:1 hydrochloric acid for an hour or two before use. For the use of a filter paper lining to facilitate ashing see S. A. Bandemer and P. J. Schaible, *Ind. Eng. Chem., Anal. Ed.*, **16**, 417 (1944).

magnesium nitrate solution, evaporate and heat as before. Dissolve the ash in 5 ml. (or more if necessary) of 6 *N* hydrochloric acid,[59] heating on a steam bath, and dilute with 5–10 ml. of water. If any appreciable amount of residue remains, filter it off on a small filter paper previously washed with hydrochloric acid, wash with a little dilute hydrochloric acid and water, and ignite the paper and its contents in a platinum crucible. Treat the residue with an appropriate amount of hydrofluoric acid and a drop or two of perchloric acid, and evaporate to fumes of the latter; repeat the evaporation to fuming after adding another drop or two of perchloric acid and a little water. Take up the residue in a few milliliters of water and combine with the main solution.

(*b*) *Wet oxidation*: Transfer 1 to 2 g. of sample (or more as required) to a small Kjeldahl flask or a 250 ml. Erlenmeyer flask with a small funnel in its mouth. Add 5 ml. of concentrated nitric acid (for 1–2 g. of sample) and 2 ml. of concentrated sulfuric acid.[60] Heat gently at first, guarding against too vigorous initial reaction. Increase the temperature somewhat, so that the digestion proceeds moderately rapidly without too great loss of nitric acid. When charring begins, add nitric acid in small portions (0.5–1 ml.), and continue heating until finally on evaporation to fumes of sulfuric acid a colorless or very pale yellow liquid is obtained.

Cool, add 2–3 ml. of water, and evaporate to white fumes; cool, add another like portion of water, and again evaporate to fumes to destroy nitrosyl sulfuric acid. Then add 10 ml. of water to the cold flask and heat to boiling. Any slight residue may usually be disregarded.

Determination of Copper. Follow (*a*), (*b*), or (*c*).

(*a*) *Directly with dithizone*:[61] To the sample solution or an aliquot of it, having a volume of approximately 10 ml. and containing not more than 3 or 4 γ of copper, add 3 drops of cresol red indicator solution followed by enough concentrated ammonium hydroxide to produce a yellow color. Add 1 ml. of buffer solution (8.3 g. of anhydrous disodium phosphate and 38 g. of citric acid in 250 ml. of water, shaken with 0.01 per cent dithizone in carbon tetrachloride to remove copper) and 10.0 ml. of dithizone in carbon tetrachloride (8 mg. per liter, best prepared fresh by accurate dilution of a stronger solution). Shake mechanically for 10 minutes.

[59] If there is a possibility of metallic copper being present (p. 318) add first a few drops each of 1:1 hydrochloric and nitric acids, evaporate to dryness, and then add concentrated hydrochloric acid and evaporate to dryness to destroy most of the nitrate.

[60] If desired, 2 ml. of 60–70 per cent perchloric may also be added.

[61] Essentially according to Morrison and Paige,[19] except treatment of the carbon tetrachloride extract with potassium iodide solution is omitted. Mercury and silver must be absent. As much as 0.2 mg. of bismuth is permissible

Obtain the transmittancy of the clear carbon tetrachloride phase at 520 mμ. Run a blank through the whole procedure.

(*b*) *Directly with diethyldithiocarbamate*:[62] To the sample solution or an aliquot of it, add 10 ml. (or less for an aliquot) of 20 per cent ammonium citrate solution, make alkaline with 1:1 ammonia as described on p. 309 and continue as described there. Run a blank through the procedure.

(*c*) *After isolation with dithizone*: Almost neutralize the solution of the decomposed sample with pure ammonium hydroxide (methyl orange as indicator) and add sufficient hydrochloric acid to make its concentration 0.05 *N*. Transfer the cold solution to a separatory funnel; the volume at this point should not exceed 50 ml. Add 5 ml. of 0.01 per cent dithizone in analytical-reagent carbon tetrachloride and shake vigorously for 2 minutes. Draw off the carbon tetrachloride phase into another separatory funnel and extract the aqueous solution with another 5 ml. portion of dithizone. If this portion remains green (substantially the same hue as before shaking) all the copper has been extracted; otherwise extract with more dithizone until the color of the latter remains unchanged.

Shake the combined extracts[63] with 5 or 10 ml. of 0.01 *N* hydrochloric acid and transfer the carbon tetrachloride phase to a 50 or 100 ml. Erlenmeyer flask. Evaporate to dryness and add 0.5–0.75 ml. of concentrated sulfuric acid and 0.2 ml. of 60 or 70 per cent perchloric acid to the residue. Heat at 200° or a little higher until the solution becomes virtually colorless, adding more perchloric acid if necessary.

Dilute the concentrated acid digest with 10 or 15 ml. of water (or dilute to 25 ml. and take a suitable aliquot if the copper content is comparatively great as shown by the color in the dithizone extraction). Almost neutralize the solution with pure ammonia and determine copper by either the dithizone method (p. 303) or the carbamate method (p. 309). If the latter procedure is to be followed, add only 1 ml. of 20 per cent ammonium citrate solution, since only traces of iron can be present. Run a blank through the whole procedure.

[62] For an alternative procedure with diethyldithiocarbamate without extraction, in which gum arabic is used to stabilize the suspension, see High.[55]

[63] If there is a possibility of the presence of traces of mercury and silver, or relatively much bismuth, shake the combined extracts with 10 ml. of 2 per cent potassium iodide solution in 0.01 *N* hydrochloric acid (add a little sulfite to destroy any free iodine). Finally wash the separated carbon tetrachloride with 5 ml. of 0.01 *N* hydrochloric acid

CHAPTER XVIII

GALLIUM

I. Separations

A. Extraction Methods

Extraction of gallium chloride from 1:1 hydrochloric acid by ethyl or isopropyl ether is a method of great practical importance for the isolation of gallium. The distribution of gallium chloride between ether and acid phases is independent of the gallium concentration, at least in dilute solutions. The value of the distribution coefficient for ethyl ether-6 *M* hydrochloric acid is approximately 17 (p. 32). The most favorable hydrochloric acid concentration is 5.5 to 6 *M*.[1] The ether extraction provides a separation from aluminum[2] and zinc (although a trace of the latter metal is said to be extracted) as well as from many other elements. Among the metal chlorides (or other metal compounds) extracted are those of iron (III), gold, thallium (III), germanium, molybdenum, rhenium, arsenic, antimony, and tin (*cf.* Table 7). Copper (II) is slightly extracted. If iron is reduced to the ferrous state, as by the use of metallic silver in finely divided form, it is not extracted.[3] At the same time, some of the elements mentioned (especially gold and thallium) are reduced to the metal or lower valence states and are then not extracted. Molybdenum is extracted to some extent under the conditions. Directions for the extraction are given on p. 327.

Gallium hydroxyquinolate can be extracted by chloroform, and separa-

[1] E. H. Swift, *J. Am. Chem. Soc.*, **46**, 2378 (1924); I. Wada and R. Ishii, *Sci. Papers Inst. Tokyo*, **34**, 787 (1937–38). The extraction of gallium chloride by isopropyl ether has recently been studied by N. H. Nachtrieb and R. E. Fryxell, *J. Am. Chem. Soc.*, **71**, 4035 (1949), who find that the optimum hydrochloric acid concentration is 7 *N*. At this acidity the extraction coefficient has the approximate value 200 for very low gallium concentrations.

[2] J. A. Scherrer, *J. Research Natl. Bur. Standards*, **15**, 585 (1935).

[3] Ordinarily there is some air-oxidation of ferrous iron in the extraction and a small amount of iron enters the ether. Such small amounts do not interfere in the subsequent determination of gallium with 8-hydroxyquinoline. Other reducing agents that have been used are hydrogen sulfide (Wada and Ishii) and metallic mercury (Swift). S. Lacroix (private communication, 1948) uses titanous chloride. The separated ether phase is washed with a hydrochloric acid solution of titanous chloride to remove traces of iron, and then shaken with a biphthalate buffer to transfer gallium to the aqueous phase.

tion from various metals can thus be achieved by regulation of the acidity and the concentration of the reagent (p. 119). This extraction method is rarely applied for the purpose of preliminary separation, since the ether extraction of the chloride is usually preferable. However, it is of great value in the determination of gallium, as will be shown later.

Cupferron precipitates gallium in mineral acid medium (2 *N* sulfuric acid)[4] and it is likely that gallium cupferrate can be extracted by chloroform and separations thus made from metals not precipitated in strongly acid solution. The precipitation technique has been applied to effect a separation from aluminum, chromium, scandium, the rare earth metals, and uranium (VI).

B. Precipitation Methods

These are of far less importance than extraction methods in the isolation of gallium, but may occasionally be of use.

Gallium hydroxide is appreciably soluble in ammonium hydroxide and an excess must be avoided in its precipitation. Aluminum hydroxide is a good collector for gallium because of the similarity in the *p*H range of precipitation of the two hydroxides and in the ionic radii of the two metal ions. By ammonia precipitation in the presence of ammonium chloride, gallium can be separated from such metals as the alkaline earths, magnesium, manganese, nickel, and, less satisfactorily, cobalt. It may be expected that gallium can be separated from iron by ammonia precipitation if mercaptoacetic acid is first added (*cf.* p. 207).

Separation of gallium from much ferric iron by precipitation of the latter with excess sodium hydroxide is usually not satisfactory.[5] According to Rienäcker a much better separation is obtained by fusing ferric and gallium oxides with sodium hydroxide (7–8 g. of the latter, extracted melt diluted to 100–200 ml. with water).[6] Only a few micrograms of gallium are adsorbed by even large amounts of iron.

A fairly satisfactory separation of gallium from indium is said to be obtainable by sodium hydroxide precipitation. Some indium remains in solution.

[4] Scherrer, *loc. cit.*; L. Moser and A. Brukl, *Monatsh.*, **51**, 325 (1929).

[5] The magnitude of the error for small quantities of gallium can be gathered from some results obtained by Wada and Ishii. They found that 250 mg. of ferric iron precipitated from a solution containing 1.0 mg. of gallium carried down 0.6 mg. when the concentration of excess sodium hydroxide was 0.5 *N*, and 0.2 mg. when the excess was 1.0 *N*.

[6] G. Rienäcker in Fresenius and Jander, *Handbuch der analytischen Chemie*, Part III, Vol. III, p. 567. Sodium hydroxide fusion has been applied by A. Majumidar and P. B. Sarkar, *Science and Culture*, **13**, 75 (1947), in the determination of gallium in bauxite (separation of aluminum and gallium from iron and titanium).

Much aluminum can be precipitated as the hydrated chloride by strong hydrochloric acid from ethereal medium.[7] A partial separation of aluminum from gallium is achieved by precipitation of the former with sodium fluoride (p. 329).

Metallic cadmium has been used to separate various metals from gallium (p. 332).

II. Methods of Determination

Two photo methods are available for the determination of traces of gallium, one based on a fluorescence reaction with 8-hydroxyquinoline and the other on a color reaction with quinalizarin. The former method is the more useful.

A. The 8-Hydroxyquinoline Method (Fluorimetric)[8]

Gallium hydroxyquinolate can be extracted from an aqueous solution at a suitable *p*H by shaking with chloroform. Gallium distributes itself between the two phases in accordance with the relation

$$\frac{[Ga^{+++}]\,[Ox'^{-}]^3}{[GaOx'_3]_{CHCl_3}} = 1.8 \times 10^{-40}$$

(at 18°, according to S. Lacroix, p. 119). The concentration of hydroxyquinolate ion, Ox'^{-}, for a given concentration of reagent, is a function of the hydrogen ion concentration as explained on p. 118. Under the conditions described below, most of the gallium will be in the chloroform phase when the *p*H of the aqueous phase is 2.6–3.0. Increasing the *p*H above 3.0 does not appreciably increase the amount of gallium in the chloroform and has the possible disadvantage of increasing the amount of other metal hydroxyquinolates extracted.

The chloroform phase shows a strong yellowish fluorescence in the near ultraviolet. Fluoride and citrate inhibit the fluorescence. With the exception of indium and scandium, no metal hydroxyquinolate imparts a fluorescence to the chloroform in the *p*H range 2.6–3.0.[9] The fluorescence

[7] E. H. Swift, *J. Am. Chem. Soc.*, **46**, 2377 (1924). *Cf.* W. Fischer and W. Seidel, *Z. anorg. allgem. Chem.*, **247**, 333 (1941).

[8] E. B. Sandell, *Anal. Chem.*, **19**, 63 (1947); see also *Ind. Eng. Chem., Anal. Ed.*, **13**, 844 (1941). For other fluorescence reagents that have been used qualitatively see Radley, *Analyst*, **68**, 369 (1943).

[9] A possible exception to this statement may be provided by lithium and beryllium in large amounts. One hundred mg. of lithium give an extremely weak fluorescence under the conditions of the test, equivalent to approximately 0.1 γ of gallium. Ten mg. of beryllium produce a fluorescence corresponding to 0.1–0.2 γ of gallium. However, it is not known whether the lithium and beryllium salts used were entirely free from gallium.

produced by these metals is much weaker than that given by gallium. At *p*H 3 the indium fluorescence is about $^1/_{500}$ as strong as that of an equal weight of gallium, and that of scandium is about $^1/_{40,000}$ as strong. At *p*H 2.6 the fluorescence intensity of indium is much less, being approximately $^1/_{10,000}$ that of gallium. As much as 30 mg. of aluminum produces no fluorescence. However, a number of metals form hydroxyquinolates which dissolve in chloroform to give colored but non-fluorescent solutions.

TABLE 53

FLUORIMETRIC DETERMINATION OF GALLIUM IN SILICATE ROCKS AFTER ETHER EXTRACTION

Sample	Ga present, *p.p.m.*	Ga added, *p.p.m.*	Ga found, *p.p.m.*	Ga recovered	
				p.p.m.	%
Solution[a]	10	8	18	8	100
Solution[b]	10	10	21	11	110
Solution[c]	10	12	21	11	90
Solution[c]	10	40	48	38	95
Diabase[d]	19	10	27	8	80
Diabase	19	16	33	14	88
Diabase	19	50	67	48	96
Dunite	0.5	10	10	9.5	95
Dunite	0.5	10	9	8.5	85
Composite of mediosilicic rocks + 0.012% Mo	14.5	—	14.5	14.5	100
Composite (No. 1) of subsilicic rocks + 0.4% Cu	12.5	—	11.5	11.5	92
Composite (No. 2) of subsilicic rocks + 0.15% V	13	—	13.5	13.5	104

[a] Composition in mg. (as sulfates and chlorides): Al_2O_3 48, Fe_2O_3 38, MgO 25, CaO 25, Na_2O 10, MnO 0.6, TiO_2 3, P_2O_5 1.2, Cu 0.08. Solution evaporated to dryness and excess sulfuric acid fumed off. Residue taken up in 6 *N* hydrochloric acid, calcium sulfate filtered off, and solution further treated as described in procedure.

[b] Calcium omitted from mixture.

[c] Composition same as [a]. Evaporated to dryness with 2.5 ml. of hydrofluoric acid and excess sulfuric acid.

[d] Percentage composition: SiO_2 52.7, Al_2O_3 14.5, Fe_2O_3 7.4, FeO 5.6, MgO 3.7, CaO 8.0, Na_2O 3.2, K_2O 1.1, TiO_2 1.8, P_2O_5 0.25, MnO 0.24, Cu 0.024, Ni 0.004, Co 0.0024, Mo 0.0002.

These colored hydroxyquinolates absorb ultraviolet and visible radiation and lead to low results. The metals thus interfering are ferric iron, quinquevalent vanadium, cupric copper, and sexivalent molybdenum. Titanium hydroxyquinolate is insoluble in chloroform under the conditions and produces an emulsion. The difficulties arising from the presence of these elements are most simply avoided by first isolating gallium by ether extraction of its chloride from hydrochloric acid medium after reduction of iron to the ferrous state with silver.

The procedure outlined above has been worked out in detail for the

determination of gallium in silicate rocks, but it can be made the basis of determination in other materials as well. It is evident from Table 53 that the common elements do not interfere. Molybdenum is a metal that will interfere if present in relatively large amounts because it is extracted by ether and gives a chloroform-soluble hydroxyquinolate in the final step. The small quantities of iron which are extracted by ether are made harmless by reduction with hydroxylamine hydrochloride. Directions for the determination of gallium in silicate rocks follow.

Apparatus

Glass-stoppered tubes, 1.8 × 15 cm., flat-bottomed, 25 ml. capacity.

Funnel with silver column. Place a plug of glass wool at the bottom of the stem of a buret funnel (stem diameter preferably 8 mm.), and fill the stem loosely to a depth of 15 mm. with powdered silver. The column should allow the passage of 5 to 7 ml. of solution per minute without suction. Since only a small amount of ferric iron has to be reduced by the silver column, it may be used for many reductions before replacement. After use rinse it with 1 to 1 hydrochloric acid and water and then dry.

Microburet, graduated to 0.01 ml., for measuring the standard gallium solution.

Ultraviolet lamp. A source supplying radiation in the near ultraviolet is satisfactory. A Westinghouse type G-5 lamp serves well.

Reagents

Hydrochloric acid, 1 to 1. Dilute concentrated hydrochloric acid (density 1.18) to twice its volume with water.

Silver powder. Prepare by reducing silver nitrate with metallic copper. Wash well with dilute sulfuric acid and then water, and dry. The powder should be finely divided. If necessary sift out the larger grains.

Ethyl ether. Use only the analytical reagent or purified grade, treated daily as follows: Shake 65 ml. (enough for four extractions of gallium) in a separatory funnel with 25 ml. of 1 to 1 hydrochloric acid to which has been added 0.05 gram of sodium hydrogen sulfite. Separate the phases. Do not wash the ether phase but rinse out the stem of the funnel by pouring a little 1 to 1 hydrochloric acid into the funnel and drawing it off. The ether thus purified must not give a yellow color when shaken with a little titanium sulfate in sulfuric acid solution.

Sodium chloride, 10 grams in 100 ml. of water.

Hydroxylamine hydrochloride, 20 grams in 100 ml. of solution.

Potassium hydrogen phthalate, 0.20 *M,* 20.41 grams of salt in 500 ml. of solution.

8-Hydroxyquinoline, 0.10 per cent. Dissolve 0.10 gram in a little water containing 0.6 ml. of 6 *N* acetic acid and dilute to 100 ml.

Chloroform, analytical reagent.

Standard gallium solution. A convenient concentration is 0.0005 per cent gallium. The solution should be 0.05 *N* in hydrochloric acid.

§ Procedure

To 0.25 gram of 100-mesh rock powder in a platinum dish add 2 ml. of 6 *N* sulfuric acid and 3 ml. of hydrofluoric acid. Evaporate to dryness and fume off the excess sulfuric acid, avoiding decomposition of ferric sulfate.

Take up the residue in 0.5 ml. of 6 *N* sulfuric acid and 1 or 2 ml. of water, evaporate to dryness, and again fume off the sulfuric acid. Treat the residue with 10 ml. of 1 to 1 hydrochloric acid, warm the covered dish gently, and stir at intervals to bring all soluble material into solution. After 0.5 hour, or when it is judged that all soluble matter has been dissolved, filter off any calcium sulfate or other insoluble matter on a small (5 cm.) fine filter paper and wash with 5 ml. of water containing a few drops of hydrochloric acid. Catch the filtrate and washings in a 25 ml. volumetric flask. (If the sample contains appreciable amounts of chromite or other mineral not decomposed by hydrofluoric acid, the residue should be treated appropriately to complete the decomposition.)

Add 0.5 gram of silver powder to the volumetric flask and swirl the solution until most of the ferric iron has been reduced, as shown by the almost complete disappearance of the yellow color. Depending upon the amount of iron and the fineness of the silver, from 1 to 5 minutes will be required. Then add 8 ml. of concentrated hydrochloric acid and dilute with water to 25 ml. After mixing for 1 minute, run the solution through the funnel containing dry silver powder in its stem and collect a little more than 10 ml. Without delay transfer 10.0 ml. of the solution to a small separatory funnel which has been rinsed with 1 to 1 hydrochloric acid and proceed with the ether extraction.

Extraction of Gallium Chloride. Add 8 ml. of ether to the separatory funnel and shake for 20 to 30 seconds with the usual precautions. When the layers have separated, drain the aqueous phase into another separatory funnel (rinsed with 1 to 1 hydrochloric acid) and shake with 5 ml. of ether. Draw off and discard the acid layer and combine the second ether extract with the first, rinsing the funnel with 1 ml. of ether. Separate any small amount of aqueous solution present and shake the ether vigorously for 10 seconds with 1 ml. of 1 to 1 hydrochloric acid. Drain off the aqueous layer as sharply as possible and shake the ether again with another 1 ml. portion of 1 to 1 hydrochloric acid. Discard the hydrochloric acid washings. After the second portion of acid has been separated, add a few drops of 1 to 1 hydrochloric acid to the funnel and draw it off without shaking to rinse out the stem of the funnel.

Run the washed ether into a 50 ml. beaker containing 0.5 ml. of sodium chloride solution and rinse the funnel with 1 or 2 ml. of ether. Cover the beaker with a watch glass and evaporate the ether at a low temperature. Remove the cover glass and allow all the water to evaporate; the walls of the beaker must be dry. Cool and add 2.00 ml. of 0.200 *N* hydrochloric acid to the dry residue. With the aid of a stirring rod distribute the acid over the lower walls of the beaker. When the residue has dissolved, transfer the solution to a flat-bottomed glass-stoppered tube and wash the beaker

and cover glass with small portions of water totaling about 3 ml. Add 1 ml. of hydroxylamine hydrochloride solution, mix, and then add 6.0 ml. of potassium hydrogen phthalate solution. After mixing, allow the solution to stand at room temperature for 20 minutes. At the same time prepare a comparison solution of the same composition (or if preferred a series of standards) and dilute to the same volume as the sample solution.

Fluorimetric Comparison. To sample and comparison solutions add 0.25 ml. of 8-hydroxyquinoline solution, mix by inversion, and then add 2.0 ml. of chloroform. Shake the sample tube vigorously for at least 30 seconds, allow the chloroform to settle, and note the intensity of the fluorescence of the latter when the tube is held vertically above an ultraviolet source in a dark room. The strength of the fluorescence serves as a guide for the initial amount of gallium to be added to the standard tube. After each addition of standard gallium solution to the comparison tube shake well for 30 seconds. When the fluorescence of the chloroform in the comparison tube is almost as strong as that in the sample tube, shake the latter for 0.5 to 1 minute, and after each addition of gallium to the comparison solution shake both tubes for about 0.5 minute. When both chloroform layers show the same fluorescence intensity shake for 1 minute to be certain that distribution equilibrium has been reached and again compare. It is permissible to make the final adjustment by adding a small quantity of gallium to the sample solution if necessary. If the fluorescence appears too strong for good comparison, more chloroform may be added to each tube. After the fluorimetric comparison the chloroform layers should be examined in daylight. The chloroform in the sample tube should be almost colorless, not appreciably different from the chloroform in the standard tube. A pronounced yellow color will be evident if an appreciable amount of molybdenum is present, and the result is then likely to be low.

Run a blank through the entire procedure. See notes for the application of a correction factor.

Notes. 1. As little as 0.05 γ of gallium in 2 ml. of chloroform gives a perceptible fluorescence when comparison is made against a blank.

2. There is no difficulty in distinguishing between two chloroform solutions differing in gallium concentration by 10 per cent, if the amount present is greater than 0.5 γ. With a little practice one can detect differences of 7, and perhaps 5, per cent.

3. Under the conditions described the fluorescence of the blank has been found to correspond to 0.1 γ of gallium, or 1 p.p.m. of sample. The fluorescence is not due to gallium, because omission of hydroxyquinoline in the mixture still results in a faint fluorescence. A trace of some organic compound derived from the ether is the source of this fluorescence. The quality of the ether is of great importance. Even some reagent-grade anhydrous ethyl ethers will give rise to a faint blue-white fluorescence in the chloroform, which makes it difficult to match sample and standard solutions. If satisfactory ether cannot be obtained the comparison solution should be a blank solution, *i.e.*, one

obtained by adding hydrochloric acid and the other reagents to the residue produced by evaporation of the ether, which has been shaken with hydrochloric acid as in the actual procedure. In this way the same hue will be shown by sample and standard solutions. Even if the blank fluorescence is very weak it may be advantageous to follow this procedure when very small quantities of gallium are to be determined.

4. Avoid the use of ordinary stop-cock grease in burets and separatory funnels. A silicone-type lubricant may be used.

5. Recoveries of gallium are slightly low, probably due in part to incomplete extraction of gallium chloride by ether. In the most accurate work a correction of 5 to 10 per cent is probably advisable.

B. The Quinalizarin Method[10]

Quinalizarin (p. 125) yields a pink to amethyst lake with gallium hydroxide. The reaction is highly sensitive (0.02 mg. of Ga per liter can be detected) but very unspecific, so that separation of most other metals is required before it can be applied. The best results are obtained when the determination is made at a *p*H of 5 in a solution containing ammonium acetate (1 *N*) and ammonium chloride (0.5 *N*).

The reaction of aluminum, beryllium, titanium, zirconium, thorium, rare earths, tin (IV), thallium (III), etc. with quinalizarin at *p*H 5.0 can be inhibited by the addition of fluoride, which in regulated excess has hardly any effect on the gallium reaction. Fluoride does not prevent the reaction of iron (III), tin (II), antimony (III), copper, lead, indium, germanium, vanadium (IV and V), and molybdenum (VI). Magnesium, manganese, iron (II), mercury (II), thallium (I), cadmium, tungsten, uranium (VI), and arsenic (V) do not give a color with quinalizarin at *p*H 5; other metals such as nickel, cobalt, etc. interfere only because of their own color. Zinc does not react if present in amounts less than 0.5 g. per liter. Metals such as silver, mercury (I), bismuth, columbium, etc. precipitate as chlorides or hydrolyze out, and the amounts left in solution do not interfere. Citrate, oxalate, and tartrate prevent the reaction of gallium as well as ferric iron and aluminum. Phosphate reduces the sensitivity of the gallium reaction.

The procedure following is that of Willard and Fogg. Because of the varied nature of the separations required, the procedure has been divided into sections. Aluminum is precipitated as sodium fluoaluminate and gallium then determined in the filtrate. Iron and indium are precipitated as the hydroxides with manganese dioxide as collector by an excess of sodium hydroxide. The weakness of the method lies in the difficulty of achieving a separation of iron and gallium. If more than about a milligram of iron is present, there is serious loss of gallium by coprecipitation

[10] H. H. Willard and H. C. Fogg, *J. Am. Chem. Soc.*, **59**, 40 (1937). Quinalizarin has been used by Majumidar and Sarkar[6] in the determination of gallium in bauxite.

with ferric hydroxide. The procedure becomes rather complicated if gallium must be separated from both iron and aluminum. In such a case iron is first separated with sodium hydroxide, the filtrate is acidified, aluminum and gallium hydroxides are precipitated with ammonia, the precipitate is dissolved in acid, and aluminum is separated with sodium fluoride. This particular procedure must be applied because large amounts of alkali salts interfere in the aluminum separation.

It is believed that the separations mentioned under IA above can, in many cases, be substituted with advantage for those described by these authors.

Special Solutions

Quinalizarin, 0.01 per cent alcoholic solution. The solution should be discarded after one week. A solution 1 to 4 days old gives the best results.

Sodium fluoride, saturated solution in water.

Standard gallium solution, 0.010 mg. Ga per milliliter.

§ Procedure

In the Presence of Aluminum. Not more than a few milligrams of potassium or 100 mg. of sodium should be present.

Add dilute ammonium hydroxide to the solution until a turbidity appears, clear the solution with 6 *N* hydrochloric acid and add an excess of 4 ml. Next dissolve 7.7 g. of ammonium acetate and 2.7 g. of ammonium chloride in the solution and dilute to 70–80 ml. Heat to 70–80° and add with stirring sufficient sodium fluoride solution to precipitate the aluminum as Na_3AlF_6 and leave an excess of 0.5 g. per liter. The precipitate should be finely crystalline. Allow the mixture to stand for an hour with occasional stirring, add a little filter paper pulp, filter off the precipitate, and wash with small portions of water containing a few drops of sodium fluoride solution. Dilute the filtrate almost to 100 ml., adjust the *p*H to 5.0 (quinhydrone electrode) and make up to 100 ml. Take an aliquot containing 1 to 10 micrograms of gallium if the color comparison is to be made in 50 ml. Nessler tubes. Prepare a series of standards containing the same amount of ammonium acetate, ammonium chloride, and sodium fluoride as the unknown solution (the *p*H of all the solutions must be the same), and add 1.0 ml. of quinalizarin solution to each tube. Compare the colors one or two minutes after mixing.

If the concentration of aluminum is less than 15 mg. per liter, gallium can be determined directly without the preliminary precipitation of sodium fluoaluminate.

In the Presence of Iron and Indium. Not more than a milligram of ferric iron may be present; as much as 100 mg. of indium is permissible.

Heat the solution, having a volume of 25 ml. or less, to boiling and add enough 4 *N* sodium hydroxide to make the final concentration 0.5 to 1 *N*. Continue boiling until the precipitate coagulates, add filter paper pulp, filter, and wash the precipitate with hot 1 per cent sodium chloride solution made alkaline with sodium hydroxide (the filter paper and pulp should be washed with hot 1.5 *N* sodium hydroxide before use). Heat the filtrate nearly to the boiling point and add 0.5 ml. of 1 per cent potassium permanganate solution followed by an equal volume of alcohol to reduce the permanganate. Continue heating until the green color has disappeared and a precipitate of manganese dioxide has been produced. Filter off the precipitate and wash as before.

Neutralize the filtrate to litmus with hydrochloric acid, and add enough ammonium chloride, ammonium acetate, and sodium fluoride to give a solution having a *p*H of 5 and a salt concentration recommended in the previous section. The ammonium chloride and ammonium acetate are conveniently added as a stock solution of *p*H 5 containing the two salts in the respective concentrations 1.5 and 3 *N*. Then determine gallium as before.

In the case of indium it is not necessary to filter off the precipitate before adding the permanganate. If the indium concentration of the solution is less than 8 mg. per liter, a separation is not necessary (in the presence of 0.5 g. sodium fluoride per liter the limit of detection of indium with quinalizarin is 10 mg. per liter).

In the Presence of Zinc and Aluminum or Iron. The procedures given above may be followed.[11] Zinc alone gives no color with quinalizarin if present in concentrations below 600 mg. per liter provided 0.5 g. of sodium fluoride is present per liter.

In the Presence of Iron and Aluminum. Separate iron as described above, and acidify the filtrate with hydrochloric acid. Precipitate aluminum and gallium with ammonia by the usual method, avoiding any large excess of ammonium hydroxide which might redissolve some gallium. Collect the precipitate in a Gooch crucible containing a layer of purified anthracene or phenanthrone.[12] (Filter paper cannot be used for the filtration because it contains traces of iron extracted by hydrochloric acid.) Transfer the anthracene mat and the precipitate to the precipitation beaker

[11] In the iron separation enough sodium hydroxide to dissolve the zinc hydroxide must be added.

[12] Purify by dissolving in hot acetone and pouring with stirring into an equal volume of concentrated hydrochloric acid. Wash with hot dilute hydrochloric acid and then hot water, and recrystallize the product from acetone and toluene. A hydrochloric extract of the purified material should give no color with quinalizarin under the conditions of the gallium determination.

and boil with dilute (6 *N*) hydrochloric acid to dissolve the hydroxides. Filter through a small filter paper, previously thoroughly washed with hot 6 *N* hydrochloric acid, to remove the filtering medium. Precipitate aluminum in the filtrate and proceed further as already described.

In the Presence of Lead, Copper, Tin, Antimony, Germanium, and Platinum. First remove germanium by boiling the solution strongly acidified with hydrochloric acid. Reduce the acidity of the remaining solution to the point where the hydrolyzable metals will just stay in solution and add a slight excess of pure 40- to 60-mesh cadmium metal. Stir until precipitation is complete, and filter off the excess cadmium and the precipitated metals. Add 2 ml. of concentrated sulfuric acid to the filtrate and evaporate to fumes to expel hydrochloric acid. Take up the residue in 75–100 ml. of water and remove cadmium from the solution by electrolysis. Precipitate traces of cadmium and other metals with hydrogen sulfide, filter, and treat the filtrate as already described.

There are no satisfactory methods for separating gallium from vanadium and molybdenum according to the authors.

TABLE 54

DETERMINATION OF GALLIUM BY THE QUINALIZARIN METHOD[a]

Foreign element mg.	Ga taken γ	Ga found γ
Al, 10	0.0	0.0
Al, 10	5.0	4.7
Al, 10	10	11
Al, 20	10	7.5
Fe, 0.5	10	9
Fe, 1.0	20	20
Fe, 2.0	10	5
In, 100	10	11
Zn, 25	5	6
Zn, 20; Fe, 1.0	5	4
Al, 15; Fe, 1.0	10	8
Pb, 100	10	12
Cu, 100	10	10
Sn, 100	50	53
Ge, 30	10	8

[a] Representative values from Willard and Fogg,[10] chosen to show performance of method with 10 γ quantities of gallium; larger quantities of gallium show smaller percentage error.

CHAPTER XIX

GERMANIUM

I. Separations

The volatility of germanium tetrachloride (boiling point 86°) makes possible an easy separation of germanium from most elements by distillation of a 1:1 hydrochloric acid solution. Less hydrochloric acid need be present if the distillation is made at a higher temperature from sulfuric acid solution (p. 339). Arsenic and fluorine are likely to accompany germanium into the distillate and cause errors in the subsequent colorimetric determination. Trivalent arsenic will distil over as the chloride. Even if arsenic is originally present in the quinquevalent state, some of it will distil unless an oxidizing environment is maintained. If a stream of chlorine, or chlorine and carbon dioxide, is passed through the flask during the distillation, all the arsenic will be retained in the latter.[1] Alternatively, potassium permanganate may be added to the flask. Another method of preventing the distillation of arsenic consists in reducing it to the arsenide by the addition of finely divided copper to the distilling flask.[2] Antimony is similarly reduced.

Fluorine, which will be present in traces after a hydrofluoric acid decomposition of a silicate sample, will distil over as fluosilicic acid, and the silica thus introduced into the solution will give high results in the colorimetric determination. This error is prevented by distilling off the fluosilicic acid from a sulfuric acid solution, then adding hydrochloric acid, and distilling the germanium tetrachloride.

Germanium may be separated from much arsenic (V) by electrolytic reduction to monogermane, GeH_4, in alkaline solution.[3] The monogermane is carried away in a stream of hydrogen, which is led through a hot tube to give a deposit of germanium.

Germanium sulfide is highly insoluble and serves well as a separation form for small amounts of the element. The sulfide is precipitated from a

[1] L. M. Dennis and E. B. Johnson, *J. Am. Chem. Soc.*, **45**, 1380 (1923); W. Geilmann and K. Brünger, *Z. anorg. allgem. Chem.*, **196**, 312 (1931); H. Lundin, *Trans. Electrochem. Soc.*, **63**, 149 (1933).

[2] W. C. Aitkenhead and A. R. Middleton, *Ind. Eng. Chem., Anal. Ed.*, **10**, 633 (1938).

[3] S. A. Coase, *Analyst*, **59**, 462 (1934).

6 *N* hydrochloric or sulfuric acid solution, which is saturated with hydrogen sulfide and allowed to stand for a day before filtration.

Tannin precipitates germanium from dilute hydrochloric and sulfuric acid solutions.[4] This is a separation from arsenic.

Germanium appears to be quantitatively coprecipitated with ferric and aluminum hydroxides in an ammonia precipitation.

Germanium tetrachloride can be extracted by carbon tetrachloride from strong hydrochloric acid medium (*e.g.*, 9 *N*). It may be possible to base a method for the isolation of germanium on this property.

II. Methods of Determination

Method B below is the more sensitive of the two methods described, but its precision is perhaps less. Both methods require the absence of silicate and phosphate.

A. The Germanomolybdate Method

Germanium yields a soluble yellow heteropoly acid with molybdenum (VI) in acid medium. In the solid state the compound is reported to have the composition $H_4[Ge(Mo_3O_{10})_4]\cdot xH_2O$.

Alimarin and Ivanov-Emin[5] first made use of the heteropoly acid for the colorimetric determination of germanium; the method has been investigated further by Kitson and Mellon.[6] The latter workers report that it is not advisable to carry out the reaction in a mineral acid medium, because the color fades rapidly and its intensity is extremely sensitive to the acid concentration (maximum intensity in the range 0.1–0.3 *N*). In an acetic acid solution conditions are more favorable. The color intensity in such a medium increases rapidly up to 3.5 *N* acetic acid and then more slowly. The concentration of molybdate, above a requisite value, has little effect on the intensity. The stability of the color increases with the acidity, the optimum acetic acid concentration being 5 *N* (at 6 *N* the solution is slightly yellow in the absence of germanium). Under the conditions of the procedure given below, the color fades slowly, the decrease in intensity corresponding to an error of less than 2 per cent after 15 minutes. Beer's law is valid up to at least 40 p.p.m. of germanium.

The most serious interference in the method is produced by phosphate,

[4] G. R. Davies and G. T. Morgan, *Analyst*, **63**, 388 (1938). Tannin precipitation of germanium from a hydrochloric acid distillate has been applied by A. Weissler, *Ind. Eng. Chem., Anal. Ed.*, **16**, 311 (1944), in determining the element in steel. The precipitation can also be made in the presence of oxalic acid as shown by H. Holness, *Anal. Chim. Acta*, **2**, 254 (1948).

[5] I. P. Alimarin and B. N. Ivanov-Emin, *Mikrochemie*, **21**, 1 (1936).

[6] R. E. Kitson and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **16**, 128 (1944).

silicate, and arsenate,[7] which also form yellow heteropoly acids (see Table 55). Among the ions that were found not to interfere when present in a concentration 100 times that of germanium the following may be men-

TABLE 55

SOME INTERFERING SUBSTANCES IN THE GERMANOMOLYBDATE METHOD[6]

Ion	Amount present, p.p.m	Error, %	Amount permissible,[a] p.p.m.
$AsO_3^{\equiv}$	5 (As)	2	5
$AsO_4^{\equiv}$	2 (As)	0	2
$B_4O_7^{=}$	500	4	200
$C_4H_4O_6^{=}$	20	0	20
F^-	50	2	50
$PO_4^{\equiv}$	2 (P_2O_5)	94	0
$SiO_3^{=}$	4	24	0
VO_3^-	2	78	0
Al^{+++}	20	14	0
Ba^{++}	50	2	50
Ca^{++}	50	2	50
Cu^{++}	50	4	25
Fe^{+++}	50	20	5
Pb^{++}	500	Ppts.	0
Ti^{++++}	500	Ppts.	0
Zn^{++}	200	2	200

[a] With 5 p.p.m. Ge.

tioned: benzoate, chloride, citrate, nitrate, oxalate, sulfate, tungstate, magnesium, manganese, mercury (I and II), and the alkali metals. Strong reducing agents, such ferrous salts, which are capable of converting germanomolybdate into the heteropoly blue must of course be absent.

The procedure of Kitson and Mellon follows.

Special Solutions

Ammonium molybdate, 2.5 per cent. Dissolve $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in warm water. Discard the solution if it becomes turbid. Store in a waxed bottle.

Standard germanium solution, 0.01 per cent germanium. Dissolve pure dry germa-

[7] According to Alimarin and Ivanov-Emin, large amounts of quinquevalent arsenic (as much as 0.1 g. in 100 ml. if a sufficiently large excess of molybdate is added for complex formation) do not interfere in their visual colorimetric method which is carried out as follows. Transfer the solution of the isolated germanium (p. 336) to a volumetric flask of such size that 5 to 50 p.p.m. of germanium will be present after dilution to volume. Add 4 ml. of 5 per cent ammonium molybdate for 100 ml. of solution and then enough nitric acid to give an acidity of 0.15 to 0.35 *N*. Keep the temperature of the solution below 25°. Prepare a standard germanium solution at the same time in a similar manner and compare the solutions after a few minutes.

nium dioxide ($GeO_2/Ge = 1.44$) in a minimum volume of 0.1 *N* sodium hydroxide (silica-free), dilute with water, make acidic with hydrochloric acid, and dilute to volume. Keep in a wax-coated bottle.

§ Procedure

Transfer the neutral sample solution (Note 1), preferably containing 0.25 to 3 mg. of germanium, to a 100 ml. volumetric flask. Add 30 ml. of glacial acetic acid, dilute with water to about 80 ml., add 10 ml. of ammonium molybdate solution, and make up to volume with water. Determine the transmittancy at 440 mμ or a shorter wave length within 15 minutes of the addition of molybdate.

Notes. 1. If germanium has been isolated as sulfide, dissolve the washed precipitate in the smallest volume of redistilled ammonium hydroxide or sodium hydroxide free from silicate and phosphate (best prepared from metallic sodium). Transfer the solution to a platinum or silver dish, add a slight excess of hydrogen peroxide to destroy the thiogermanate, and boil the solution to decompose the remaining peroxide. Then cool and neutralize the solution with dilute sulfuric acid. Instead of isolating germanium by sulfide precipitation from the hydrochloric acid distillate (p. 339) as prescribed by Alimarin and Ivanov-Emin, and Kitson and Mellon, it would seem preferable in most cases (especially when germanium tetrachloride has been distilled with a limited amount of hydrochloric acid from sulfuric acid medium) simply to neutralize the distillate and then proceed with the colorimetric determination. The reagents must be as free as possible from silica. In any event a blank must be run.

2. Hydrochloric or nitric acid can be used for acidification of the solution, in place of acetic acid, if the transmittancy is determined as soon as possible after adding molybdate. The concentration of hydrochloric or nitric acid should lie between 0.1 and 0.2 *N*, and the transmittancy should be determined within 5 minutes after mixing.[8]

B. The Heteropoly Molybdenum Blue Method

The germanomolybdate complex, like the molybdate complexes of phosphate, arsenate, and silicate, may be reduced by suitable reagents to a soluble blue substance containing molybdenum in a lower valence state. Poluektov[9] has given a procedure based on this fact, which he applied to the determination of germanium after separation as the chloride and sulfide. Ferrous sulfate is used as the reducing agent. This procedure has been modified and applied directly to the hydrochloric acid distillate of germanium.[10]

Boltz and Mellon[11] have recently studied the molybdenum blue method. They also use ferrous sulfate as reducing agent, but work in a more acidic

[8] Experiments of R. Ko, University of Minnesota, 1948.

[9] N. S. Poluektov, *Z. anal. Chem.*, **105**, 23 (1936).

[10] A.-G. Hybbinette and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **14**, 715 (1942).

[11] D. F. Boltz and M. G. Mellon, *Anal. Chem.*, **19**, 875 (1947). For the use of hydroquinone as reducing agent in the molybdenum blue method, see W. Fischer and H. Keim, *Z. anal. Chem.*, **128**, 443 (1948). These authors isolate germanium by sulfide precipitation.

solution than did Poluektov, the advantage claimed being more rapid and stronger color development. According to them, at least 1 ml. of 10 per cent ammonium molybdate must be present in 25 ml. of final solution for maximum color intensity. The excess of ferrous sulfate must be kept fairly constant. The acid concentration when the germanomolybdic acid complex is formed is important. An acidity of 0.1 to 0.2 *N* in sulfuric acid is recommended. Likewise the acidity at the time of reduction is important. The color intensity increases markedly up to about 1.6 *N*, after which it does not increase much up to 3.2 *N*. A final acidity of 1.5 to 2 *N* is recommended. It appears that the germanomolybdic acid is unstable under the conditions, since the longer the time interval between the formation of the complex and its reduction to the heteropoly blue, the weaker the color.

Beer's law holds as high as 4 p.p.m. of germanium; at higher concentrations less color is obtained than expected. Among non-interfering ions (concentration 500 p.p.m.) may be mentioned aluminum, ammonium, cadmium, calcium, chromium (III), cobalt, copper (II), magnesium, manganese, nickel, silver, zinc, acetate, arsenate, arsenite, bromide, chloride, citrate, nitrate, oxalate, and tungstate. The following ions interfere, the percentage error with 500 p.p.m. in the determination of 3 p.p.m. of germanium being indicated in parentheses: ferric iron (83), fluoride (8), phosphate (6.5), silicate (45), and vanadate (61). (The sign of the error is not stated by the authors mentioned.) Barium, bismuth, and lead salts produce precipitates under the conditions.

Special Solutions

Ammonium molybdate, 10 per cent aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$.

Reducing solution. Mix 2 per cent ferrous ammonium sulfate hexahydrate solution with 4 *N* sulfuric acid in the volume ratio 1:4.

Standard germanium solution, 0.01 per cent Ge. See p. 335.

§ Procedure

To 20 ml. of neutral sample solution (containing not more than 0.4 mg. of germanium) in a 50 ml. volumetric flask add 0.75 ml. of 4 *N* sulfuric acid, followed by 1 ml. of ammonium molybdate solution and, immediately thereafter, 25 ml. of the reducing solution. Dilute to the mark, mix, and obtain the transmittancy at 830 mμ.

III. Special Applications of the Heteropoly Molybdenum Blue Method: Germanium in Silicate Rocks and Minerals[10]

By suitable modification, the procedure given below can be applied to materials other than those mentioned.[12] The method of decomposition is

[12] Since silicate rocks are very low in arsenic, no special measures are included in the procedure for retaining it in the distilling flask. When appreciable quantities of arsenic are present, the distillation should be made in the presence of chlorine or alternatively of copper, as mentioned on p. 333.

based on the assumption that the sample can be brought into solution completely by hydrofluoric acid attack.

Apparatus

The all-glass (Pyrex) distilling apparatus of Scherrer (p. 182) may conveniently be used for the distillation of the germanium tetrachloride. The flask should preferably have a volume of 100 ml. The end of the condenser tube should be drawn to a narrow point. A test tube, drawn to a narrow taper at the lower end, is used as a receiver to hold the sodium hydroxide solution in which the germanium tetrachloride is absorbed; it should have a capacity of at least 12 ml. and should be well paraffined to prevent attack by the sodium hydroxide solution.

Special Solutions

Ammonium molybdate. Dissolve 6.00 g. of $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$ in about 35 ml. of water, add a cooled mixture of 16.0 ml. of concentrated sulfuric acid (sp. gr. 1.84) with 35 ml. of water, dilute the solution to 100 ml. with water, and preserve in a paraffined bottle.

Ferrous ammonium sulfate. Dissolve 10.0 g. of the hydrated salt in water containing 1.5 ml. of 6 *N* sulfuric acid and dilute to 500 ml.

Sodium acetate. Dissolve 67.5 g. of sodium acetate trihydrate in water and dilute to 200 ml. Keep the solution in a paraffin-lined bottle.

Ammonium molybdate-ferrous ammonium sulfate reagent. This solution is unstable and must be prepared immediately before use. Add successively with shaking 10 ml. of ammonium molybdate solution, 10 ml. of ferrous ammonium sulfate solution, and 25 ml. of sodium acetate solution to 50 ml. of water and dilute to 100 ml. with water. Allow the reagent to stand 5 minutes before use.

Sodium hydroxide. Dissolve 25 g. of analytical quality reagent as low as possible in silica in 100 ml. of water and store the solution in a paraffined bottle.

Standard germanium solution, 0.01 per cent Ge or GeO_2. Dissolve a weighed amount of pure dry germanium dioxide in a few milliliters of water to which a drop or two of dilute sodium hydroxide (silica-free) has been added, neutralize with dilute sulfuric or hydrochloric acid, add a drop or two of acid in excess, and make up to volume.

§ Procedure

Weigh 1.0 g. of rock powder into a platinum dish and add a few milliliters of water, 6 ml. of 1:1 sulfuric acid, 0.5 to 1 ml. of concentrated nitric acid, and 10 ml. of hydrofluoric acid. Evaporate slowly on a hot plate until the sulfuric acid just starts to fume, cool, add a few milliliters of water and again evaporate to fumes. Repeat the addition of water and evaporation at least two times, never letting the mixture fume strongly. Transfer the decomposed sample to the distilling flask with 1:1 sulfuric acid (chloride-free) and water. The total volume of the solution should be approximately 50 ml., of which 35 ml. should be 1:1 sulfuric acid.

Removal of Residual Hydrofluoric Acid. To remove traces of fluoride, bubble air slowly through the solution and raise the temperature to 140° C. Maintain the temperature at this figure during the distillation by the slow addition of water through the funnel. In this manner distil over and dis-

card 150 ml. of liquid. Allow the distilling flask to cool, add 15 ml. of water and, while passing air through the solution, distil until a temperature of 120° is reached. Catch the distillate in a paraffined drawn-out test tube containing 1 ml. of 25 per cent sodium hydroxide solution and 1 ml. of water. Neutralize the distillate with 1:1 hydrochloric acid, using phenolphthalein as indicator, add a drop of sodium hydroxide, and then acidify with acetic acid and add the mixed ammonium molybdate-ferrous ammonium sulfate reagent as described below under "Colorimetric determination," except use the whole solution instead of an aliquot. Prepare the comparison solution by adding the reagent to a solution having the same composition as the neutralized distillate. If the distillate shows no color when compared against the reference solution, all hydrofluoric acid has been expelled from the solution in the distilling flask and germanium may be distilled over as described in the next section; if a color is shown distil again at 140° as already described until a negative result is obtained.

TABLE 56

DETERMINATION OF GERMANIUM IN SILICATE ROCKS

Sample	Germanium present[a] %	Germanium found %	Error %
Granite	0.0005	0.0005	0.0000
Granite	0.0010	0.0009	−0.0001
Granite	0.0030	0.0029	−0.0001
Granite	0.0058	0.0050	−0.0008
Granite[b]	0.00026	0.00028	+0.00002
Granite[c]	0.00026	0.00030	+0.00004
Diabase	0.0008	0.0007	−0.0001
Diabase	0.0014	0.0013	−0.0001
Diabase	0.0056	0.0052	−0.0004

[a] Includes the germanium originally present in the samples as determined by method described (0.00026% in granite, 0 00014% in diabase).

[b] Contained 0 05% Cl.

[c] Contained 0.01% As.

Distillation of Germanium Tetrachloride. Add 2 ml. of 1:1 hydrochloric acid and 2 ml. of water to the cool contents of the distilling flask, and distil while bubbling air through the solution until the temperature reaches 120°.[13] Collect the distillate in the drawn-out test tube containing 2.00 ml. of 25 per cent sodium hydroxide solution. At the end of the distillation, neutralize the solution with 1:1 hydrochloric acid, transfer to a 25 ml. volumetric flask, and make up to volume with water.[14]

[13] Approximately 5 ml. of liquid should distil over.

[14] With minimal amounts of germanium omit the dilution to volume and use the whole of the distillate instead of an aliquot in the subsequent colorimetric determination.

Allow the distilling flask to cool, add 2 ml. of 1:1 hydrochloric acid and 2 ml. of water, and distil as before. Neutralize the solution, transfer to a 25 ml. volumetric flask and make up to the mark with water. With small amounts of germanium practically all is found in the first distillate but with quantities in the neighborhood of 25 γ a small amount is found in the second distillate.

Colorimetric Determination of Germanium. Prepare two standard germanium solutions as follows. Measure out two portions of germanium oxide solution containing, for example, 5 and 10 γ of germanium, add 10 ml. of water, 1.5 ml. of 1:1 hydrochloric acid and 2.00 ml. of 25 per cent sodium hydroxide solution. Neutralize the solutions carefully with 1:1 hydrochloric acid (phenolphthalein as indicator) and dilute to 25 ml. In a similar manner prepare a blank solution for the color comparison by neutralizing 2.00 ml. of sodium hydroxide and diluting to 25 ml.

Take a 10 ml. aliquot of each standard, of the two germanium distillates and of the blank. Make each solution basic with a drop of 25 per cent sodium hydroxide and then acidify with 0.10 ml. of 1:1 acetic acid. Add 10.0 ml. of ammonium molybdate-ferrous ammonium sulfate reagent, mix and dilute to 25 ml. with water. After 15 minutes compare the germanium distillates and the standards against the blank solution in a photoelectric photometer, using a red filter.[15] The standard series method of comparison may also be used. The color intensity of the solutions increases slowly on standing and the readings should therefore be made after the period of standing specified. Although germanium in appreciable amounts is very unlikely to occur in the reagents, it is nevertheless advisable to run a blank through the procedure, especially since any contamination by silica will then be revealed.

[15] The extinction is proportional to the concentration up to about 1.5 p.p.m. of germanium in the solution, but at higher concentrations the color intensity is less than demanded by the concentration.

CHAPTER XX

GOLD

I. Separations

A. Precipitation Methods

The easy reducibility of gold to the metal provides a basis for its isolation from most elements.[1] Gold may be readily precipitated from extremely dilute, acid solutions by such reducing agents as stannous chloride, zinc, and magnesium if a suitable collector is used.[2] Mercury, mercurous chloride, lead, and tellurium have been used as collectors. Tellurium is very useful for the purpose. The precipitate of elemental tellurium, produced by reduction with stannous chloride, contains the gold as telluride. The precipitate may be dissolved in aqua regia; the tellurium in the solution does not interfere if gold is determined by the rhodanine method. If tellurium must be removed, as when determination of gold with stannous chloride is to follow, the precipitate can be ignited strongly to volatilize tellurium oxide. Directions for the tellurium coprecipitation are given later in this chapter in connection with the rhodanine method for the determination of gold.[3] By the use of this method, gold can be separated from much iron, copper, lead, and other metals (Table 58). Palladrum, platinum, mercury, and more or less silver will be coprecipitated together with the gold. Small amounts of other metals will contaminate the precipitate, but ordinarily will do no harm because only a very small quantity

[1] Passing reference may be made to the familiar method of isolation used in fire assaying in which the sample is fused with a mixture of lead oxide, a reducing agent, and a "flux," whereby the gold is collected in a lead button, from which after cupellation and parting it is recovered as the pure metal. Although in this process the gold is finally weighed, there is no reason why the metal could not be dissolved and determined colorimetrically, if its amount was so small as to preclude accurate weighing.

[2] W. E. Caldwell and K. N. McLeod, *Ind. Eng. Chem., Anal. Ed.*, 9, 530 (1937), precipitate gold and silver by adding magnesium metal and mercuric chloride to a hydrochloric acid solution. The final determination is made by cupellation and weighing Gold in concentrations of 0.001 p.p.m. was recovered within the limits of experimental accuracy. These authors also describe a procedure for isolating gold by coprecipitation with a mixture of mercury and mercury amino salt obtained by adding mercurous nitrate to an ammoniacal sample solution.

[3] W. B. Pollard, *Analyst*, 62, 597 (1937), also uses tellurium as a collector for gold in a volumetric method, but precipitates it with sulfur dioxide from a 1:10 hydrochloric acid solution. He was able to recover 0.01 mg. of gold quantitatively from about 10 liters of solution, using 200 mg. of tellurium.

of tellurium need be used, and the absolute amounts of the contaminants will therefore be negligibly small.

Gold can be precipitated with various organic reducing agents such as metol, *p*-phenylenediamine, and hydroquinone[4] in hot 1:10 hydrochloric acid solution. Palladium, platinum, tellurium, and selenium are not precipitated under these conditions, and palladium and platinum at least show little tendency to contaminate the precipitate of gold. The possibility of precipitating gold in this manner from highly dilute solutions has not been investigated.

In the determination of gold in sea water, ammonium sulfide has been used as precipitant for the gold with lead sulfide as the collector.[5] This method permits the quantitative recovery of gold from solutions containing 1 γ in 1000 liters.

Incomplete recovery of gold in very low concentrations (2.5 γ in 100 ml.) by hydrogen sulfide precipitation from 1 per cent acetic acid solution with lead as collector has been reported.[6] Losses in the subsequent determination by cupellation rather than incomplete precipitation may be the cause of the incomplete recovery.

Charcoal has been used as an adsorbent for gold in its determination in the water of streams.[7] The charcoal is ashed after adsorption, the ash brought into solution, and gold determined with stannous chloride or rhodanine reagent (p. 346).

B. Extraction Methods

The extractability of chloroauric acid from hydrochloric acid medium, and of bromoauric acid from hydrobromic acid, by ether and ethyl acetate[8] provides not only a method of isolating small amounts of gold but also a method for separating it from most of the platinum metals as well as other elements. The extraction of chloroauric acid by ethyl ether has been studied by Mylius,[9] although not especially from the standpoint of isolating small quantities of gold. The partition coefficient (ether/aqueous phase) has a value of about 50 for 3 to 6 *N* hydrochloric acid (Table 7). Since the solutions studied were not very dilute, it is not known whether the coefficient has the same value for extremely low gold concentrations.

[4] F. E. Beamish, J. J. Russell, and J. Seath, *Ind. Eng. Chem., Anal. Ed.*, **9**, 174 (1937); J. Seath and F. E. Beamish, *ibid.*, **9**, 373 (1937).

[5] F. Haber, *Z. angew. Chem.*, **40**, 303 (1927); F. Haber and J. Jaenicke, *Z. anorg. allgem. Chem.*, **147**, 156 (1925).

[6] G. Lunde, *Mikrochemie*, **5**, 118 (1927).

[7] C. K. Kropachev, *Sovet. Zolotoprom.*, **1935**, No. 8, 46.

[8] V. Lenher and C. H. Kao, *J. Phys. Chem.*, **30**, 126 (1926).

[9] F. Mylius, *Z. anorg. Chem.*, **70**, 203 (1911); F. Mylius and C. Hüttner, *Ber.*, **44**, 1315 (1911).

Bromoauric acid is a better extraction form for gold than is chloroauric acid.[10] Isopropyl ether is a more satisfactory solvent than ethyl ether, ethyl acetate, or hexone. The hydrobromic acid concentration of the aqueous phase should be 2.5 to 3 *M*. At this acid concentration the concentration of gold seems to have little effect on the completeness of the extraction. When the volumes of isopropyl ether and aqueous phases are equal, one extraction removes 98 to 100 per cent of the gold from a solution containing 0.1 mg. in 10 ml. With the exception of osmium as tetroxide, the platinum metals are not appreciably extracted. The extraction of ferric iron increases with the hydrobromic acid concentration. With 100 mg. of ferric iron in about 10 ml. of solution, the percentage of iron going into about an equal volume of isopropyl ether is 0.14, 0.14, and 1.0 in 2.0, 2.5, and 2.9 *M* hydrobromic acid solutions respectively.

II. Methods of Determination

Gold may be determined colorimetrically by reduction to the metal, which under suitable conditions gives fairly stable colloidal suspensions; by the formation of a slightly soluble red-colored compound with dimethyl- or diethylaminobenzylidenerhodanine, which also yields a colloidal dispersion; by conversion into bromoaurate ion, which has a moderately strong color; and by oxidation of certain organic compounds which yield strongly colored products with auric gold. All of these methods are subject to various interferences, and gold must usually be separated from the other constituents of the sample before it can be determined. The colloidal gold method is less sensitive than the others and, moreover, has other disadvantages which usually make the other methods more suitable for a trace determination. The rhodanine method has been studied in greater detail than the others from the standpoint of determining extremely small amounts of gold in the presence of large quantities of associated elements.

A. The Stannous Chloride Method

Various reagents have been used for the reduction of auric solutions to obtain a colloidal dispersion of gold suitable for use in colorimetric analysis. Stannous chloride is as good as, if not better than, any that have been proposed for the purpose.[11]

As well known, the color and stability of colloidal gold suspensions are

[10] W. A. McBryde and J. H. Yoe, *Anal. Chem.*, **20**, 1094 (1948). *Cf.* p. 345 of this book.

[11] For the use of α-naphthylamine hydrochloride as a colorimetric gold reagent see I. A. Paul'sen and S. M. Pevzner *J. Applied Chem. U.S.S.R.*, **11**, 697 (1938); *Chem. Abstracts*, **32**, 6972 (1938).

greatly dependent upon the electrolyte concentration of the solution. The standard solutions for the construction of the reference curve or for comparison must have the same acid and salt concentration as the sample solution. Frequently this condition can be fulfilled only by isolating the

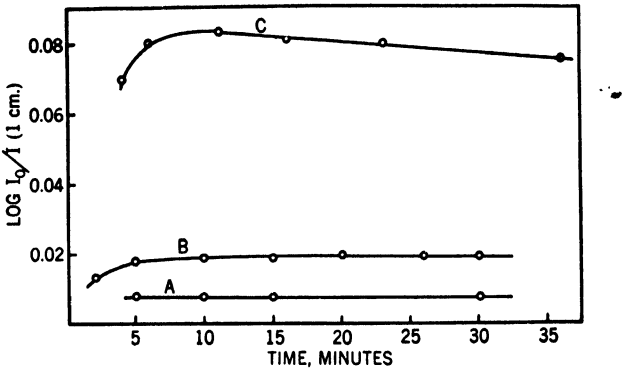


Fig. 37. Relation between time and optical density of gold suspension in the stannous chloride method at various gold concentrations: (*A*) 0.44 p.p.m., (*B*) 1.1 p.p.m., (*C*) 4.4 p.p.m., Au. HCl concentration *ca.* 1 *N*.

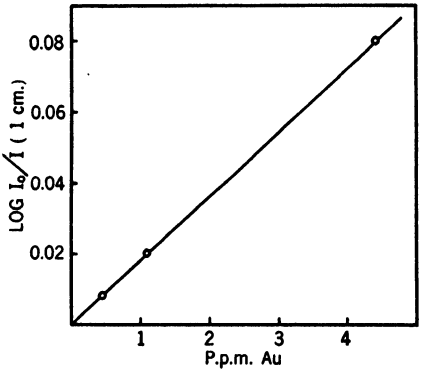


Fig. 38. Determination of gold by the stannous chloride method. Two ml. 10 per cent stannous chloride added to 20 ml. of gold solution in 1 *N* hydrochloric acid, solution diluted to 25 ml. with water and extinction determined after 20 minutes. No filter used.

gold and bringing it into solution again. Fink and Putnam[12] have shown the important role played by the hydrochloric acid concentration in the stannous chloride method for gold. At low acidities, 0.1 *N* or less, the colloidal solution has a yellow color and at higher acidities, in the neighborhood of 0.5 *N*, it has a purplish color, which passes into blue at still higher

[12] C. G. Fink and G. L. Putnam, *Ind. Eng. Chem., Anal. Ed.*, **14**, 468 (1942).

acidities. Color development is more rapid at low acidities than at high. Moreover the suspension formed in weakly acid solutions is more stable than that produced in more strongly acid medium. For these reasons it is advisable to work at low acidities. However, satisfactory results can be obtained at relatively high acidities. Figures 37 and 38 show the relation between color intensity on the one hand and time and concentration on the other in approximately 1 *N* hydrochloric acid solution.

Determination of gold with stannous chloride demands the absence of platinum, palladium, ruthenium, tellurium, selenium, silver (except in very low concentrations), mercury, and some other metals such as tungsten which give fairly strongly colored reduction products under the conditions.

Special Solutions

Stannous chloride, 10 per cent solution of the dihydrate in 1 *N* hydrochloric acid. This solution should be prepared fresh weekly.

Standard gold solution, 0.001 per cent Au as chloroauric acid in 0.1 *N* hydrochloric acid. This solution is best prepared fresh at reasonable intervals by diluting a 0.01 or 0.1 per cent gold solution. The latter may be obtained by dissolving pure gold in a few milliliters of aqua regia, evaporating just to dryness on the steam bath, adding a milliliter or two of concentrated hydrochloric acid, evaporating nearly to dryness, and making up to volume with 1 *N* hydrochloric acid.

§ Procedure

The sample solution may contain 10 to 100 γ of gold (III) in a volume of 20 ml. or less, and should preferably be only slightly acid (0.05 *N* in hydrochloric acid). If necessary, however, one may work with a solution 1 *N* in hydrochloric acid. Dilute with water to about 20 ml. in a 25 ml. volumetric flask and add all at once 2 ml. of stannous chloride solution. Make up the volume to the mark with water, mix, and allow to stand 20 minutes. Then determine the transmittancy. It is hardly necessary to use a filter, although slightly lower transmittancies will be obtained with green light. The standard solutions for the reference curve must have the same acidity and the same concentration of extraneous salts as the sample solution.

B. The Bromoaurate Method[13]

A moderately sensitive method for gold may be based on the formation of orange-colored bromoaurate ion by addition of hydrobromic acid to a gold (III) solution. In acid medium (*p*H 2 or less) the color is stable.

[13] McBryde and Yoe.[10] These authors also describe the application of the bromoaurate method to the determination of gold in ores and concentrates. Gold is isolated by coprecipitation with tellurium followed by isopropyl ether extraction.

The amount of chloride present must not be more than three times that by weight of bromide, else the full color is not developed because of appreciable reversal of the reaction

$$AuCl_4^- + 4\ Br^- \rightleftharpoons AuBr_4^- + 4\ Cl^-$$

It appears that mixed ions, such as $AuCl_3Br^-$, may also be formed. The law of Beer is followed. Ions that lead to high results include iron (III), chromium, nickel, palladium, platinum, and rhodium. Colorless ions generally do not interfere. As much as 1000 p.p.m. of tellurium (IV) may be present. Phosphate and fluoride do not interfere; nitrate and sulfate are without effect.

Gold can be separated from the platinum metals, except osmium as the tetroxide, and most of any ferric iron present by extraction with isopropyl ether from hydrobromic acid medium as already mentioned under IB. Small amounts of iron coextracted with gold can be made harmless with phosphoric acid.

§ Procedure

Adjust the volume of the sample solution to 10–12 ml. and add 5 ml. concentrated hydrobromic acid. Extract twice with 15 ml. of isopropyl ether (free from alcohols). Combine the ether extracts and wash with 5 ml. of 4 *M* hydrobromic acid. Remove gold from the ether phase by shaking with one 20 ml. and two 10 ml. portions of water. Add 1 ml. of concentrated hydrobromic acid to the combined water extracts and heat on the water bath to remove ether. If iron may be present, add 0.5 ml. of concentrated phosphoric acid. Dilute the solution to volume and find the transmittancy at 380 mμ.

C. The Rhodanine Method[14]

In slightly acidic solution, *p*-diethylaminobenzylidenerhodanine (p. 128) yields slightly soluble red or red-violet products with auric gold, silver, palladium (II), platinum, mercury, and copper (I). A sensitive method for the determination of gold may be based on this reaction.[15]

The colloidal suspension of the gold compound (believed to contain gold in the univalent state) is quite stable, and there is no necessity for using a protective colloid at low gold concentrations, for which the procedure is intended. A suitable acidity for the reaction is 0.12 *N* in hydrochloric acid.

[14] E. B. Sandell, *Anal. Chem.*, 20, 253 (1948).

[15] The reagent has been used by B. K. Merejkovsky, *Bull. soc. chim. biol.*, 15, 1336 (1933), for the determination of gold in biological samples. The procedure given here differs considerably from that of Merejkovsky.

At lower acidities, *e.g.*, 0.075 *N*, the sensitivity is greater but the reproducibility is poorer (Fig. 39). It is evident that the acidity must be closely controlled. Under the condition specified in the procedure below, the full color intensity of the suspensions is attained in 1 to 2 minutes, after which it decreases. The rate of fading is illustrated by the following data obtained for a 1.1 p.p.m. gold suspension in 0.12 *N* hydrochloric acid in the presence of fluoride (extinction versus time in minutes after mixing): 3 minutes, 0.113; 5, 0.112; 12, 0.107; 18, 0.104; 30, 0.100. The concentration-extinction curve is a straight line up to at least 2 p.p.m. of gold, but

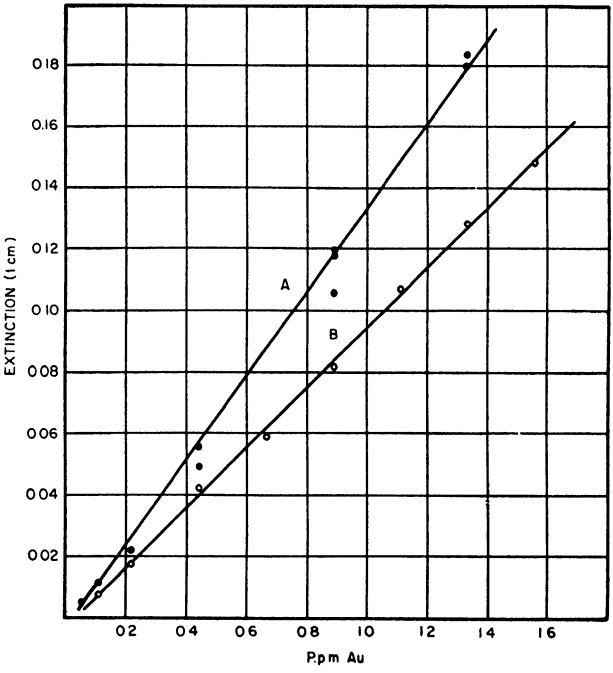


Fig. 39. Determination of gold with *p*-diethylaminobenzylidenerhodanine in 0.075 *M* hydrochloric acid (A) and in 0.12 *M* hydrochloric acid (B). Green filter.

it does not quite pass through the origin (extinction of reagent subtracted). The photometric technique can be used to determine as little as 0.5 γ of gold in a volume of 5 ml. when a 1 cm. cell is used. Below this amount visual comparison in narrow tubes can be applied if an absorption cell of greater thickness is not available. The limit of detectability is approximately 0.05 γ under the conditions of the procedure below.

The concentration of silver ion in a saturated solution of silver chloride in 0.1 *N* hydrochloric acid is too small to give a color with the reagent. Fifty micrograms of mercury (II) under the same conditions give no color.

Palladium reacts even more sensitively than gold with the reagent. However, small quantities of palladium (up to 3 γ) can be made harmless with dimethylglyoxime, which does not impair the gold reaction. Platinum

TABLE 57

PHOTOMETRIC DETERMINATION OF GOLD WITH DIETHYLAMINOBENZYLIDENERHODANINE AFTER COPRECIPITATION WITH TELLURIUM

Gold taken, γ	Gold found, γ	
	0.075 *M* HCl	0.12 *M* HCl
0.5	—	0.6
1.0	0.9	0.95
2.0	2.05, 1.75	1.95
2.5[a]	—	2.55
2.5[b]	—	2.4
3.0	2.9	2.85
4.0	—	3.9
5.0	4.7	5.0
7.0	7.75	—
8.0	—	8.3

[a] 1.1 mg. of Ag present.
[b] 500 mg. of ferric iron (as sulfate) present.

TABLE 58

DETERMINATION OF GOLD WITH DIETHYLAMINOBENZYLIDENERHODANINE BY VISUAL COMPARISON AFTER COPRECIPITATION WITH TELLURIUM

Addition	Gold taken, γ	Gold found, γ
None	0	0.0
	0.3	0.4
0.2 mg. Ag	0	0.0
0.5 mg. Ag	0.5	0.5
0.5 gram Fe (as ferric sulfate)	0	0.0
	0.2	0.2
	0.3	0.3
	0.5	0.5
0.5 gram Fe (as ferric sulfate), 0.005 mg. Ag	0.5	0.55
0.5 gram Fe (as ferric sulfate), 0.02 mg. Ag	0.2	0.2
0.5 gram Fe (as ferric sulfate), 0.2 mg. Ag	0.2	0.25
0.5 gram Cu (as cupric sulfate)	0	0.0
	0.3	0.25
0.6 gram Pb (as nitrate)[a]	0	0.0
	0.3	0.35
0.5 gram As_2O_3, 0.05 gram Sb (III)[b]	0.3	0.25

[a] Total volume *ca.* 90 ml. Some lead chloride precipitated; dissolved by washing tellurium precipitate with 25 ml. of hot 1 to 4 HCl.
[b] Volume 70 ml. at time of precipitation.

reacts much less sensitively than gold. A solution containing 0.8 p.p.m. of platinum (IV) in 1 *N* hydrochloric acid showed no color after 20 minutes. Stronger solutions may give a color, especially on long standing; it may be that quadrivalent platinum is reduced to the divalent state, which is the form probably reacting.

Because of its oxidizing action, ferric iron produces a brownish coloration with the rhodanine reagent. The interference of small amounts of iron (0.1 mg.), such as might be carried down in the tellurium precipitate in the isolation of gold, can be prevented by the addition of a little sodium fluoride. Strong oxidizing agents such as bromine and chlorine give a coloration similar to that produced by gold. Some distilled water has been found to contain enough free chlorine to give false results. Electrolytes seriously disturb the determination because of their effect on the colloidal suspension; the color intensity is decreased.

The gold-rhodanine compound is soluble in chloroform and an extraction procedure has been proposed for the colorimetric determination.[16]

The following procedure includes directions for the isolation of gold by coprecipitation with elemental tellurium produced by stannous chloride as reducing agent.

Special Solutions

p-Diethylaminobenzylidenerhodanine, 0.05 gram in 100 ml. of absolute ethyl alcohol. The solid dissolves slowly. The solution is stable.

Stannous chloride, 20 grams of the dihydrate in 100 ml. of 2 *N* hydrochloric acid, prepared fresh at reasonable intervals. Any insoluble material should be removed by filtration.

Tellurium tetrachloride, 1 mg. of tellurium per ml. Treat 100 mg. of precipitated tellurium with 1 or 2 ml. of nitric acid and evaporate to dryness. Add 1 ml. of hydrochloric acid and again evaporate to dryness. Dissolve the residue in 10 ml. of concentrated hydrochloric acid and dilute to 100 ml. with water.

Sodium fluoride, 1 gram in 100 ml. of water.

Standard gold solution, 0.001 per cent gold as chloroauric acid in 0.10 *M* hydrochloric acid. This solution is conveniently obtained by diluting a 0.010 per cent gold stock solution in 1.0 *M* hydrochloric acid with water.

§ Procedure

The sample solution (0.1 to 10 micrograms of gold) may conveniently have a volume of 50 ml. It should not contain strong oxidizing agents such as nitric acid.

[16] N. S. Poluektov, *Trudy Vsesoyus. Konferentsii Anal. Khim.*, 2, 393 (1943); *Chem. Abstracts*, 39, 3494, gives the following directions. The gold solution is acidified with a few drops of 1 *N* nitric acid and treated with 0.5–1.0 ml. of reagent (1 ml. of 0.03 per cent alcoholic *p*-dimethylaminobenzylidenerhodanine, 13 ml. of benzene, and 36 ml. of chloroform). The mixture is shaken vigorously and the color of the benzene-chloroform layer (pink-violet) is compared with standards. The limit of detectability is 0.1–0.2 γ of gold in 5 ml. Silver does not interfere if separated as chloride.

Add enough hydrochloric acid to make its concentration 2.5 *N*, and 0.2 ml. of tellurium solution. Mix, and add 5 ml. of stannous chloride solution or more as required to reduce iron and copper and produce a brown colloidal precipitate of tellurium, followed by an excess of 3 to 5 ml. Heat to boiling and keep near the boiling point for 0.5 hour or until the precipitate is well coagulated. Collect the precipitate in a small porous porcelain filter crucible (7 ml.). Wash the precipitation beaker and the crucible with five portions of 1 to 4 hydrochloric acid of 5 ml. each. Wash carefully to remove all iron and other foreign substances.

Add 1 ml. of aqua regia (1 volume of nitric acid to 3 volumes of hydrochloric acid) to the precipitation beaker, moisten the walls with the aid of a stirring rod, heat almost to boiling, and pour the solution into the crucible. By the use of a stirring rod bring the acid into contact with the tellurium on the walls of the crucible, and when all or most of the precipitate has been dissolved draw the solution through the crucible, catching the liquid directly in a 20 ml. Pyrex beaker. Add 1 ml. more of aqua regia to the beaker and repeat the operation as described to complete the solution of any remaining tellurium. Then wash the beaker and crucible with two portions of water of a few milliliters each. Evaporate the solution to dryness on the steam bath, avoiding prolonged heating of the dry residue. Allow the beaker to cool and add 0.01 ml. of aqua regia. By means of a stirring rod moisten the bottom and lower sides of the beaker with the drop of acid, so that all the residue is wetted. Set the beaker aside to permit the acid to evaporate at room temperature. (Conveniently the beaker is allowed to stand overnight under a large inverted beaker to protect from dust.)

Prepare standards containing 0, 0.2, and 0.4 microgram of gold by transferring the proper amount of standard gold solution to the glass-stoppered tubes, adding 0.30 ml. of 2.0 *M* hydrochloric acid and water (redistilled) to make the volume almost 4 ml., followed by 0.25 ml. of sodium fluoride solution, and mixing. (It would be more correct in principle to prepare the standards by evaporating to dryness after the addition of aqua regia and tellurium and further treating in the same manner as the sample solution, but this is believed to be an unnecessary refinement.)

Determination of Gold. When the tellurium residue is entirely dry, add exactly 0.30 ml. of 2.0 *M* hydrochloric acid to the beaker and bring into contact with all of the solid by the use of a stirring rod. Add 1 ml. of water and stir. If the solution is clear, transfer it to a tube and rinse the beaker carefully with small portions of redistilled water to make the total volume in the tube 3.5 ml. If the solution is turbid (silver chloride), filter through a small porous porcelain filter crucible, catching the filtrate directly in a

tube, and wash with small portions of water to give a total volume of 3.5 ml. (or 4 ml., if the final volume is to be 5 ml.).

Add 0.25 ml. of sodium fluoride solution to the sample and standard tubes and mix by inversion. Now add 0.30 ml. of rhodanine reagent to each tube and mix at once by inverting three times. Bring the volume of each solution to the mark (4.5 or 5 ml.) with water and again mix by inverting three times. In a few minutes the colors will have reached their full intensity and, if the sample is less strongly colored than the 0.4 microgram standard, find the gold content by visual comparison, examining the tubes axially against a white background. If the gold content of the sample falls between two standards, a more exact comparison can be made by mixing the two standards in a small beaker, dividing the mixture between the two tubes, and again comparing.

If more than 0.4 microgram of gold is present in the sample solution, transfer the latter to a dry absorption cell, and obtain the transmittancy with a green filter exactly 10 minutes (or other fixed time) after the addition of the rhodanine reagent. To establish the standard curve take 0, 0.5, 1.0, 2.5, 5, 7.5, and 10 micrograms of gold, add enough 2.0 *M* hydrochloric acid to make the total volume equal to 0.30 ml. (bear in mind that the standard gold solution is 0.10 *M* in hydrochloric acid), treat with sodium fluoride and rhodanine reagent as described, and dilute to volume. A plot of extinction versus concentration should give a straight line.

The absorption cell should be cleaned with dilute hydrochloric acid after each reading to dissolve any precipitate that may have been deposited on the walls.

D. Methods Involving Formation of Strongly Colored Organic Compounds by the Oxidizing Action of Auric Gold

Various organic substances are oxidized by auric salts to intensely colored products, and several methods for the determination of gold based on this principle have been described. Such methods are unspecific, for other strong oxidizing agents will produce the same colored products, but they are nevertheless valuable in certain cases.

1. o-Tolidine Method

Chloroauric acid converts *o*-tolidine into a yellow compound in mineral acid solution. Interfering substances include free chlorine, osmium tetroxide, ruthenium salts, ferric iron, vanadate, tungstate, and nitrite.[17] The reagent has been used for determination of gold in the indirect measurement of the thickness of gold plating.[18] It was found that the maximum

[17] W. B. Pollard, *Analyst*, **44**, 94 (1919); *Bull. Inst. Mining Met.*, No. 223 (1923).

[18] W. S. Clabaugh, *J. Research Natl. Bur. Standards*, **36**, 119 (1946).

color intensity was attained 1 to 3 minutes after the addition of *o*-tolidine and that the intensity remained constant for 10 to 30 minutes if the reagent was pure (recrystallized from sulfuric acid solution). From 1 to 4 γ of gold in 25 ml. could be determined with an average deviation of 4 per cent when a 5 cm. absorption cell was used. Silver, copper, nickel, and zinc in amounts of 500 γ did not interfere. The general directions of Clabaugh follow.

§ Procedure

To the evaporation residue (obtained by evaporating the last portion of the solution at room temperature with the aid of a jet of air to prevent decomposition of chloroauric acid), containing from 0.5 to 10 γ of gold, add 25 ml. of tolidine reagent solution. Transfer the mixed solution to a 5 cm. absorption cell and obtain the transmittancy at 437 mμ.

The reagent solution is prepared by saturating 1 *N* sulfuric acid with purified *o*-tolidine and diluting with 19 volumes of 1 *N* sulfuric acid. Commercial *o*-tolidine can be purified by recrystallizing three times from hot 2 *N* sulfuric acid solution. The hot solution should be filtered through porous porcelain or fritted glass, not paper.

2. Malachite Green Method[19]

In faintly acid medium the leuco compound of malachite green, $PhCH(C_6H_4NMe_2)_2$, is oxidized by trivalent gold to malachite green and the originally colorless solution becomes blue-green. Iridium must be absent. Fluoride may be added to decolorize ferric iron. In brief, the determination is carried out as follows. One milliliter of reagent (0.05 g. of leuco malachite green in a mixture of 15 ml. alcohol and 35 ml. acetate buffer of *p*H 3.6) is added to the sample solution whose *p*H has been brought to 3.6 by the addition of acetate buffer, and the liquid is boiled for two minutes. After cooling, comparison is made against a similar standard with the aid of a yellow filter. When very small amounts of gold are involved, the malachite green formed can be extracted with chloroform. The author states that he was able to determine 3×10^{-6} per cent gold in a copper coin by the use of this method.

3. o-Dianisidine Method

Auric gold yields a red color with *o*-dianisidine in weakly acid solution, and this substance has been used as an indicator in a volumetric method

[19] L. M. Kul'berg, *Zavodskaya Lab.*, **5**, 170 (1936).

for the element.[3,20] It may also be used for a colorimetric determination. Approximately 50 ml. of sample solution, containing only a few drops of mineral acid, are treated with 0.5 ml. of 5 per cent potassium bifluoride (buffer) and 0.1 ml. of 0.1 per cent *o*-dianisidine in 0.05 *N* hydrochloric acid. The color may be compared after 10–15 minutes. Any chlorine, bromine, or nitrosyl chloride originally present must be removed. This can be done by allowing a stream of air to impinge on the sample solution having as small a volume as possible (a few milliliters).

The *o*-dianisidine method has been used by Block and Buchanan[21] in the determination of gold in biological fluids after destruction of organic matter with sulfuric acid and hydrogen peroxide, and oxidation of the gold with aqua regia.

E. The Mercurous Chloride Method[22]

When mercurous chloride is shaken with a gold solution, reduction of gold to the metal occurs on the surface of the particles and the precipitate becomes pink or purple. This behavior provides a method for determining 0.1 to 100 γ of gold by comparison against a series of standards. Gold is reduced in strongly as well as in slightly acid solutions. Palladium likewise is reduced by mercurous chloride over a wide range of acid concentration, whereas platinum is reduced in slightly acid medium at room temperature, both metals coloring the mercurous chloride gray. Selenium and tellurium react in 6 per cent to concentrated hydrochloric acid solutions and arsenic (III) above 27 per cent acid. Iodide also colors the mercurous chloride. Oxidizing agents, including iron (III) and copper (II), interfere by preventing the precipitation of the gold. Mercurous chloride alone has a tendency to turn gray when shaken with a hydrochloric acid solution. This effect is reduced if the hydrochloric acid is first boiled with mercurous chloride and filtered.

§ Procedure

To 1–2 ml. of the sample solution, neutral or slightly acid and containing 0.1–10 γ Au, add 5 ml. of cold 0.5 *N* hydrochloric acid previously boiled with a little mercurous chloride and filtered. Add 0.10 g. of mercurous chloride and shake in a glass-stoppered tube for 2–3 minutes. Allow the

[20] A. R. Jamieson and R. S. Watson, *Analyst*, **63**, 702 (1938).

[21] W. D. Block and O. H. Buchanan, *J. Biol. Chem.*, **136**, 379 (1940).

[22] G. G. Pierson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 437 (1934); **11**, 86 (1939). The principle of this method was already known to F. Haber.

mercurous chloride to settle and compare with a series of standards similarly treated.

III. Special Applications

The stannous chloride-tellurium precipitation procedure already described can be used to separate gold from large quantities of iron, copper, lead, arsenic, and other metals. If this method of isolation is combined with a sensitive final determination (as with the rhodanine reagent and possibly with *o*-tolidine), as little as 0.1 p.p.m. of gold can readily be determined in a variety of materials. Sulfide minerals can generally be decomposed with nitric acid or aqua regia, with final treatment with hydrochloric acid to eliminate nitrate.

As an example of the application of the rhodanine method, we give directions for the determination of minute amounts of gold in plant material.[14]

§ Procedure

Ash the sample in a porcelain dish at low redness (not higher than 500° C.) in the customary manner. Take enough material to yield several grams of ash. Burn off as much as possible of the carbon. Transfer from 1 to 2 grams of ash to a small porcelain dish or a 20 ml. porcelain crucible (for an expected gold content of 0.2 microgram or more, a 1 gram sample is sufficient). Add a few milliliters of water followed by 2 ml. of concentrated nitric acid (for 1 gram of sample) added in small portions; keep the vessel covered with a watch glass. Evaporate to dryness on the steam bath

TABLE 59

RECOVERY OF GOLD FROM ASH OF LOMBARDY POPLAR LEAVES

Gold present, p.p.m.			Gold found, p.p.m.
Original	Added	Total	
0.10[a]	0.13	0.23	0.27
0.10	0.20	0.30	0.30
0.10	0.33	0.43	0.45

[a] Average of 0.13 and 0.08 p.p.m.

or low-temperature hot plate, gradually heat to low redness, and keep at that temperature for about 15 minutes or until brown fumes cease to come off.

Add 5 ml. of 1 to 1 hydrochloric acid to the residue and evaporate to dryness. Add another 5 ml. portion of dilute hydrochloric acid and evaporate to dryness again to destroy any remaining nitrate. Take up the residue in a mixture of 5 ml. of concentrated hydrochloric acid, 5 ml. of water, and 2 ml. of saturated bromine water. Heat almost to boiling while stirring at

intervals and filter through a sintered-glass crucible. Wash with 10 ml. of 1 to 1 hydrochloric acid and a few portions of water.

Transfer the filtrate and washings to a 100 ml. beaker, dilute to 50 ml., and add 0.2 ml. of tellurium solution followed by 5 ml. or more as required of stannous chloride solution. Then continue as in the general procedure described above.

Note. Complete destruction of carbon in the ashing is a necessity. Any colloidal carbon remaining is carried down by the tellurium precipitate and may give a color in the final solution. The nitric acid treatment followed by ignition ensures the destruction of all carbon.

CHAPTER XXI

INDIUM

I. Separations

Indium (III) sulfide can be precipitated quantitatively only in weakly acidic solution (acetic acid-acetate). However, it is carried down in strongly acid solution by various members of the hydrogen sulfide group, so that hydrogen sulfide precipitation of these metals should not be used as a method of separation from indium.[1] Possibly zinc or antimony (III) will serve as collectors in the sulfide precipitation of indium in weakly acidic medium. Indium can be separated from cadmium, nickel, cobalt, manganese, and, less successfully, from zinc and copper by precipitation with ammonium hydroxide in the presence of an ammonium salt at a *p*H of 5 or 6. Similar separations are effected by the use of sodium sulfite, potassium cyanate,[2] and other reagents which bring the *p*H of the solution to a value at which indium hydroxide or a basic salt is precipitated. These separations have been applied to comparatively concentrated indium solutions and very little is known about the behavior of very small amounts of indium under the conditions.

Indium chloride is not extracted from hydrochloric acid solution by ether (a separation from gallium), but indium bromide can be extracted from 4.5 *N* hydrobromic acid solution by ether.[3] Among the metals extracted from hydrobromic acid medium under the conditions are gallium, iron (III), gold (III), thallium (III), molybdenum (VI), rhenium, and small amounts of zinc and tellurium. Since the extractability of some metal halides by ether is a function of the metal concentration in the aqueous phase, further investigation is needed before this method can be recommended for the isolation of microgram quantities of indium.

Indium 8-hydroxyquinolate can be extracted from weakly acidic solutions by chloroform. Certain separations can thus be effected as noted

[1] I. Wada and S. Ato, *Sci. Papers Inst. Tokyo*, **1**, 57 (1922/24), found that bismuth and cadmium sulfides have a lesser tendency to carry down indium in 0.6 *N* acid medium than do the sulfides of lead, copper, and mercury.

[2] L. Moser and F. Siegmann, *Monatsh.*, **55**, 14 (1930), carry out the separation from cadmium, zinc, copper, nickel, and cobalt by adding an excess of potassium cyanide and boiling with potassium cyanate to precipitate indium hydroxide.

[3] I. Wada and R. Ishii, *Sci. Papers Inst. Tokyo*, **34**, 787 (1937/38).

under II (also see p. 115). Aluminum hydroxyquinolate is extracted less easily than indium hydroxyquinolate, and gallium hydroxyquinolate more easily than the latter, but the values of the constants are such that good separations do not appear possible on the basis of *p*H regulation alone (p. 119).

Ferric iron, and very likely gallium, can be separated from indium by extraction of the cupferrates of the former with chloroform from mineral acid medium (p. 142).

II. Methods of Determination

A. The 8-Hydroxyquinoline Method

The strong yellow color of indium hydroxyquinolate in chloroform solution provides the basis for a colorimetric method for the determination of minute amounts of indium.[4] The distribution of indium between aqueous and chloroform phases is governed by the relation

$$\frac{[InOx'_3]_{CHCl_3}}{[In^{+++}][Ox'^{-}]^3} = \text{constant.}$$

The value of the constant is 2×10^{33} at 18° according to S. Lacroix.[5] By using a sufficiently large amount of 8-hydroxyquinoline and adjusting the *p*H to a value that will provide an adequate concentration of oxinate ion, Ox'^{-}, the fraction of the total indium transferred to the chloroform phase can be brought as close as desired to 1.

Maximum absorption is shown by the chloroform solution at about 400 mμ. Under the conditions of the procedure given below, Beer's law is obeyed up to approximately 20 p.p.m. of indium in the chloroform. The extraction of indium is complete or nearly so in the *p*H range 3.2–4.5 under these conditions. The upper *p*H value has no real significance; it only indicates the acidity at which the formation of indium hydroxide or a basic salt becomes marked. If hydroxyquinoline is added to the aqueous solution before it is made basic the range can be extended upward. According to Lacroix (p. 117) the range for virtually complete extraction of indium hydroxyquinolate is *p*H 3.0– > 5.0.

At *p*H 3.5 the following metals interfere by giving a colored chloroform extract: aluminum, gallium, thallium (III), tin (II), bismuth, copper, iron

[4] T. Moeller, *Ind. Eng. Chem., Anal. Ed.*, **15**, 270 (1943).

[5] See p. 117 for a discussion of the equilibria involved in such an extraction. The value of the constant given above seems to be smaller than the true value, because it is based on a solubility product of indium hydroxyquinolate which was determined in a solution containing alcohol, in which the solubility is greater than in water.

(III), vanadium (V), molybdenum (VI), nickel, and cobalt (slightly). Among the metals not extracted at this *p*H are magnesium, calcium, strontium, zinc, cadmium, mercury (II), tin (IV), lead, manganese, chromium (III), and silver. It has been shown that indium can be determined in the presence of small quantities of zinc, lead, and cadmium.

A small amount of 8-hydroxyquinoline enters the chloroform phase at *p*H 3.5, but its effect on the transmission is provided for by the standard curve.

Chloroform solutions of indium hydroxyquinolate fluoresce strongly in the near ultraviolet and indium may thus be determined fluorimetrically at very low concentrations (*cf.* the corresponding method for gallium). This method has not yet been investigated in a systematic manner, but it is believed that it will be found superior to the colorimetric method for very small quantities of indium.

§ Procedure

Adjust the *p*H of the sample solution (25 ml.) to 3.5 and extract with five 5 ml. portions of 0.01 *M* solution of 8-hydroxyquinoline in chloroform. Dilute to volume (25–50 ml.) with chloroform and obtain the extinction of the solution at 400 mμ.

B. The Dithizone Method

May and Hoffman[6] have investigated the determination of microgram quantities of indium by the use of dithizone. The optimum *p*H range for the extraction by a carbon tetrachloride solution of dithizone is 5.2–6.3, and by a chloroform solution 8.3–9.6. Cyanide in moderate amount does not hinder the extraction, but citrate or tartrate does. The wave length of maximum absorption in both solutions lies at 510–520 mμ. The carbon tetrachloride solution of indium dithizonate is markedly light sensitive, the chloroform solution less so. Beer's law applies.

These authors describe a tentative method for the determination of indium in the presence of other metals, particularly zinc. In the proposed method, indium and various other metals (p. 115) are first isolated by chloroform extraction of the hydroxyquinolates at *p*H 4 from a citrate-containing solution. After destruction of the hydroxyquinoline, indium, gallium, aluminum, etc. are extracted by chloroform from an aqueous citrate-cyanide solution at *p*H 8.5 by the joint use of cupferron and dithizone. Either of these reagents alone does not provide a satisfactory recovery of indium. Indium is then transferred from the chloroform to

[6] I. May and J. I. Hoffman, *J. Washington Acad. Sci.*, **38**, 329 (1948).

water solution by shaking with 1:99 nitric acid. The final determination is made by adding 5 ml. of ammonia-cyanide mixture (200 ml. of 10 per cent potassium cyanide and 150 ml. of concentrated ammonia diluted to 1 liter) to 50 ml. of the 1:99 nitric acid solution and shaking with 15 ml. of 0.001 per cent (*w/v*) dithizone in chloroform for 1 minute. This method allows the determination of small amounts (*ca.* 10 γ) of indium in the presence of 10 mg. of zinc, copper, and lead. Aluminum, tin, and some other metals interfere.

CHAPTER XXII

IRIDIUM

I. Separations

Iridium is precipitated as the hydrous dioxide by adding sodium bicarbonate to a boiling acid solution containing bromate until a *p*H of 6 is reached.[1] Palladium and rhodium are also precipitated, but not platinum (IV); osmium and ruthenium must be removed from the solution by volatilization of the tetroxides before the hydrolytic precipitation is made. Palladium is then precipitated as the dimethylglyoxime compound, and rhodium is precipitated with titanous chloride in the filtrate. Some iridium is carried down by the metallic rhodium, and the precipitate must be dissolved in hot concentrated sulfuric acid and the precipitation repeated. Iridium is thus left with titanium which is precipitated with cupferron (double precipitation is necessary). The organic matter in the filtrate is destroyed with nitric and sulfuric acids. The procedure outlined has been used only on the macro scale and it is not known how well it will work when very low concentrations of iridium and the other metals must be dealt with. The addition of a little ferric iron should help to gather iridium in the hydrous oxide precipitation, the ionic radii of iron (III) and iridium (IV) being very similar (p. 25).

II. Methods of Determination

The direct colorimetric methods for iridium are not as sensitive as would be desired. The strong red-brown color of $IrCl_6^=$ allows moderately low concentrations of iridium to be determined. The visual sensitivity is in the neighborhood of 2 γ Ir per cm.[2] Trivalent iridium can be oxidized to the quadrivalent state with a slight excess of chlorine water. The color intensity is the same in 0.1 and 2 *N* hydrochloric acid. Possibly the interference of platinum and rhodium can be circumvented by determining the transmittancy of the solution before and after the addition of a suitable reducing agent which will convert $IrCl_6^=$ into the much less strongly colored chloroiridite ion without affecting the chloro complexes of the other metals.

A characteristic color reaction for iridium may be obtained by evaporating the solution to fumes with sulfuric acid and adding nitric acid or potas-

[1] R. Gilchrist, *Bur. Standards J. Research*, **12**, 291 (1934); **9**, 547 (1932). R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

sium periodate and again heating. A blue color is produced which becomes violet when the solution is diluted with nitric acid (water destroys the color). A similar color is obtained when an iridium solution is evaporated to fumes with perchloric acid. Unfortunately this reaction is not very sensitive, no more so than the chloroiridate test.

The indirect colorimetric determination of iridium rests on the rather strong oxidizing power of chloroiridate ion, which is able to convert various organic compounds into strongly colored products. Two reagents which have been used are benzidine[2] and leuco-malachite green.[3] Khlopin carries out the determination by adding 0.10 ml. of benzidine solution (1 g. benzidine dissolved in 10 ml. of glacial acetic acid and diluted to 50 ml. with water) to 10 ml. of very nearly neutral sample solution of chloroiridate (5 γ or more Ir) and comparing the blue color against standards having the same composition as the sample.

[2] V. G. Khlopin, *Ann. inst. platine*, 324 (1926).

[3] See p. 352.

CHAPTER XXIII

IRON

I. Separations

A special study of the isolation of minute quantities of iron, with special reference to the determination of iron in reagent chemicals, was made by Stokes and Cain.[1] These authors separate ferric iron as the hydroxide with hydrous manganese dioxide[2] as collector, and as the sulfide with cadmium sulfide as collector. Precipitation of iron as hydroxide may be applied in its isolation from solutions of the alkalies and alkaline earth metals, zinc, lead, cadmium, and other metals whose hydroxides are precipitated at a higher *p*H than ferric hydroxide or which can be kept in solution by an excess of ammonium hydroxide. Phosphate does not prevent complete precipitation of iron. The method cannot be used in the presence of tartrate, citrate, oxalate, pyrophosphate, arsenate, arsenite, or organic matter in general, which may prevent complete precipitation of ferric hydroxide. When such substances are present, iron is precipitated with ammonium sulfide in the presence of a little cadmium.[3] This method is limited to samples free from appreciable amounts of metals giving slightly soluble sulfides, except those soluble in excess ammonium sulfide. Directions for these procedures are given on p. 373.

Precipitation of iron with ammonium sulfide in the presence of tartrate serves to separate it from titanium, uranium, vanadium, phosphate, and some other elements less likely to interfere in the colorimetric determination.

Precipitation of iron by cupferron and neo-cupferron in acid medium is of importance as a separation from chromium, cobalt, nickel, manganese and a number of other elements which may prove disturbing in some of the

[1] H. N. Stokes and J. R. Cain, *J. Am. Chem. Soc.*, 29, 409, 443 (1907).

[2] This collector was used instead of aluminum hydroxide because the colorimetric procedure employed by the authors mentioned called for solution of the precipitate in thiocyanic acid in which aluminum hydroxide cannot be dissolved completely. It may also be pointed out that the manganese precipitate can be used to gather iron when sodium hydroxide is used for precipitation.

[3] For the determination of iron in sea water after precipitation with ammonium sulfide with basic magnesium salts as collector, see N. W. Rakestraw, H. E. Mahncke, and E. F. Beach, *Ind. Eng. Chem., Anal. Ed.*, 8, 136 (1936).

colorimetric methods. Ferric cupferrate can be extracted with a number of organic solvents (ether and chloroform).[4]

Extraction of ferric 8-hydroxyquinolate with chloroform from an acetic acid-acetate medium is occasionally of value in isolating traces of iron.

Iron in the ferrous state can be extracted by shaking a solution of *p*H 8 to 9 with a chloroform solution of isonitrosoacetophenone.[5] Many other heavy metals also form chloroform-soluble complexes with the reagent.

Much copper can be removed by electrolytic deposition from acid solution; small amounts can be removed by dithizone extraction in dilute mineral acid medium (p. 296).

II. Methods of Determination

There is no lack of colorimetric reagents for iron, but comparatively few are well suited for the determination of traces of iron. Some reagents react with ferric iron, others with ferrous. The former generally have the disadvantage that they cannot be used in the presence of appreciable concentrations of such ions as fluoride and pyrophosphate which form stable complexes with trivalent iron in acid medium, in which the color reaction must be carried out. In such cases better results can frequently be obtained by resorting to a reagent reacting with ferrous iron, which does not form such complexes or at least less stable ones.

Some characteristics of common colorimetric reagents for iron are given in Table 60. For the most accurate determination of minute amounts of iron, the use of *o*-phenanthroline (or the similar reagent α,α'-bipyridyl) is recommended. It reacts with ferrous iron. In its use, account must be taken of the possible interference of copper, nickel, and cobalt, which also react in very low concentrations. Thiocyanate is quite useful at times, but suffers from the disadvantage of giving a product whose color fades rather rapidly. Reagents which require adjustment of the *p*H within a narrow range are obviously not very desirable, and those that require a neutral or basic medium for reaction are of limited practical value.

A. The Thiocyanate Method

Thiocyanate is still extensively used for the determination of iron, even though other reagents may give better results. In spite of its limitations,

[4] R. Paulais, *Compt. rend.*, **206**, 783 (1938). *Cf.* S. M. Berman, J. J. Chap, and D. M. Taylor, *J. Assoc. Official Agr. Chem.*, **20**, 635 (1937). A. B. Beck, *Australian J. Exptl. Biol. Med. Sci.*, **23**, 311 (1945), isolates iron from a solution of ashed bio material by extracting the cupferron complex with chloroform or carbon tetrachloride at *p*H 1 or 2. A separation from copper and cobalt cannot be achieved in this way. These metals can be removed by first extracting with dithizone and α-nitroso-β-naphthol respectively at suitable acidities. See also p. 142.

[5] F. Kröhnke, *Ber.*, **60**, 527 (1927); E. Abrahamczik, *Mikrochemie ver. Mikrochim. Acta*, **25**, 240 (1938).

which are often not too serious, the thiocyanate is a valuable one in applied analysis. The reagent is cheap and readily available, and has the decided advantage over other reagents that it can be used in strongly acid medium. Moreover, the procedure is simple and rapid.

TABLE 60

PROPERTIES OF SOME REAGENTS FOR THE COLORIMETRIC DETERMINATION OF IRON[a]

Reagent	Sensitivity,[b] γ Fe/cm.²	Stability of color	pH range	Effect of excess reagent	Beer's law
α,α′-Bipyridyl	0.007 (522 mμ)	1 year	3–9	None	Obeyed
2,2′,2″-Terpyridyl	0.005 (552 mμ)	1 year	3–10	None	Obeyed
Disodium-1,2-dihydroxybenzene-3,5-disulfonate	0.009 (480 mμ)	Months or years[c]	8.5–>9.5[d]	None	Obeyed
Ferron	0.015 (610 mμ)	1–2 weeks	2.7–3.1	Change in hue	Not obeyed
4-Hydroxybiphenyl-3-carboxylic acid	0.03 (575 mμ)	1 day	*ca.* 3	Increases intensity	Obeyed
Mercaptoacetic acid	0.014 (540 mμ)	Several hours	7–12	None	Obeyed
Nitroso-R salt	0.0023 (720 mμ) 0.007 (620 mμ)	6 hours	3.9–5.1		Obeyed
o-Phenanthroline	0.005 (508 mμ)	6 months or more	2–9	None	Obeyed
Salicylaldoxime	0.011 (480 mμ)	1 day	6.2–6.6	None	Obeyed
Salicylic acid	0.03 (520 mμ)	2–3 days	2.5–2.7	Increases intensity	Obeyed
Sulfosalicylic acid	0.01 (430 mμ filter)	1 day or more	7		Obeyed
Thiocyanate	0.008 (480 mμ)	Fades rapidly unless stabilized	0.05–>1 *N*	Increases intensity	Slight deviation
Thiocyanate and acetone	0.004 (480 mμ)	Fades	0.05–>1 *N*	Increases intensity	Slight deviation

[a] This table is partly based on data given by J. T. Woods and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 554 (1941).

[b] Number of micrograms of iron in a column of solution of 1 cm.² cross section giving an extinction of 0.001.

[c] Color increases slightly first 18 hours, then constant.

[d] Blue color in weakly acidic medium, which is less sensitive than red color in basic solution.

More than one product can be formed when thiocyanate reacts with ferric ion. Depending upon the thiocyanate concentration, a series of complexes represented by $[Fe(CNS)_n]^{+3-n}$, where $n = 1 \ldots 6$, can be obtained. At low thiocyanate concentrations the colored species is predominantly $[Fe(CNS)]^{++}$, as shown by a number of investigators (see references on p. 130). At 0.1 *M* thiocyanate concentration the product is

mostly $[Fe(CNS)_2]^+$.[6] Above 0.2 *M* thiocyanate, negatively charged complex ions seem to predominate. The colors of all these complexes are red and there is not much difference in hue although there is a shift of maximum absorption toward higher wave lengths with increasing thiocyanate concentration (Table 61). Babko has reported values for the *K*'s of the reaction:

$$Fe^{+++} + n\ CNS^- \longrightarrow [Fe(CNS)_n]^{+3-n}.$$

Log K_n is respectively 2.3, 1.94, 1.4, 0.8, and 0.02 for $n = 1 \ldots 5$. Since thiocyanic acid is a strong acid the concentration of thiocyanate ion is affected but little by a change in the hydrogen-ion concentration of the solution.

TABLE 61

SHIFT IN WAVE LENGTH OF MAXIMUM ABSORPTION IN IRON–THIOCYANATE SYSTEM WITH CHANGE IN THIOCYANATE CONCENTRATION[a]

Concentration of ammonium thiocyanate, per cent (*w/v*)	Absorption maximum, mμ
0.02	450
0.2	456
1.0	470
2.0	477
4.0	480
7.5	480

[a] Ovenston and Parker.[7] In 1.7 *N* sulfuric acid.

The color intensity of an iron-thiocyanate solution depends upon a number of factors such as the excess of thiocyanate, the kind of acid present, and the time of standing.[7] A relatively large excess of thiocyanate is desirable. Not only is the sensitivity increased by increasing the thiocyanate concentration, but the color intensity then remains more nearly constant when the acidity is varied. Moreover a high concentration of thiocyanate reduces the errors due to chloride, phosphate, and other ions forming complexes with ferric iron in acid solution. A final concentration of thiocyanate of about 0.3 *M* is generally satisfactory. Care must be taken to have the same concentration of thiocyanate in the unknown and

[6] A. K. Babko, *J. Gen. Chem.* (*U.S.S.R.*), **16**, 1549 (1946); *Chem. Abstracts*, **41**, 4732 (1947). *Cf.* H. S. Frank and R. L. Oswalt, *J. Am. Chem. Soc.*, **69**, 1321 (1947).

[7] For more or less general studies of the thiocyanate method see J. T. Woods and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 551 (1941); C. A. Peters and C. L. French, *ibid.*, **13**, 604 (1941); G. J. Truter, *Onderstepoort J. Vet. Sci. Animal Ind.*, **21**, 305 (1947); T. C. J. Ovenston and C. A. Parker, *Anal. Chim. Acta*, **3**, 277 (1949).

the standards, because a relatively small difference leads to a fairly large change in color intensity. Metals such as cadmium and mercury which form complexes with thiocyanate bleach the iron color and the effect can be overcome only partially by adding more thiocyanate when these metals are present in fair amounts.

The acidity of the solution plays a minor role in determining the color strength provided enough acid is present to prevent appreciable hydrolysis of the iron, and the acid does not form a complex with ferric-iron. Thus when nitric acid is used for acidification the color intensity is virtually constant in the range 0.05 to 0.8 *N*. Even with hydrochloric acid the color intensity is but slightly lower in 1 *N* than in 0.1 *N* solution when the solution is 0.3 *M* in thiocyanate (Fig. 40). Moreover in 0.1 *N* hydro-

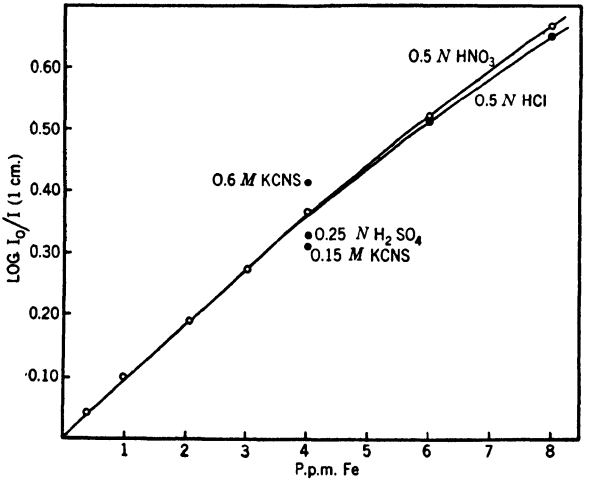


Fig. 40. Determination of iron by the thiocyanate method (green filter). All solutions, except as indicated, 0.3 *M* in KCNS. Curve for 0.1 *N* HCl solutions is practically coincident with 0.5 *N* HNO_3 curve.

chloric acid solution the color strength is the same as in nitric acid solution. Sulfuric acid reduces the color intensity in accordance with expectations. In order to avoid error, the same amount of sulfuric acid must be present in both unknown and standard (see Fig. 41).

The ferric-thiocyanate system does not in general[8] follow Beer's law. The color intensity does not increase quite proportionately with the iron concentration (Fig. 40). The magnitude of the resulting error can be seen from the figure. In 0.5 *N* nitric acid, with a standard containing 4 p.p.m.

[8] According to Woods and Mellon, Beer's law is obeyed up to 10 p.p.m. of iron in hydrochloric acid solution of *p*H 1.5–1.65.

of iron the error is +3.5 per cent for an unknown containing 2 p.p.m. of iron and *ca.* −6 per cent for 6 p.p.m. of iron (green filter used). The error is larger in hydrochloric acid solution.

Another source of error in the method arises from the fading of the ferric thiocyanate color when the solution is exposed to light, because of the reduction of ferric iron by thiocyanate or its decomposition products. In diffuse daylight a solution containing 4 p.p.m. of iron in 0.5 *N* HCl and 0.3 *M* thiocyanate shows approximately a 10 per cent decrease in color intensity after 10 minutes. The fading appears to be somewhat slower at lower acidities. At least in the initial stage, the fading is directly proportional to the time (Fig. 42). In 0.5 *N* nitric acid solution the fading ceases after about fifteen minutes and the color intensity then increases, eventually becoming stronger than it was originally.[9] This behavior is due to a reaction between the nitric acid and thiocyanate which results in the formation of a yellow-brown product. In the absence of iron this reaction becomes evident only after an hour or so in diffuse daylight.

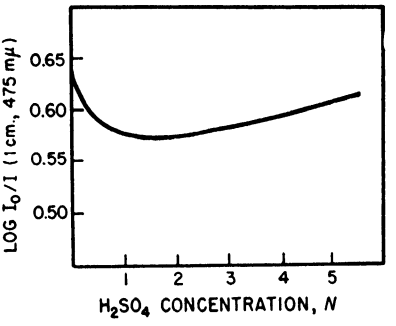


Fig. 41. Effect of concentration of sulfuric acid on color intensity in the ferric iron–thiocyanate system. (According to Ovenston and Parker.)

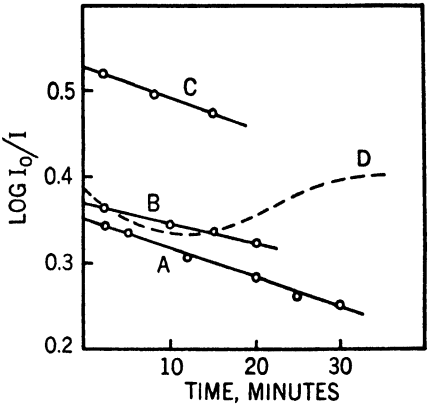


Fig. 42. Effect of time on ferric thiocyanate color intensity. Solutions exposed to diffuse daylight; strength of light only approximately the same in the different experiments, so that curves are only roughly comparable. *A.* 4 p.p.m. Fe in 0.5 *N* HCl. *B.* 4 p.p.m. Fe in 0.1 *N* HCl. *C.* 6 p.p.m. Fe in 0.1 *N* HCl. *D.* 4 p.p.m. Fe in 0.2 *N* HNO_3.

[9] According to H. A. Daniel and H. J. Harper, *J. Assoc. Official Agr. Chem.*, **17**, 286 (1934), it is more satisfactory to develop the thiocyanate color in 1 per cent nitric acid medium than in hydrochloric acid medium because of the greater stability of the color and freedom from the effect of metal chlorides.

The fading of the ferric thiocyanate color can be greatly decreased by adding certain oxidizing agents in regulated amount. Persulfate and hydrogen peroxide[10] have been used for the purpose. The favorable effect of small quantities of persulfate is demonstrated in Fig. 43. The slow rise in extinction with time is due to the formation of the yellow oxidation product of thiocyanate. If the extinction of the solution is determined immediately after the addition of thiocyanate the use of an oxidizing agent to stabilize the color is usually not necessary.

Temperature affects the color intensity and stability of ferric thiocyanate solutions. Ovenston and Parker[7] found that the color intensity decreased

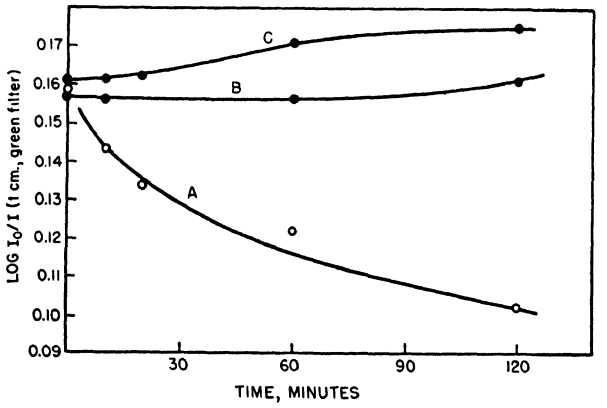


Fig. 43. Effect of persulfate on fading of ferric thiocyanate color in aqueous medium. *A*. No persulfate. *B*. Solution 1.8×10^{-2} *M* in potassium persulfate. *C*. Solution 3.6×10^{-2} *M* in persulfate. All solutions contained 1.25 p.p.m. of iron and were 1.5 *N* in hydrochloric acid and 0.5 *M* in potassium thiocyanate. (Data of Ruth Goodhope, University of Minnesota.)

by about 7 per cent when the temperature was raised from 15 to 30°, in the presence of persulfate as stabilizing agent. The rate of fading is greater at higher temperatures; the difference is not very pronounced in the absence of persulfate, but is marked in the presence of this substance after the initial period of stability has been passed. These experiments were carried out in 1.7 *N* sulfuric acid and the transmittancy of the solutions was measured at 546 mμ.

The following ions especially interfere in the determination:

[10] C. A. Peters, M. M. MacMasters, and C. L. French, *Ind. Eng. Chem., Anal. Ed.*, 11, 502 (1939). The slightly acidic solution (0.01 *N* in hydrochloric acid) is made 0.001–0.003 *M* in hydrogen peroxide. More hydrogen peroxide than this produces a yellow color with thiocyanate, especially if the solution is acid.

1. Fluoride, metaphosphate, pyrophosphate,[11] oxalate, etc. which form complexes with ferric iron in acid solution. Sulfate and phosphate interfere if present in appreciable amounts. As much as 500 p.p.m. of P_2O_5 as orthophosphate may be present without producing any serious error.
2. Silver and mercurous mercury which yield insoluble thiocyanates.
3. Copper,[12] bismuth, titanium, uranium, and molybdenum, which give yellow or orange colors of greater or less intensity; ruthenium (pink), osmium (blue). The interference of cobalt (due largely to the pink color of cobaltous ion itself under the conditions of the determination) can be avoided by making the transmittancy measurements at two suitable wave lengths.[13] Manganese should not be present in large amounts.
4. Mercury (II), cadmium, zinc, and antimony (III), which form complexes with thiocyanate and reduce the intensity of the iron-thiocyanate color.

Addition of a miscible organic solvent having a low dielectric constant intensifies the iron thiocyanate color. Acetone[14] and 2-methoxyethanol ("methyl cellosolve")[15] have been recommended for the purpose. In 60 per cent acetone solution the color is about twice as strong as in water. It has been shown that there is less interference from such ions as fluoride and oxalate in a water-acetone solution than in water alone. Thus Woods and Mellon found that in order to keep the error below 2 per cent not more than 30 and 0 p.p.m. of F^- and $C_2O_4^=$ could be present in water solution, whereas the limits of the same ions were 400 and 30 p.p.m. in 60 per cent acetone solution. The fading of the iron color is slower in acetone solution than

[11] The interference of metaphosphate and pyrophosphate can be prevented or greatly reduced by adding aluminum (as nitrate) to form stable complexes, according to H. E. Wirth, *Ind. Eng. Chem., Anal. Ed.*, **14**, 724 (1942). It may be mentioned that Wirth found the interference of pyrophosphate and phosphate to be greater in solutions of *p*H 1 (and higher) than in those of *p*H 0.5 or less; metaphosphate interfered seriously even in strongly acid solutions. Vanossi (see reference on p. 370) has also used aluminum to prevent the interference of complex phosphates and fluoride.

[12] The copper reaction is rather sensitive, being perceptible with 0.1 mg. of the metal; the colored compound is extracted by ethyl acetate and other organic solvents.

[13] E. A. Brown, *Ind. Eng. Chem., Anal. Ed.*, **17**, 228 (1945), uses filters with maximum transmittancies at 425 and 525 mμ, respectively.

[14] See for example W. Marriott and C. G. Wolf, *J. Biol. Chem.*, **1**, 451 (1906); J. T. Woods and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 551 (1941).

[15] H. W. Winsor, *Ind. Eng. Chem., Anal. Ed.*, **9**, 452 (1937). A solution of thiocyanate in water plus 2-methoxyethanol soon turns yellow on exposure to light whereas the acetone solution is not appreciably changed. It is not known whether the difference in behavior is due to an impurity in the former solvent.

in water. General use of acetone to increase the sensitivity (with certain methods of observation) and color stability is not possible because of the slight solubility of many salts in acetone-water mixtures. Moreover cobalt gives an intense blue color with thiocyanate in the presence of acetone (p. 279).

TABLE 62

DETERMINATION OF IRON WITH THIOCYANATE

Concentration Fe p.p.m.	Acid concentration	Extinction (1 cm. cell, green filter)
4.0	0.05 *N* HNO_3	0.358
4.0	0.2 *N* HNO_3	0.358
4.0	0.5 *N* HNO_3	0.367
4.0	0.8 *N* HNO_3	0.364
0.4	0.5 *N* HNO_3	0.041
1.0	0.5 *N* HNO_3	0.100
2.0	0.5 *N* HNO_3	0.190
3.0	0.5 *N* HNO_3	0.275
6.0	0.5 *N* HNO_3	0.520
8.0	0.5 *N* HNO_3	0.666
4.0	0.1 *N* HCl	0.368
4.0	0.5 *N* HCl	0.360
4.0	0.8 *N* HCl	0.356
4.0	1.0 *N* HCl	0.358
2.0	0.1 *N* HCl	0.193
6.0	0.1 *N* HCl	0.520
8.0	0.1 *N* HCl	0.663
2.0	0.5 *N* HCl	0.186
6.0	0.5 *N* HCl	0.511
8.0	0.5 *N* HCl	0.648
4.0	0.25 *N* H_2SO_4	0.328

The ferric thiocyanate complex may be extracted from aqueous solution by amyl alcohol, a mixture of amyl alcohol and ether,[16] a mixture of the monobutyl ether of ethylene glycol and ethyl ether,[17] ethyl acetate,[18] etc. Extraction with an organic solvent has a number of advantages. The sensitivity can be increased by concentrating the complex in a small volume of the immiscible solvent; the precision is increased at the same time if the original concentration was very low. Moreover, the color intensity of the thiocyanate complex is appreciably stronger, as a rule, in the organic solvent

[16] H. N. Stokes and J. R. Cain, *J. Am. Chem. Soc.*, 29, 409 (1907).
[17] A. Bernhard and I. J. Dekter, *Science*, 75, 517 (1932).
[18] R. Vanossi, *Anales soc. quim. argentina*, 29, 48 (1941).

than in aqueous medium. At least with some solvents the stability of the color is greater than it is in water.[19]

Isobutyl alcohol has been recommended for the extraction.[20] It is very important to use a pure product. The alcohol should be redistilled before use (b.p. 106–107°). There is no fading of the iron color for at least several

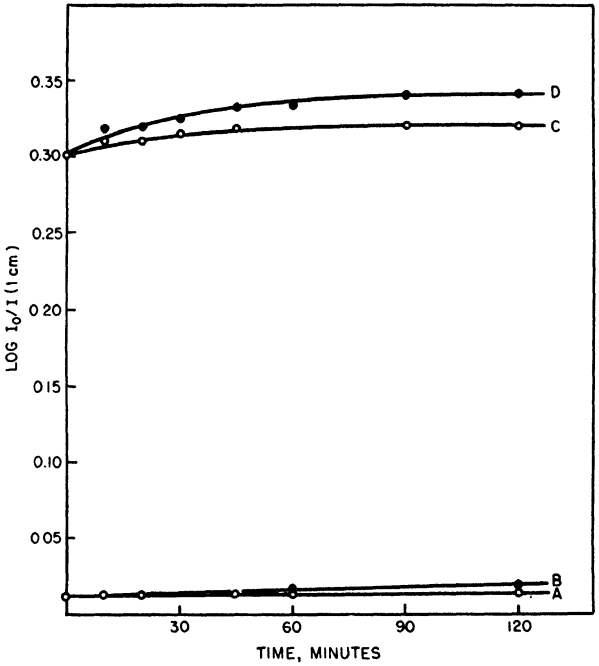


Fig. 44. Stability of ferric thiocyanate in isobutyl alcohol. Aqueous solution (40 ml.), 1.5 *N* in HCl and 0.5 *M* in potassium thiocyanate, extracted with 25 ml. redistilled isobutyl alcohol. *A*. Blank with no persulfate present in the aqueous solution. *B*. Blank with persulfate (3.6×10^{-2} *M*) in aqueous solution. *C*. 1.25 p.p.m. Fe with no persulfate. *D*. 1.25 p.p.m. Fe with persulfate (3.6×10^{-2} *M*) in aqueous solution. (Data obtained by Ruth Goodhope, University of Minnesota.)

hours in a good grade of alcohol, although there seems to be a slight increase in the color intensity for about one-half hour after extraction (Fig. 44). It has been recommended that persulfate be added before the extraction in order to make the color more stable. In our experience the addition of

[19] It has been noted that extracts of ferric thiocyanate in amyl alcohol soon become yellowish, especially if the extraction is made from a relatively acid aqueous solution. This discoloration may be due to some impurity (perhaps peroxide) in the solvent and is not attributable to the alcohol itself.

[20] J. B. Thompson, *Ind. Eng. Chem., Anal. Ed.*, 16, 646 (1944).

persulfate in the extraction method serves no useful purpose if the iron complex is extracted as soon as the thiocyanate has been added (Fig. 44). However, if the extraction must be delayed for any reason after the addition of thiocyanate, persulfate will stabilize the complex in aqueous solution as already noted.

An unusual method of obtaining a stable solution of the thiocyanate complex involves extraction with ethyl ether saturated with sufur dioxide.[21]

Iron may be oxidized to the ferric condition by the addition of a slight excess of potassium permanganate to the acid solution. The excess permanganate is quickly reduced in acid solution by thiocyanate and no colored products are formed. Hydrogen peroxide may also be used (p. 368).

Immediately following are general directions for determining iron with thiocyanate. Directions for determining very small amounts of iron after isolation by precipitation as the hydroxide and sulfide are then given on p. 373.

Reagents

Potassium thiocyanate, 1.5 *M* or other convenient concentration. A good grade of reagent may generally be used without purification. The salt may be tested for iron by adding a milliliter or two of acetone to 1–2 g.; the solution should show no color. If purification seems desirable, add a few milligrams of an aluminum salt to the solution, precipitate aluminum hydroxide with a few drops of ammonia, and filter off the precipitate which will contain the iron.

Hydrochloric or nitric acid. Except in the determination of extremely small amounts of iron, the best grade of acid may be used without purification. If purification is necessary, distil in all-Pyrex apparatus and store the acid in Pyrex or other resistant glass. Any oxides of nitrogen in nitric acid should be removed by drawing filtered air through the diluted acid.

Acetone. The reagent quality product may be used without purification.

Standard iron solution, 0.100 mg. Fe per ml. Dissolve 0.1000 g. electrolytic iron or iron wire for standardization in 50 ml. of 1:3 nitric acid, boil to expel oxides of nitrogen, and dilute to 1 liter with iron-free water. If desired, more dilute solutions can be prepared from this solution by diluting with 0.2 *N* nitric acid.

§ General Procedure

Ordinary Procedure. The sample solution may conveniently contain up to 10 p.p.m. of Fe (III) after final dilution to volume if a photoelectric photometer with a 1 cm. cell is used, and up to 20 p.p.m. of iron if a Duboscq colorimeter is employed. The acidity may vary from 0.05 to 1 *N* in nitric or hydrochloric acid.

Add sufficient thiocyanate, accurately measured, to make the final concentration about 0.3 *M*, dilute to volume with water, and determine the transmittancy of the mixed solution *at once*. Use a filter showing maximum

[21] H. Ginsberg, *Metallwirtschaft*, **16**, 1107 (1937); K. Steinhauer and H. Ginsberg, *Z. anal. Chem.*, **104**, 385 (1936).

transmission at or near 480 mμ. The standard series method may also be used, but the colorimetric titration technique should be avoided.

The standard iron solutions used in the construction of the reference curve should contain approximately the same amount and kind of acid as the unknown, especially if hydrochloric acid is used for acidifying. The concentration of thiocyanate must be the same in the standards and unknown. If sulfuric acid is present in the sample an equal amount must be added to the standards. The temperature should be approximately constant.

Procedure with Acetone. In the absence of precipitable salts, the use of acetone to increase the intensity of the color and its stability may be advantageous. The acidity of the sample solution and thiocyanate concentration may be the same as before. Add sufficient acetone, exactly measured, to give a 50 to 60 per cent solution by volume, make up to volume, and obtain the transmittancy without undue delay. The standards must have the same composition as the sample solution. Use the same filter as above.

Extraction with an Immiscible Organic Solvent. See p. 386.

Determination of Traces of Iron with Thiocyanate after Precipitation as Hydroxide and Sulfide

In the procedure given below, traces of iron are coprecipitated with hydrous manganese dioxide or cadmium sulfide according to the method of Stokes and Cain (*loc. cit.*) and finally determined with thiocyanate in acetone medium to increase the sensitivity and the stability of the color. It is of course possible to determine iron by any other sensitive method after its isolation, account being taken of the possible effect of the coprecipitating agent and other extraneous substances.

Reagents

Hydrochloric acid. If only a small amount of hydrochloric acid is needed in preparing the sample for analysis, the analytical reagent may be used without purification, but if a large volume is required the acid should be distilled in Pyrex, or still better, hydrogen chloride obtained by dropping sulfuric acid into hydrochloric acid should be absorbed in redistilled water.

Ammonium hydroxide. Pass pure ammonia into water, or distil concentrated ammonium hydroxide. Keep the solution in a ceresin-coated bottle.

Potassium permanganate, 0.5 per cent aqueous solution.

Cadmium chloride or sulfate, 0.1 *M* aqueous solution. If removal of traces of iron in the salt is considered advisable, use the manganese dioxide method described in the procedure below.

Sodium potassium tartrate, 20 per cent. Remove iron as sulfide with cadmium sulfide as collector (see procedure below).

Ammonium sulfide solution. Prepare from pure hydrogen sulfide (not from ferrous sulfide + acid) and pure ammonia.

Thiocyanate reagent. To 20 ml. of 1.5 *M* potassium thiocyanate and 8 ml. of 1:1 hydrochloric acid add 50 ml. of reagent-grade acetone and dilute to 100 ml. with water.

Ethyl alcohol.

§ Procedure

Preparation of Sample. Acids such as hydrochloric, nitric, sulfuric, etc. should be evaporated nearly to dryness in fused silica (not in platinum which invariably contains iron extracted by acid), with provision for exclusion of dust and prevention of dripping back of condensed liquid into the container. There is no loss of iron in the evaporation of hydrochloric acid.

Ammonia should be evaporated nearly to dryness in silica or platinum.

Salts should, in general, be dissolved in water acidified with hydrochloric acid. As much as 10–20 g. of solid may be taken.

Precipitation of Iron as Hydroxide with Hydrated Manganese Dioxide as Collector. The solution may conveniently have a volume of 50 or 100 ml., although larger volumes may be used, and if possible at least 1 γ iron should be present. The equivalent of at least 1 ml. of 1:1 hydrochloric acid should be present. For each 100 ml., add 0.5 ml. of potassium permanganate solution and sufficient ammonium hydroxide to give a distinct odor, followed by 1 ml. of ethyl alcohol. If metals such as zinc, lead, etc. are present in large amounts, add only enough ammonia to give a very slight permanent precipitate. Heat to boiling and keep near the boiling point until the precipitate of $MnO_2 \cdot xH_2O$ has coagulated well.

Collect the precipitate on a small loose-textured filter paper (5 cm. diameter) which previously has been washed with warm dilute hydrochloric acid and then with water. Wash the precipitate with a few portions of water, and then with a few milliliters of acetone, which first has been poured into the precipitation vessel to remove water. Shake out any acetone in the stem of the funnel and allow most of the acetone in the paper and precipitate to evaporate. Pour 5 ml. of thiocyanate reagent into the cold precipitation vessel to dissolve any precipitate on its walls and transfer the solution to the filter paper. Catch the solution in a dry 10 ml. volumetric flask and wash the paper with more of the reagent, finally making the volume up to the mark with the reagent. If these operations are carried out without undue delay there will be no important loss of acetone by evaporation from the solution.

Immediately obtain the transmittancy of the solution, using a suitable filter (p. 373). The calibration curve is constructed by pipetting 0.10, 0.20, and 0.30 ml. of 0.001 or 0.002 per cent iron solution (prepared by diluting a stronger solution, p. 372) into a dry 10 ml. volumetric flask, diluting to volume with the acetone reagent solution, and determining the transmittancy.

The effect of the water introduced through the iron solution may be disregarded. A blank must be run to find the amount of iron in the reagents.

Precipitation of Iron as Sulfide with Cadmium Sulfide as Collector. To the neutral or only slightly acid solution, which has been treated with sufficient pure sodium potassium tartrate if aluminum, chromium, etc. are present, add 1 ml. of cadmium solution and a slight excess of ammonium sulfide (or enough to dissolve any sulfides soluble in excess reagent). Allow the mixture to stand for one-half to one hour with occasional stirring. Collect the precipitate on a small washed paper filter and wash with water to which a little ammonium sulfide has been added. Dissolve the precipitate in warm 1:1 hydrochloric acid and return the solution to the precipita-

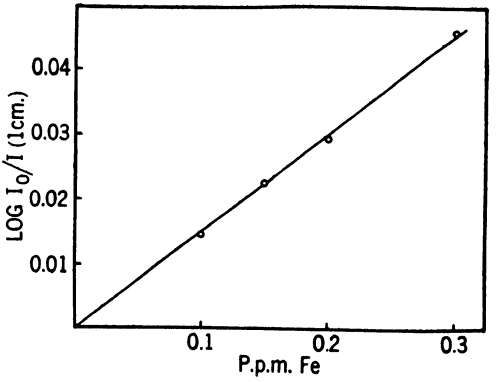


Fig. 45. Determination of low concentrations of iron by the thiocyanate-acetone method (green filter). 50 per cent by volume of acetone.

tion vessel. Boil out hydrogen sulfide and precipitate iron as hydroxide with manganese dioxide collector as described above.

If the original solution contained tartrate, oxalate, etc., dissolve the precipitate in warm dilute nitric acid, add potassium permanganate solution in excess and heat the solution until any organic matter has been decomposed.

B. The *o*-Phenanthroline Method[22]

A good sensitive method for the determination of iron is based on the formation of an orange-red complex, $[(C_{12}H_8N_2)_3Fe]^{++}$, between *o*-phenanthroline and ferrous iron. The color intensity is independent of the acidity

[22] W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1938); A. Thiel, H. Heinrich, and E. van Hengel, *Ber.*, **71B**, 756 (1938); L. G. Saywell and B. B. Cunningham, *Ind. Eng. Chem., Anal. Ed.*, **9**, 67 (1937).

in the *p*H range 2–9 with the reagent concentration recommended below; below *p*H 2 the color develops slowly and is much weaker. The complex is very stable and solutions show no change in color after many months. Beer's law is closely followed.

The equilibria and kinetics in the ferrous iron-phenanthroline system have been investigated.[23] *o*-Phenanthroline behaves as a monoacidic base; the dissociation constant of phenanthrolinium ion, PhH^+, is 1.1×10^{-5} at 25°. The value of the equilibrium constant for the reaction between ferrous ion and phenanthrolinium ion is

$$\frac{[FePh_3^{++}][H^+]^3}{[Fe^{++}][PhH^+]^3} = 2.5 \times 10^6 \ (25°).$$

Ferric iron can be reduced with hydroxylamine hydrochloride, hydroquinone, or, less preferably, sulfur dioxide. When citrate is present hydroquinone must be used as reducing agent.

Aside from colored ions, the following interfere to a greater or less extent.[24] Silver and bismuth give precipitates. Certain divalent metals such as cadmium, mercury, and zinc form slightly soluble complexes with the reagent and, moreover, reduce the intensity of the iron color, but the interference can be diminished by adding a larger excess of reagent. The maximum permissible concentration of these ions for 2 p.p.m. of iron is approximately 50 p.p.m. of Cd, 1 p.p.m. of Hg and 10 p.p.m. of Zn. Mercury (I) may be present up to 10 p.p.m. (*p*H 3–9). Beryllium (50 p.p.m.) does not interfere if the *p*H lies between 3.0 and 5.5; below the former *p*H a stable complex is formed with the reagent and above the latter *p*H the hydroxide is precipitated. Molybdenum (VI) does not interfere above *p*H 5.5 but in more acid solutions it gives a turbidity. Tungstate decreases the color intensity but 5 p.p.m. of W does no harm. Copper may not exceed 10 p.p.m. and in the presence of this element the *p*H must lie between 2.5 and 4.0. Nickel interferes by producing a change in hue and raising the transmittancy below 540 mμ, so that no more than 2 p.p.m. may be present. Cobalt gives a yellow color and should not exceed 10 p.p.m. at *p*H 3–5. Tin (II) should not exceed 20 p.p.m. for *p*H 2–3, and tin (IV) should not be above 50 p.p.m. (*p*H 2.5).

If the *p*H is kept above 6 and 3 respectively, oxalate and tartrate in concentrations as high as 500 p.p.m. do not interfere. In the presence of

[23] I. M. Kolthoff, T. S. Lee, and D. L. Leussing, *Anal. Chem.*, **20**, 985 (1948); *J. Am. Chem. Soc.*, **70**, 2348, 3596 (1948).

[24] Fortune and Mellon, *loc. cit.* The results cited above were obtained by the use of hydroxylamine hydrochloride as reducing agent and adjustment of the *p*H with hydrochloric acid or ammonia.

pyrophosphate the *p*H must be above 6; then 50 p.p.m. of $P_2O_7^{\equiv\equiv}$ causes an error of only 1 per cent with 2 p.p.m. of iron.[25] Phosphate may be present up to 20 p.p.m. of P_2O_5 (*p*H 2–9).[26] Fluoride (500 p.p.m.) does not interfere if the *p*H is kept above 4.0. Chloride and sulfate are without effect, at least in moderate amounts. If perchlorate is present in more than small amounts, a precipitate of the slightly soluble *o*-phenanthroline perchlorate may be produced.

A great advantage of *o*-phenanthroline over some other iron reagents lies in the possibility of using it in slightly acidic solutions, so that hydroxides, phosphates, etc. of many metals are not precipitated. However, phosphate, and more particularly pyrophosphate and metaphosphate, may cause difficulties. Some *o*-phenanthroline procedures that have been described do not yield correct results when applied to various bio materials containing much phosphorus. It is essential that iron be present in a form that will react completely with phenanthroline in a reasonable period of time. This means that the conditions in the determination must be such that iron will not be bound in pyrophosphate and other stable complexes and that slightly soluble phosphate precipitates containing iron will be prevented from forming. Procedures in which sodium acetate is used to adjust the acidity to a *p*H of 3.5 are generally not adequate for bio samples because of the danger of precipitating ferric and aluminum phosphates.[27] The precipitation of these is prevented by the addition of citrate and the latter may also be used to reduce the acidity of the initially acid solution to a *p*H in the range 2.5 to 5, as shown by Bandemer and Schaible.[28] These authors further show that it is important to add the sodium citrate to the acid solution of the sample after the *o*-phenanthroline and hydroquinone have been added. Satisfactory recoveries of iron from ashed samples could then be obtained if the treated solution was allowed to stand 30 minutes at a temperature above 20°. The procedure is given below.

[25] F. C. Hummel and H. H. Willard, *Ind. Eng. Chem., Anal. Ed.*, **10**, 14 (1938), found that as much as 50 mg. of P as pyrophosphate in 25 ml. of solution of *p*H 3.5 did not interfere in the determination of 0.2 mg. of iron if the mixture was allowed to stand at least one-half hour after the addition of *o*-phenanthroline and reducer (hydroquinone).

[26] According to J. A. Brabson, O. A. Schaeffer, A. Truchan, and L. Deal, *Ind. Eng. Chem., Anal. Ed.*, **18**, 554 (1946), an amount of orthophosphoric acid equivalent to 2 g. of phosphorus does not interfere if the *p*H is 6 ± 1.

[27] H. Cowling and E. J. Benne, *J. Assoc. Official Agr. Chem.*, **25**, 555 (1942), have shown that if relatively much aluminum is present with phosphate, low results are obtained for iron in such a procedure because iron is carried down in the aluminum phosphate precipitate formed in the weakly acidic medium. To avoid this difficulty, these authors propose addition of citrate before *p*H adjustment with acetate.

[28] S. L. Bandemer and P. J. Schaible, *Ind. Eng. Chem., Anal. Ed.*, **16**, 317 (1944).

α,α'- (or 2,2'-) Bipyridyl and 2,2',2''-Terpyridyl.[29] These reagents are very similar to *o*-phenanthroline, and may be used in place of it, but for general use have no advantages. Terpyridyl has the disadvantage of being very sensitive to cobalt and copper, and nearly as much so to nickel.

Special Solutions

Hydroquinone, 1 per cent solution in water.

Sodium citrate, 250 g. in 1 liter of solution.

o-Phenanthroline, 0.5 per cent solution of the monohydrate in water. Warm to effect solution. Keep in the dark. Discard if any color develops.

§ Procedure

Take an aliquot portion of the sample solution, having a low mineral acid concentration and containing 0.01–0.2 mg. of iron (photometer, 1 cm. cell), and transfer to a 25 ml. volumetric flask. Determine by the use of a similar aliquot portion containing a few drops of bromphenol blue the volume of sodium citrate required to bring the *p*H to about 3.5. Add to the working aliquot 1 ml. each of hydroquinone and *o*-phenanthroline solutions and then the requisite amount of citrate solution. Allow to stand for an hour above 20° to assure complete reduction of iron, make up to volume and determine the transmittancy with the aid of a filter showing maximum transmission at 480–520 mμ (optimum 508 mμ).

Note. An alternative procedure with hydroxylamine hydrochloride as reducing reagent is the following; it may be applied in the absence of aluminum and phosphate which are likely to cause difficulty as already mentioned. Adjust the *p*H of the slightly acid solution to 3–6 with sodium acetate solution after the addition of 1 ml. of 10 per cent hydroxylamine hydrochloride. Add 1 ml. of *o*-phenanthroline (0.5 per cent), mix, dilute to the mark, and obtain the transmittancy of the solution after 5 or 10 minutes (or after 1 hour if much pyrophosphate is present). The standards should be treated in the same manner, and should preferably have the same final *p*H as the sample solution.

C. Mercaptoacetate (Thioglycolate) Method[30]

In ammoniacal medium, mercaptoacetate (as the ammonium salt $HS\cdot CH_2COONH_4$) reacts with iron to yield a soluble red-purple product. The color is a function of the total iron present, both ferrous and ferric iron reacting; the course of the reaction is obscure. The reaction must be carried out in basic medium; precipitation of metal hydroxides can be

[29] M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **14**, 862 (1942). This paper contains further references on the use of these reagents.

[30] H. W. Swank and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 7 (1938); E. Lyons, *J. Am. Chem. Soc.*, **49**, 1916 (1927); N. L. Allport, *Colorimetric Analysis*, p. 55 (1947). The choice of mercaptoacetic acid as the third iron reagent for description above is somewhat arbitrary. Sulfosalicylic acid may perhaps be considered the equal of mercaptoacetic acid.

prevented by adding citrate. A number of metals, including cobalt, nickel, lead, bismuth, mercury (I), uranium (UO_2^{++}), silver and gold produce colors, more or less strong, with the reagent. The colors due to cobalt (yellow-red) and uranyl (orange) ions are very strong (about as intense as with iron itself). Manganese gives an amber color if the solution is shaken or stirred (air-oxidation) but the color fades in a few minutes and as much as 100 p.p.m. of the element does not interfere. Certain metals, among them copper (1 mg.), arsenic (III) (> 100 mg.), tin (II), zinc (> 10 mg.), and cadmium bleach the iron color, although this effect

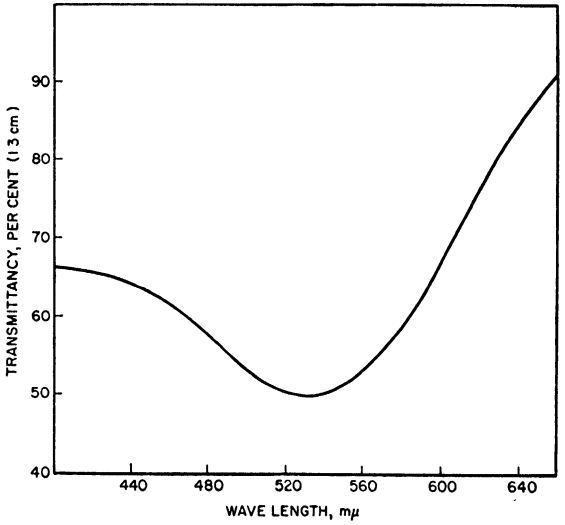


Fig. 46. Transmission curve of iron-mercaptoacetate complex; 5 p.p.m. of iron. (Data of L. Lund.)

can be diminished by the addition of more reagent. Very high concentrations of salts of the alkali metals decrease the color intensity somewhat. On the other hand, anions have but a slight effect on the color. As much as 5000 p.p.m. of chloride, fluoride, orthophosphate, tartrate, oxalate, citrate, and acetate ion do not interfere. Pyrophosphate in a concentration of 5000 p.p.m. of P_2O_5 causes an error of −8 per cent with 1 p.p.m. of iron. Nitrous acid and cyanide must be absent. Molybdate gives a yellow color in relatively high concentrations. Tungsten (> 20 p.p.m.) as tungstate yields a blue color with the reagent.

Beer's law is closely followed by the color system and the color intensity is independent of the exact concentration of the reagent and the *p*H in the range 6–11. The color is fairly stable (at least 6 hours in diffuse light and 12 hours or more in the dark when the solutions are kept in Erlenmeyer

flasks, in which the area exposed to air is large). Shaking tends to restore the color of a faded solution (air-oxidation).

§ Procedure

Add 2 ml. of ammonium mercaptoacetate (neutralize a 10 per cent by volume solution of mercaptoacetic acid with ammonium hydroxide) and then 10 ml. of 3 or 4 *M* ammonia to the approximately neutral solution and dilute to 100 ml. with water. Compare with a similar standard in any convenient way or measure the transmittancy.

The final concentration of the solution may conveniently be 0.05–0.2 mg. Fe in 100 ml. Maximum absorption is shown by the solution at 530–540 mμ. It is advisable to measure or compare the color soon after it has been developed.

When metals precipitated in basic medium are present, citrate (*e.g.*, 5 ml. 10 per cent ammonium citrate) may be added to keep these in solution.

D. Other Methods

Among the plethora of other reagents that have been proposed or used for the determination of iron the following may be mentioned: Sulfosalicylic acid,[31] salicylic acid,[32] salicylaldoxime,[33] 7-iodo-8-hydroxyquinoline-5-sulfonic acid (ferron),[34] 8-hydroxyquinoline,[35] acetylacetone,[36] gallic acid,

[31] F. Alten, H. Weiland, and E. Hille, *Z. anorg. allgem. Chem.*, **215**, 81 (1933); A. Thiel and E. van Hengel, *Ber.*, **70**, 2491 (1937); A. Thiel and O. Peter, *Z. anal. Chem.*, **103**, 161 (1935); K. Dietrich and K. Schmitt, *ibid.*, **111**, 176 (1937); R. Bauer and J. Eisen, *Angew. Chem.*, **52**, 459 (1939) (determination of iron in aluminum); R. Pfeiffer, *Z. anal. Chem.*, **126**, 81 (1943) (determination of iron in chrome baths). The latest study of this reagent has been made by L. C. E. Kniphorst, *Chem. Weekblad*, **42**, 311 (1946), with special reference to the determination of iron in food products. Manganese interferes and in its presence iron must be separated with zinc oxide according to this author. Interference of copper is prevented by cyanide. Much phosphate is without effect. The reaction must be carried out in basic medium. See V. I. Kuznetsov, *Zavodskaya Lab.*, **12**, 278 (1946); *Chem. Abstracts*, **40**, 7053 (1946).

[32] J. P. Mehlig, *Ind. Eng. Chem., Anal. Ed.*, **10**, 136 (1938); R. O. Scott, *Analyst*, **66**, 142 (1941); A. K. Babko, *Chem. Abstracts*, **40**, 7041.

[33] D. E. Howe and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **12**, 448 (1940).

[34] J. H. Yoe, *J. Am. Chem. Soc.*, **54**, 4139 (1932); J. H. Yoe and R. T. Hall, *ibid.*, **59**, 872 (1937); H. W. Swank and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 406 (1937).

[35] A slightly soluble green-black ferric oxinate is formed at *p*H 2–3 which can be extracted with chloroform or filtered off and dissolved in alcohol (J. Lavollay, *Bull. soc. chim. biol.*, **17**, 432 (1935)). Vanadium reacts similarly.

[36] A. Combes, *Compt. rend.*, **105**, 868 (1887); H. Pulsifer, *J. Am. Chem. Soc.*, **26**, 967 (1904).

pyrocatechol,[37] pyramidone,[38] alloxantin,[39] nitroso-R salt,[40] isonitrosodimethyldihydroresorcinol,[41] disodium-1,2-dihydroxybenzene-3,5-disulfonate,[42] 4-hydroxybiphenyl-3-carboxylic acid,[43] cupferron,[44] protocatechuic acid,[45] kojic acid,[46] various dioximes,[47] ammonium sulfide,[48] ferrocyanide, hydrobromic acid, and hydrochloric acid.[49]

III. Applications

A. Glass Sand

§ Procedure[50]

Fuse 0.5 g. of sample with 5 g. of sodium carbonate. Treat the melt with dilute hydrochloric acid, evaporate to dryness, and remove silica in the usual way by double dehydration with hydrochloric acid. Combine the silica precipitates, ignite, and volatilize silica in the customary manner with hydrofluoric-sulfuric acid. Fuse the non-volatile residue with a gram of sodium carbonate, dissolve the melt in dilute hydrochloric acid, and add the solution to the filtrate from the silica. Add 1 ml. of concentrated nitric acid to the solution, boil for a minute or two, and add an excess of ammonia. Allow the precipitate to settle, filter, and wash with hot water. Dissolve the precipitate in 10 or 20 ml. of 1:1 hydrochloric acid and dilute the solution to 100 ml. in a volumetric flask. Determine iron in a 25 ml.

[37] A. L. Bernoulli, *Helv. Chim. Acta*, **9**, 835 (1926).

[38] H. W. van Urk, *Pharm. Weekblad*, **63**, 1121 (1926).

[39] G. Denigès, *Compt. rend.*, **180**, 519 (1925).

[40] C. P. Sideris, *Ind. Eng. Chem., Anal. Ed.*, **14**, 756 (1942); C. P. Sideris, H. Y. Young, and H. H. Q. Chun, *ibid.*, **16**, 276 (1944). See also *Anal. Chem.*, **19**, 1014 (1947).

[41] S. C. Shome, *Anal. Chem.*, **20**, 1205 (1948).

[42] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944). For some characteristics of this reagent see p. 576. Copper and especially titanium interfere by giving strong colors with the reagent.

[43] J. H. Yoe and A. E. Harvey, Jr., *J. Am. Chem. Soc.*, **70**, 648 (1948). Copper (II) and uranium (VI) also react.

[44] See p. 363 (Paulais).

[45] R. S. Pereira, *J. Biol. Chem.*, **137**, 417 (1941). See also *Chem. Abstracts*, **36**, 3114.

[46] M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 612 (1941).

[47] M. Griffing and M. G. Mellon, *Anal. Chem.*, **19**, 1017 (1947).

[48] L. Roelen, *Z. anal. Chem.*, **117**, 385 (1939). A bluish green colloidal dispersion of ferrous sulfide is formed in a basic tartrate medium; the method is useful for determining iron in aluminum.

[49] See p. 131 and also R. Havemann, *Angew. Chem.*, **54**, 263 (1941).

[50] G. E. F. Lundell and H. B. Knowles, *J. Am. Ceram. Soc.*, **11**, 122 (1928). Also see A. Thürmer, *Glashütte*, **68**, 857 (1938). J. J. Diamond, *J. Am. Ceram. Soc.*, **31**, 243 (1948), treats the sample with hydrofluoric-sulfuric acids, fuses the residue successively with sodium carbonate and potassium pyrosulfate and determines iron with *o*-phenanthroline (hydroxylamine hydrochloride as reducing agent).

aliquot by the thiocyanate or other method. Run a blank through the procedure.

B. Water

The following simple method[51] is adequate in most cases for the determination of iron in natural waters.[52] The presence of the usual forms of organic matter (clear samples) does not appear to affect the results. The procedure cannot be used if copper is present, since it gives a reaction approximately as sensitive as that of iron; the presence of copper is revealed by a change in hue. The high concentration of thiocyanate specified in the method increases the sensitivity and tends to reduce interference by substances forming complexes with ferric iron. As much as 1000 p.p.m. of sodium hexametaphosphate or pyrophosphate reduces the color from 1 to 5 p.p.m. of iron by less than 10 per cent. The small effect of these ions is to be attributed to the high acid concentration and the heating called for in the procedure. The usual fading of the thiocyanate color must be borne in mind.

§ Procedure

To 30 ml. of sample in a 2-ounce French square bottle or in a small flask, add 20 ml. of 4 *N* hydrochloric acid and heat in a water bath just below the boiling point for 20 minutes. Cool to room temperature and add a drop of 0.5 per cent potassium permanganate or enough to maintain a color in the solution for a minute. Add 5.0 ml. of potassium thiocyanate solution (30 g. in 100 ml.) and compare at once with a suitable series of standards (see p. 372 for preparation of standard iron solution). If less than 0.4 p.p.m. of iron is present use 50 ml. Nessler tubes for the comparison. For the preparation of permanent color standards consult the original paper.

C. Bio Materials

It is strange that there still are uncertainties in the colorimetric determination of iron in bio samples and that there is no unanimity regarding

[51] F. J. Hallinan, *Ind. Eng. Chem., Anal. Ed.*, **15**, 510 (1943).

[52] If the iron content is less than 0.1 p.p.m. or if the sample contains relatively large amounts of organic matter, evaporate 100 ml. to dryness in a silica or porcelain dish and, if there is evidence of organic material, ignite the residue gently. (Alternatively the sample can be evaporated in Pyrex and organic matter destroyed with a little nitric and perchloric acid.) Heat the residue with 20 ml. of 4 *N* hydrochloric acid to bring iron into solution and continue as in the procedure above. The phenanthroline or mercaptoacetate method can also be applied, and it is necessary to use one of these if traces of copper are present. Any appreciable amount of material not dissolved by hydrochloric acid, as for example silica, had best be examined for traces of iron by the usual methods when the most accurate results are required. See D. H. Caldwell, *J. Am. Water Works Assoc.*, **38**, 727 (1946), for determination of iron with *o*-phenanthroline.

the most suitable procedure in spite of the large amount of work that has been done. In recent years the *o*-phenanthroline (or the similar α,α'-bipyridyl) method has been used by many workers and is perhaps regarded as the best by the majority. However, the thiocyanate method with extraction has been applied with apparently good results. Procedures based on the use of both these reagents are given below.

Decomposition of the sample may be effected by ignition or by wet oxidation. Destruction of organic matter by ignition has some attractive features: the blank can be kept low and a relatively small sample can be used since the volume of the final solution is easily kept small. On the other hand, all the iron present in the sample may not be recovered unless precautions are taken. There is a possibility of loss of iron by interaction of the ash with the material of the dish (silica or porcelain) if too high a temperature is used or the quantity of ash is very small, apparently by volatilization if much chloride is present,[53] and as a result of retention by silica or other insoluble material remaining after treatment of the ash with acid. Pyrophosphate is formed on ignition and if much is present it must be converted to phosphate by heating the acid solution or allowing it to stand for some time, before iron can be determined satisfactorily. These difficulties are avoided in wet-oxidation with acids.

Directions are given below for both methods of decomposing the sample. The exact procedure will vary to some extent from one bio material to another, and these directions should be looked upon merely as a guide which may require greater or less modification for a particular sample. The *o*-phenanthroline (or α,α'-bipyridyl) method is recommended for the final determination of the iron; it is not subject to error by the presence of sulfate, phosphate, and the trace metals of bio materials occurring in the usual quantities.[54] Much copper can be precipitated with hydrogen sulfide in acid solution or removed by dithizone extraction. If copper does not exceed 0.2 mg. in a final volume of 25 ml. it will not interfere appreciably.

Those wishing further information on the determination of iron in materials of biological origin are referred to the recent papers mentioned below.[55]

[53] According to C. Hoffman, T. R. Schweitzer, and G. Dalby, *Ind. Eng. Chem., Anal. Ed.*, 12, 454 (1940), such losses are prevented by treating the sample with sodium hydroxide solution before ignition.

[54] S. H. Jackson, *Ind. Eng. Chem., Anal. Ed.*, 10, 302 (1938), encountered an interfering substance or substances, not identified, in certain food products, which led to low results in the α,α'-bipyridyl method, whether organic material was destroyed by ignition or wet-oxidation. He recommends separation of the iron by precipitation as sulfide in ammoniacal solution to avoid this error.

[55] (a) Thiocyanate method: R. Stugart, *Ind. Eng. Chem., Anal. Ed.*, 3, 390 (1931); H. L. Roberts, C. L. Beardsley, and L. V. Taylor, *ibid.*, 12, 365 (1940); C. Hoffman, T. R. Schweitzer, and G. Dalby[53]; Truter.[7] (b) Mercaptoacetate method: G. Leavell,

(*continued on next page*)

1. o-Phenanthroline Method

§ Procedure

Ashing by Ignition. Take 3–4 g. of sample for iron contents in the neighborhood of 10 p.p.m. and ash at 550° C. in a silica or porcelain dish.[56] A muffle furnace, not a burner, should be used. Add 5 ml. of 1:2 hydrochloric acid and warm until it is judged that all soluble material has been brought into solution. Dilute with water and filter through a small paper (previously washed with hot dilute hydrochloric acid) into a 25 or 50 ml. volumetric flask. Wash with small portions of hot water. If there is a significant amount of insoluble material (carbon, silica, etc.), ignite the paper and its contents in a platinum crucible[57] until a light-colored residue is obtained. Add a drop or two of 1:1 sulfuric acid followed by 1–2 ml. of hydrofluoric acid and evaporate to fumes of sulfuric acid. Cool, rinse down the sides of the crucible with water, add 1–2 drops of sulfuric acid, and again evaporate to fumes. Add 1–2 ml. of water to the crucible, warm and rinse into the volumetric flask (filter the solution in the crucible if it is not quite clear after diluting with more water).

Dilute the solution in the volumetric flask to the mark and determine iron in a suitable aliquot (10/25 for 10–20 p.p.m. of iron in the sample) with *o*-phenanthroline (or α,α'-bipyridyl) according to the general directions on p. 378.[58] A blank must be run.

Wet Oxidation. Transfer 1–2 g. of sample (at least 20 γ of iron should be present) to a small Kjeldahl flask,[59] moisten with water, and add 5 ml.

and N. R. Ellis, *Ind. Eng. Chem., Anal. Ed.*, **6**, 46 (1934); R. A. Koenig and C. R. Johnson, *J. Biol. Chem.*, **142**, 233 (1942). (c) *o*-Phenanthroline and α,α'-bipyridyl method: Jackson;[54] F. C. Hummel and H. H. Willard, *Ind. Eng. Chem., Anal. Ed.*, **10**, 14 (1938). L. G. Saywell and B. B. Cunningham, *ibid.*, **9**, 67 (1937). R. A. Koenig and C. R. Johnson, *J. Biol. Chem.*, **143**, 159 (1942); R. H. Thorp, *Biochem. J.*, **35**, 672 (1941); K. H. Schaefer, *Biochem. Z.*, **304**, 417 (1940). V. E. Munsey, *J. Assoc. Official Agr. Chem.*, **27**, 396 (1944); Bandemer and Schaible, *loc. cit.*; W. J. S. Pringle, *Analyst*, **71**, 491 (1946). (d) Sulfosalicylic acid method: L. C. Kniphorst, *loc. cit.*

[56] If there is a possibility of volatilization of iron (appreciable amounts of chloride present), 4–5 ml. of 1 *N* sodium hydroxide solution may be mixed with each gram of sample before drying and igniting. It is more difficult to burn off the carbon when sodium hydroxide is added, and it may be necessary to extract the black residue with dilute acid to remove the coating of salts, filter, wash with hot water, and then ash the paper and its contents.

[57] The crucible should be heated before use in 1:1 hydrochloric acid for several hours to remove iron.

[58] In analyzing samples of about the same weight of similar materials it is usually not necessary to find the volume of sodium citrate required for *p*H adjustment of each sample. An average volume can be used for the series, since the color intensity is independent of the *p*H in the range 2.5 to 5 or higher.

[59] A 250 ml. Erlenmeyer flask may also be used. Place a small funnel in the mouth of the Erlenmeyer.

of concentrated nitric acid and 2 ml. of concentrated sulfuric acid. Heat gently. When charring begins, add nitric acid in small portions (a few drops at the time)[60] and continue until on evaporation to fumes of sulfuric acid a colorless or very pale yellow liquid is obtained. Cool, add 2–3 ml. of water and evaporate to white fumes; cool, add another 2 ml. portion of water, and again evaporate to fumes.[61] Add 10 ml. of water and heat to boiling. Cool and dilute the solution to 25 ml. in a volumetric flask.[62]

Transfer a 10 ml. aliquot to a 25 ml. volumetric flask, and add 1.0 ml. of aqueous 0.5 per cent *o*-phenanthroline solution, 1.0 ml. of fresh 1 per cent hydroquinone solution, 5 ml. of sodium citrate solution (250 g. per liter), and enough 1:1 ammonium hydroxide to give a *p*H of 3.5–4. (The amount of ammonia required may be found by adding bromphenol blue or methyl orange to a 5 ml. aliquot of the sample solution, treated with the solutions mentioned, and titrating with the ammonia solution.) Dilute to the mark with water, mix, and determine the transmittancy at 508 mμ after 1 hour. Standards for the reference curve should be treated in the same manner as the sample solution. Deduct the correction for iron in the reagents.

2. Thiocyanate Method

According to Thompson,[63] iron can be determined accurately in food products by decomposing the sample with sulfuric-nitric-perchloric acid and extracting the iron thiocyanate complex with isobutyl alcohol. The isobutyl alcohol must be of adequate purity; recovered products previously used in iron or thiamin determinations cannot be used because they result in rapid fading of the color. The advantage of the method lies in the high acidity which is preserved throughout the procedure, so that difficulties due to separation of calcium and other phosphates are avoided. Such amounts of phosphate as are likely to be present probably will not affect the color intensity appreciably.[64] The effect of traces of copper has not been investigated. The directions of Thompson follow.

[60] If desired, the oxidation can be finished with perchloric acid. Add 1 ml. of the 60 per cent acid after the preliminary oxidation with nitric acid and heat at a slightly higher temperature than before until white fumes appear. If the solution is not colorless at this point continue the heating, adding more perchloric acid if necessary. Then continue as in the procedure above, adding water and evaporating to fumes to destroy any nitrosyl sulfuric acid that may be present.

[61] If calcium sulfate separates, destroy nitrosyl sulfuric acid by adding 1 ml. of 30 per cent hydrogen peroxide (or ammonium persulfate, p. 440) to the warm concentrated sulfuric acid. Heat for 5 minutes.

[62] If the solution should contain any insoluble material, filter through a very small ash-free paper into the volumetric flask. The washed residue on the filter paper should preferably be examined for any iron it may contain (*cf.* p. 384).

[63] J. B. Thompson, *Ind. Eng. Chem., Anal. Ed.*, 16, 646 (1944).

[64] The possible effect of sulfate on the color intensity is not mentioned by Thompson.

§ Procedure

Decomposition of Sample. Transfer 3 to 5 g. of sample to a 300 ml. Kjeldahl flask, add 10 ml. of redistilled nitric acid, and warm slightly. After subsidence of vigorous reaction, add 2 ml. of concentrated sulfuric acid and boil gently until charring begins. Add nitric acid a few milliliters at the time, or preferably dropwise, until oxidation is almost complete as shown by only slight darkening on evolution of sulfuric acid fumes. Remove the flame and allow the flask to cool slightly. Add 1 ml. of 70 per cent perchloric acid and continue the heating until the liquid clears; it may be necessary at this point to add a few more drops of nitric acid to complete the oxidation. Heat to the point where copious fumes of sulfuric acid appear and perchloric acid has been eliminated. The solution should now be colorless, or, at most, a light straw color. Cool, add 40 ml. of water, and boil until sulfuric acid fumes appear in abundance. Continue heating for 5 minutes to assure complete elimination of nitric and perchloric acids. Cool, add 10 ml. of water, transfer to a 100 ml. volumetric flask, and make up the cold solution to the mark.

The following alternative method of decomposition is advantageously used for foods of high fat content. To a suitable weight of sample in a 300 ml. Kjeldahl flask, add 5 ml. of 30 per cent hydrogen peroxide (reagent quality, without stabilizer) and 2 ml. of concentrated sulfuric acid, and heat gently until charring begins. Add 5 ml. more of hydrogen peroxide and continue heating until charring again occurs. Then continue as described in the preceding paragraph, beginning with the addition of nitric acid, a few milliliters at the time.

Photometric Determination. To a 25 ml. aliquot of the prepared solution in a 125 ml. separatory funnel, add successively with swirling, 5.0 ml. of concentrated hydrochloric acid, 1.0 ml. of 2 per cent potassium persulfate[65] (prepare fresh every few days and store in a refrigerator), and 10.0 ml. of 20 per cent potassium thiocyanate solution. Now add 25.0 ml. of isobutyl alcohol (b.p. 106–107°, redistilled from Pyrex) and shake for 2 minutes. Draw off the aqueous layer, invert and slowly revolve the funnel to dislodge water droplets on the walls, and allow to stand for 10 minutes. Draw off the small amount of water that has separated and transfer the alcohol layer to a dry 50 ml. Erlenmeyer flask. Immediately before reading the transmittancy of the solution, add about 0.1 g. of anhydrous sodium sulfate (avoid adding too much) and agitate to remove droplets of water. Determine the transmittancy at 485 mμ. If the color

[65] Persulfate need not be added if the extraction is made as soon as the thiocyanate has been added. See p. 371.

intensity is too great ($> 50\ \gamma$ iron), take a smaller aliquot diluted to 25 ml. with water.

Establish the standard curve by taking from 0 to 50 γ of iron (p. 372) in a solution containing 5.0 ml. of hydrochloric acid and treating exactly as described above. Beer's law is followed. Run a blank through the procedure.

CHAPTER XXIV

LEAD

I. Separations

Important methods for the separation and isolation of small amounts of lead include dithizone extraction, sulfide precipitation, electrolytic deposition of lead dioxide or lead, coprecipitation of lead sulfate with strontium or barium sulfate, and precipitation of lead chromate or phosphte. The nature of the sample decides which method must be used in any particular case; sometimes two methods must be used in conjunction with each other for satisfactory isolation.

A. Dithizone Extraction

This frequently provides the most satisfactory means of separating lead. Lead can be completely extracted from a slightly basic solution, containing citrate or tartrate to prevent the precipitation of foreign metal hydroxides, by a small excess of dithizone in either carbon tetrachloride or chloroform. With the latter solvent the optimum *p*H range in citrate-cyanide medium has been reported as 8.5–11 (see Fig. 17)[1] and with the former as approximately 8–10.[2] Both the upper and lower *p*H limits can be extended somewhat by increasing the excess of dithizone. The *p*H range also is dependent on the nature of the anions present; the lower limit of the range is raised when ions forming complexes with lead are present.[3]

In the presence of cyanide as complex-former the only other metals extracted are bismuth, thallium, stannous tin and possibly indium (p. 358). However, a number of substances may cause difficulties. Ferric iron in

[1] P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **19**, 134 (1936).

[2] H. Müller, *Z. anal. Chem.*, **113**, 164 (1938).

[3] L. P. Biefeld and T. M. Patrick, *Ind. Eng. Chem., Anal. Ed.*, **14**, 275 (1942), found that under otherwise constant conditions (50 per cent excess of dithizone), lead was extracted by chloroform to the extent of 90 per cent at a *p*H of (*a*) 6.3 in hydrochloric acid-cyanide medium, (*b*) 6.8 in acetate solution, (*c*) 7.3 in tartrate-ammonia solution, (*d*), 8.5 in cyanide-citrate-ammonia solution. In ammoniacal citrate-cyanide medium a *p*H of 9.5 was required for virtually complete extraction when 50 ml. of solution containing 100 γ of lead, 1.5 ml. of concentrated ammonia, and enough citric acid to give a *p*H of 9.5, was shaken with 0.0015 per cent dithizone solution, the volume of the latter being such as to provide a 50 per cent excess over the theoretical amount.

alkaline cyanide medium gives ferricyanide which oxidizes dithizone, and when it is present in more than small amounts the *p*H should be kept as low as is consistent with the complete extraction of the lead, or hydroxylamine hydrochloride should be added. Copper also tends to oxidize dithizone in basic medium; the oxidizing tendency appears to depend on the ratio of cyanide to copper, being weaker when the excess of cyanide is small. Large amounts of cyanide render the extraction of lead more difficult, and there is accordingly a limit to the quantity of foreign metals that may be present. The alkaline solution must be free from any precipitate that is likely to occlude lead (*cf.* p. 111). The dithizone extraction fails in the presence of much calcium (or magnesium) and phosphorus. The phosphates of these metals are only slightly soluble in the ammoniacal citrate solution and carry down lead strongly. Tartrate is less effective than citrate in keeping phosphates in solution. Stannic acid also carries down lead, and when much tin is present it must be removed, preferably by volatilization as the bromide (see p. 412).

Bismuth in small amounts (< 0.5 or 1 mg.) has been separated from lead by extraction with dithizone in chloroform solution at *p*H 2.[4] The reaction is sluggish at this acidity. According to Fischer and Leopoldi,[5] bismuth should be extracted at *p*H 2.8 to 3.0 when a carbon tetrachloride solution of dithizone is used. These authors state that the extraction of bismuth is not quite complete at *p*H 3, but the amount remaining is too small to interfere in the subsequent colorimetric dithizone determination. At *p*H 3.6 to 4.0 lead may be slightly extracted. It is possible to determine lead with fair accuracy in the presence of as much as 5 mg. of bismuth by extracting all of the lead together with some of the bismuth from a solution containing a relatively high concentration of cyanide and then separating the co-extracted bismuth at *p*H 3 (see p. 400). Bambach and Burkey[6] separate lead and bismuth from each other by shaking the chloroform solution of the dithizonates with a buffer solution (phthalate) of *p*H 3.4. Lead goes into the aqueous phase and bismuth remains in the chloroform except

[4] C. E. Willoughby, E. S. Wilkins, Jr., and E. O. Kraemer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 285 (1935). M. K. Horwit and G. R. Cowgill, *J. Biol. Chem.*, **119**, 553 (1937), extract bismuth at *p*H 3.0–3.5. Clifford was able to separate 100 γ of bismuth from 15 γ of lead by making two extractions according to the method of Willoughby and coworkers. When 500 γ of bismuth were present, two extractions did not remove all the bismuth, but three extractions gave a complete separation. In this connection it may be mentioned that Clifford, *J. Assoc. Official Agr. Chem.*, **21**, 217 (1938), has used cupferron to remove bismuth partially and iron (III) completely from lead; the cupferrates of bismuth and iron are extracted from acid medium by ether (chloroform should also be suitable).

[5] H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **119**, 182, 184 (1940).

[6] K. Bambach and R. E. Burkey, *Ind. Eng. Chem., Anal. Ed.*, **14**, 904 (1942).

when relatively much of it is present, in which case a little finds its way into the water layer, from which it can then be extracted with dithizone.

By fractional extraction from cyanide solution, lead can be separated tolerably well from thallium (see p. 401). Another method of separation of these two metals is based on the extraction of lead at *p*H 6.0–6.4. According to Clifford[7] 50 γ of lead can be separated cleanly from 1000 γ of thallium (I) by extracting at this *p*H with three 20 ml. portions of dithizone in chloroform (100 mg. per liter).

When determining lead in samples such as silicates and biological materials containing only minute amounts of heavy metals reacting with dithizone, it is frequently advantageous to isolate the lead by extracting the alkaline citrate solution (no cyanide present) with dithizone and then shaking the carbon tetrachloride (or chloroform) extract with dilute acid (0.02 *N* or stronger hydrochloric or nitric). Lead dithizonate is thus decomposed and ionic lead transferred to the aqueous phase, in which it is then readily determined. This procedure separates lead from copper (whose dithizonate is not appreciably decomposed by dilute acid) and iron, which are undesirable constituents of a solution in which lead is to be determined by the dithizone method, since they oxidize dithizone in basic medium as already mentioned. In many cases no special preliminary separation of lead from a cyanide solution is necessary; the metal is determined directly in the presence of others such as zinc after addition of cyanide by extraction with a standard dithizone solution.

B. Sulfide Precipitation

Minute quantities of lead cannot be completely precipitated by hydrogen sulfide in dilute mineral acid solution, even if a collector such as copper or silver sulfide is used.[8] One must precipitate at a *p*H of about 3 in the presence of citrate to keep ferric and other phosphates in solution. A little copper is added as a collector.[9] Resort must be made to sulfide precipitation of lead in dealing with samples (bone-ash for example) containing much phosphate and calcium or magnesium, which are not amenable to dithizone extraction.

Small amounts of lead (0.002 to 0.03 per cent) have been successfully isolated from steel high in nickel and chromium by sulfide precipitation. The almost neutral solution is saturated with hydrogen sulfide and a few

[7] P. A. Clifford, *J. Assoc. Official Agr. Chem.*, 26, 26 (1943).

[8] I. T. Rosenqvist, *Am. J. Sci.*, 240, 359 (1942).

[9] See for example, E. C. Dawson and A. Rees, *Analyst*, 71, 417 (1946); A. G. Francis, C. O. Harvey, and J. L. Buchan, *ibid.*, 54, 725 (1929). These authors precipitate the sulfides at a *p*H of 4–5. Mercuric sulfide has been used as collector for lead in its detection and may also be of value in quantitative work; see F. Feigl and N. Braile, *Analyst*, 69, 147 (1944).

drops of ammonium hydroxide are then added to precipitate iron sulfide which carries down the lead (p. 408).

C. Electrolytic Deposition as Lead Metal or as Dioxide

Isolation of lead by electrodeposition as the metal from a solution of decomposed bio material has been recommended.[10] The lead is deposited on a rotating gauze cathode (5–6 volts, 0.2–0.5 ampere) from an ammoniacal citrate medium. Microgram quantities of lead can thus be recovered practically completely from 20–50 ml. of solution. The deposition of iron and copper is minimized by addition of potassium cyanide. The method has found little application.

Electrodeposition of lead dioxide is frequently applied in the separation of small amounts of lead. For the conditions of electrolysis see p. 403. In the absence of considerable amounts of such substances as iron and phosphate it appears that satisfactory recoveries of lead can be obtained (see Table 66). Bambach and Cholak (*loc. cit.*) obtained poor recoveries of lead as dioxide from solutions containing iron or phosphorus when electrolyzing by the A.O.A.C. and other methods.

D. Coprecipitation with Strontium Sulfate

Mixed crystal formation between strontium and lead sulfates may be made the basis of a good method for the isolation of minute quantities of lead at high dilutions (p. 22). Rosenqvist[8] found that practically complete recovery of lead could be obtained in this way. The precipitate of strontium-lead sulfate is fused with sodium carbonate and the melt leached with water to obtain strontium-lead carbonate which may be dissolved in acid after thorough washing to remove sulfate.

E. Precipitation as Chromate or Phosphate

Lead chromate is but slightly soluble in weakly acid solutions (acetic acid-acetate) and is sometimes used as an isolation form for small amounts of the metal. In nearly neutral solution (*p*H 6.6–7.4) a double chromate of lead and potassium is precipitated (see the reference on p. 114). Probably barium chromate can be used as a collector for lead chromate.

Minute amounts of lead can be successfully isolated by addition of ammonia to a solution containing calcium and phosphate.[11]

[10] K. Bambach and J. Cholak, *Ind. Eng. Chem., Anal. Ed.*, **13**, 504 (1941).

[11] L. T. Fairhall, *J. Biol. Chem.*, **60**, 485 (1924); L. T. Fairhall and R. G. Keenan, *J. Am. Chem. Soc.*, **63**, 3076 (1941). According to the latter authors coprecipitation of lead with calcium oxalate is not satisfactory. Phosphate coprecipitation has also been applied by S. Kaye, *J. Lab. Clin. Med.*, **28**, 1171 (1943), and J. Cholak, D. M. Hubbard, and R. E. Burkey, *J. Ind. Hygiene Toxicol.*, **30**, 59 (1948).

II. Methods of Determination

A. The Dithizone Method

Dithizone is doubtless the best reagent for the determination of traces of lead. When properly carried out, the dithizone method gives excellent results,[12] but there are a number of sources of error that must be guarded against (p. 110).

The first procedures[13] described for the determination of lead were based on mono-color colorimetry, either of the red lead dithizonate or of the equivalent amount of dithizone obtained by shaking the solution of lead dithizonate in the organic solvent with a dilute acid. Such a method involves a source of error, because the excess of dithizone in the organic solvent must be removed by shaking with a weakly alkaline solution, and in this washing some lead may be lost as already pointed out (p. 100). Since the loss of lead increases with the alkalinity of the wash solution, the natural tendency is to use a very weakly basic solution, but then the extraction of dithizone becomes more difficult and some of it may be left in solution (the use of a suitable filter in the color comparison minimizes this error). Clifford and Wichmann[14] have given some figures on the extent of loss of lead dithizonate on washing. When 25 ml. of a carbon tetrachloride solution of lead dithizonate containing 35.8 γ of lead were shaken with an equal volume of 1:200 ammonia for one minute, 6.4 γ of lead were found in the aqueous phase. In an actual determination the loss would be smaller because less ammonia is used in washing, and excess dithizone is originally present. If chloroform is used as the solvent the loss in a single washing is smaller but this is counterbalanced by the larger number of extractions required to remove dithizone completely from this solvent. In order that good results may be obtained in the mono-color method, the standard solution must be prepared in the same manner as the unknown and must contain very nearly the same amount of lead. The standard series method is preferable to the balancing method. The standard series technique when properly applied is of course not subject to the errors mentioned.

[12] For a comparison of the spectrographic, dithizone, and diphenylcarbazide methods for the determination of lead in bio material see J. Cholak, D. M. Hubbard, R. R. McNary, and R. V. Story, *Ind. Eng. Chem., Anal. Ed.*, 9, 488 (1937). These authors conclude that the dithizone and spectrographic methods give equally good results, although the latter is preferable when only a limited amount of sample is available. Results by the diphenylcarbazide method are low (−0.07 mg.), but the method is useful when relatively large quantities of lead are involved.

[13] H. Fischer and G. Leopoldi, *Wiss. Veröffentlich. Siemens-Konzern*, 12, 44 (1933); *Z. angew. Chem.*, 47, 90 (1934).

[14] P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, 19, 140 (1936).

1. The Mixed-Color Method

In this method the lead is first brought into a solution having a definite volume and acidity. This is readily done by extracting the sample solution with dithizone as many times as may be necessary to remove all of the lead, and then shaking the carbon tetrachloride or chloroform lead dithizonate solution with dilute acid to transfer lead to the aqueous phase. After bringing the solution to a suitable *p*H by adding an ammoniacal citrate (or tartrate) solution, together with cyanide, it is shaken with an excess of a chloroform solution of dithizone. Depending upon the *p*H employed, more or less of the excess dithizone remains in the chloroform or carbon tetrachloride phase.

The concentration of lead dithizonate in the organic solvent originally containing a fixed concentration of dithizone is found by measuring the absorption of blue-green light by the lead dithizonate in solution and referring the results to a standard curve which has been established under the same conditions. A linear relation is found between extinction and the concentration of lead dithizonate if sensibly monochromatic light is used in the measurements, since dithizone and lead dithizonate obey Beer's law in carbon tetrachloride and chloroform.

From what has already been said (p. 388), it is evident that we have a certain choice in the *p*H at which lead can be shaken out of the aqueous phase. In the older procedures the aqueous phase was adjusted to a *p*H of about 9.5 when a chloroform solution of dithizone was to be used in the extraction. At this *p*H much of the excess dithizone remains in the chloroform layer (p. 101). However, it is possible to work at a higher *p*H and still obtain quantitative extraction of lead; the advantage of such a procedure lies in the lower concentration of dithizone remaining in the chloroform layer. It has recently been shown that the extraction of lead can be made complete, or virtually so, by extracting with a chloroform solution of dithizone at a *p*H of 11.5.[15] At this high alkalinity very little dithizone remains in the chloroform and the method is to all intents and purposes a mono-color method. Under these conditions it is possible to determine lead over a wide range of concentrations by using a single standard dithizone solution. It appears that lead dithizonate, in chloroform, extracted from aqueous solutions of high *p*H (under the conditions of the procedure on p. 397) is as stable as when extracted at *p*H 9.5.

The following directions are particularly intended for the determination of traces of lead in bio material after suitable preparation of sample (p. 409), but they may be applied in many cases to other classes of material with but little modification. The procedure for the isolation of lead and

[15] L. J. Snyder, *Anal. Chem.*, **19**, 684 (1947).

its final determination at *p*H 9.5 is similar to that of a number of workers.[16] The procedure calling for a *p*H of 11.5 in the final determination seems generally superior to that carried out at *p*H 9.5, but we will give directions for both methods. The *p*H 9.5 method has been widely used and is known

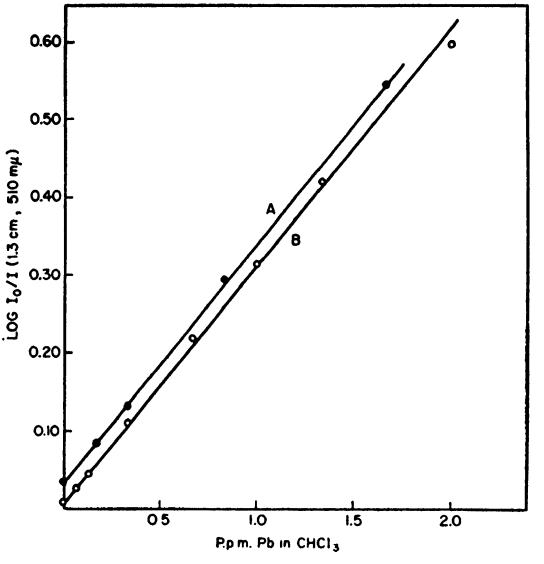


Fig. 47. Determination of lead with dithizone by extraction at *p*H 11.2. Approximately 30 ml. of sample solution containing citrate, cyanide, hydroxylamine hydrochloride, and ammonia extracted with 10 ml. of 0.005 per cent dithizone solution in chloroform; a 2 ml. aliquot of the extract was diluted to 15 ml. (A) and a 5 ml. aliquot to 15 ml. (B) with chloroform. (Based on data of Russell Frazier, Minnesota Department of Health.)

to give reliable results. The two methods have been compared.[17] Slightly superior accuracy was shown by the high *p*H procedure, but that at *p*H 9.5 was slightly more reproducible. The procedure at the lower *p*H is subject to serious error from the presence of phosphate (as little as 0.5 mg. causes low results), whereas at *p*H 11.5 as much as 5 mg. of phosphate does no harm.

[16] Especially K. Bambach, *Ind. Eng. Chem., Anal. Ed.*, **11**, 400 (1939); K. Bambach and R. E. Burkey, *ibid.*, **14**, 904 (1942); D. M. Hubbard, *ibid.*, **9**, 493 (1937); P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, **19**, 130 (1936). For a procedure by which lead and bismuth can be co-determined by measurement of the transmittancy of the carbon tetrachloride solution of the dithizonates at *ca.* 450, 510, and 560 mμ, see P. A. Clifford, *J. Assoc. Official Agr. Chem.*, **26**, 26 (1943).

[17] J. Cholak, D. M. Hubbard, and R. E. Burkey, *Anal. Chem.*, **20**, 671 (1948).

TABLE 63

DETERMINATION OF LEAD BY THE DITHIZONE MIXED-COLOR METHOD AT *p*H 11.5[a]

Lead taken, γ	0.0	8.0	20.0	40.0	60.0	80.0	100.0
Lead found, γ	0.3	7.2	19.7	40.0	60.7	80.0	99.7

[a] Representative data from Snyder[15]. Procedure as on p. 397, except 25 ml. of 0.006 per cent *w/v* dithizone solution used.

TABLE 64

DETERMINATION OF LEAD BY THE DITHIZONE MIXED-COLOR METHOD AT *p*H 9.5 (CHLOROFORM, 510 mμ)

Lead taken, γ	2.0	5.0	10.0	20.0	30.0	40.0	50.0
Lead found, γ	2.0	5.0	11	20	30	41	49.5

Reagents

Water. Distilled from Pyrex. It should give no test for lead.

Chloroform. Redistilled (p. 108).

Dithizone solution (A), 50 mg. of dithizone (not specially purified) in 1 liter of chloroform. Protect from light.

Dithizone solution (B), 50 mg. of purified[18] dithizone in 1 liter of redistilled chloroform. Keep in the dark, preferably in a refrigerator. One per cent alcohol may be added to make the solution more stable (p. 108).

Ammonium hydroxide. Pass ammonia from a cylinder into cold redistilled water until saturated, or if tank ammonia is not available, distil a concentrated solution.

Nitric acid, 1:100. Dilute colorless concentrated acid, previously distilled from Pyrex if necessary,[19] with 100 times its volume of water.

Ammonium citrate solution, 50 g. in 100 ml. of water. Make the solution ammoniacal (*p*H 9) and shake with successive portions of dithizone (solution A) until all lead has been removed. Remove any excess dithizone by shaking with chloroform.

Potassium cyanide solution, 10 g. in 100 ml. of water. If necessary, potassium cyanide can be freed from lead as follows. Prepare an approximately saturated solution (50 g. in 100 ml. of solution) and shake with successive small portions of dithizone until all lead has been removed (green color in final chloroform extract). Extract the dithizone in the aqueous layer with chloroform, and dilute to 10 per cent.

Hydroxylamine hydrochloride solution, 20 g. in 100 ml. of water. If necessary, lead and other heavy metals may be removed in the following way. Add ammonium hydroxide to 20 g. of the reagent in about 65 ml. water containing a few drops of *m*-cresol purple until a yellow color appears and then add a milliliter of 5 per cent solution of sodium diethyldithiocarbamate. Extract the solution with chloroform until the metal carbamates and all of the excess reagent are removed. Complete extraction of reagent may be tested by shaking the chloroform extract with a dilute copper solution; no yellow color should appear. Then add hydrochloric acid (redistilled if necessary) to the hydroxylamine hydrochloride solution until the indicator turns pink, and dilute to 100 ml. with water.

[18] Some commercial products do not require purification, in which case the same dithizone solution can be used for the preliminary extraction and the final determination.

[19] Concentrated analytical-reagent acid may contain 10–30 γ lead per liter.

Ammonia-cyanide solution (for final determination of lead at *p*H 9.5), 20 g. of potassium cyanide and 150 ml. of concentrated (sp. gr. 0.90) ammonia diluted to 1 liter with distilled water.

Ammonia-cyanide-sulfite solution (for final determination of lead at *p*H 11.5). Dilute 350 ml. of concentrated ammonium hydroxide (density 0.90) and 30 ml. of 10 per cent potassium cyanide solution to 1 liter and dissolve 1.5 g. of sodium sulfite in the solution.

Standard lead solution, 0.00100 per cent in 1:100 nitric acid. This solution is preferably prepared fresh before use by dilution of a 0.100 per cent solution (0.160 g. of dried lead nitrate in 100 ml. of solution acidified with nitric acid).

§ Procedure

Isolation of Lead.[20] Transfer the sample solution, or a suitable aliquot of it, containing from 1 to 100 γ of lead, to a glass-stoppered separatory funnel. Add 15 ml. of ammonium citrate and 1 ml. of hydroxylamine hydrochloride solution together with a few drops of thymol blue indicator. Next add ammonium hydroxide until the solution is basic, and then 5 ml. (or more if required) of potassium cyanide solution. Adjust the *p*H of the solution to 9.0–9.5 (green-blue to blue color of indicator), add 2 to 5 ml. of dithizone solution A, and shake for 15 seconds. If the amount of lead present is not known even approximately, it is usually advisable to add the dithizone in increments of, say, 1 ml. with shaking after each addition until the color begins to deviate from the pure red of lead dithizonate, in order that an idea of the amount present may be gained for use later in the final determination.[21] One milliliter of pure 0.005 per cent dithizone is equivalent to about 20 micrograms of lead.

Draw off the chloroform into another separatory funnel, extract the sample solution with another portion of dithizone (2–5 ml.), add this extract to the first, and extract a third time if necessary. The last extract should show no mixed color. Shake the combined chloroform extracts with 10 to 20 ml. of water containing a drop of 1:1 ammonia, draw off the chloroform into a separatory funnel, extract the aqueous solution with 1 or 2 ml. of dithizone, and add the latter to the main dithizone extract.

Shake the chloroform extract for one-half minute with 15 ml. of 1:100 nitric acid and transfer the aqueous phase to a separatory funnel or to a 25 ml. volumetric flask if an aliquot is to be taken. Shake the chloroform phase with 9–10 ml. of the dilute nitric acid and combine the latter with the previous portion. If the presence of bismuth is suspected, it may be tested for and removed at this point (see note 4). Remove any droplets

[20] It may be pointed out that the preliminary isolation of lead is not always required. In some instances a direct determination may be feasible after hydroxylamine hydrochloride has been added to reduce iron and copper.

[21] The amount of lead present need not be estimated so closely if the final determination is to be made at *p*H 11.5. In that case the preliminary extraction can usually be made with successive 5 ml. portions of dithizone.

of dithizone by shaking with a little chloroform and drawing off. Swirl the solution in the funnel to collect droplets of chloroform into one globule and draw this off, leaving the bore of the stopcock filled with chloroform. If there is a film or drop of chloroform on the surface of the aqueous solution, allow the funnel to stand unstoppered until it has evaporated. Dry the stem of the funnel with a roll of filter paper.

Determination of Lead. The isolated lead may be determined by either of the following methods:

(*a*) *At pH 11.5.*[22] To the lead solution (in 1:100 nitric acid and having a volume of 25 ml.) contained in a separatory funnel, add 75 ml. of ammonia-cyanide-sulfite mixture. For quantities of lead up to 100 γ run in 7.5 ml. of dithizone solution B and 17.5 ml. of chloroform (total volume of chloroform phase thus 25 ml.). Shake for 1 minute and allow the phases to separate. If the chloroform layer appears clear it may be run directly into a 1 cm. absorption cell, a few drops first being allowed to run out of the stem of the funnel to displace any chloroform in the bore of the stopcock. If it seems necessary, the chloroform can be filtered through a small plug of glass wool in a very small funnel or in the stem of the separatory funnel itself (reject the first few drops). At the same time run a blank by treating 25 ml. of 1:100 nitric acid as just described for the unknown solution. Measure the transmittancy of the solutions at 510 mμ without undue delay.

If the amount of lead is less than 10 γ it is preferable to use 10 ml. of a chloroform-dithizone solution containing 10 mg. of dithizone per liter. Absorption cells with a stratum thickness greater than 1 cm. should be used for very small amounts of lead.

(*b*) *At pH 9.5.* If an aliquot of the solution containing the isolated lead is taken, dilute to 25 ml. with 1:100 nitric acid. Depending on the approximate amount of lead, as estimated from the volume of dithizone required in the preliminary extraction, add a suitable volume (accurately measured) of standard dithizone solution prepared by diluting solution B with pure chloroform:[23]

Range of lead, γ	Dithizone concentration, mg. per liter	Volume of dithizone, ml.
0–5	5	5
0–10	10	5
0–25	10	10
0–50	10	20
0–100	10	40

[22] These directions are essentially those of Snyder,[15] except the maximum amount of lead provided for is 100 γ; a weaker solution of dithizone is used.

[23] The cell length to be used in the subsequent photometry of the solution will depend

(*continued on next page*)

Then add 5.0 ml. of ammonia-cyanide mixture, shake for 1 minute, and allow the phases to separate. The chloroform phase should show a mixed color, indicating that an excess of dithizone is present. Run a small volume of the chloroform solution through the stem of the funnel to displace the chloroform in the bore of the stopcock, and deliver the remainder of the clear solution into an appropriate absorption cell which is covered or stoppered to prevent evaporation. (If the chloroform phase contains suspended droplets of water or appears turbid, it may be filtered through a small plug of glass wool; reject the first portion of the filtrate.) Determine the extinction of the solution at 510 mμ (a Wratten compound filter No. 45 and No. 5 may be used). Use water as the reference liquid. Obtain the standard curve for each lead range by taking appropriate amounts of lead in 50 ml. of 1:100 nitric acid, saturating with chloroform, and proceeding as in the case of the sample solution. The 0.005 per cent stock solution (B) of dithizone in pure chloroform should show little change in a period of a few weeks if kept in the dark at 10° C. However, the transmittancy of the dilute dithizone solutions prepared from it by dilution should always be determined when the determination is made to avoid error due to a possible change in concentration from that existing at the time the standard curve was constructed.

Notes. 1. The amount of lead found must be corrected for lead introduced in the reagents, or from the apparatus, by running a blank through all the steps of the procedure, including the preparation of the sample.

2. The final solution of lead dithizonate should not be exposed to strong light. It is said that it may be kept for 12 hours without appreciable change if stored in an ice box and protected from evaporation. However, the best policy is to determine the transmittancy of the solution as soon as it has been obtained, especially if very small amounts of lead are involved.

3. Phosphate is an undesirable impurity in potassium cyanide since it may precipitate lead in the final solution and cause low results as noted above, especially if the solution is allowed to stand for some time before extraction with dithizone. Therefore, as soon as the ammonia-cyanide solution has been added to the sample solution the latter should be shaken with dithizone. Potassium cyanide may be purified by preparing a hot saturated solution and boiling down, but usually such purification is not necessary.[24]

4. To separate bismuth from lead proceed as follows. Add 2 drops of thymol blue indicator to the solution and adjust the *p*H to 3.0 or a slightly greater value by carefully adding dilute (1 *N*) ammonia until the indicator shows its full yellow color (add thymol

upon the type of instrument, *i.e.*, whether a visual or photoelectric photometer, and upon the filter, if one is used. If the solution is too strongly colored for satisfactory transmittancy measurement it should be diluted to a definite volume with pure chloroform.

[24] P. A. Clifford, *J. Assoc. Official Agr. Chem.*, **20**, 192 (1937). He reports that sodium cyanide usually contains more phosphate than does potassium cyanide and its use should be avoided. Sulfide is of course a very undesirable impurity; it sometimes occurs in cyanides in small quantities.

blue to an equal volume of water for comparison). Shake the solution with 1–2 ml. of 0.001 per cent (weight/volume) dithizone for 2 minutes. If the chloroform remains green no appreciable amount of bismuth is present. An orange or mixed color shows bismuth, which then must be removed by shaking with successive small portions (2–3 ml.) of 0.005 per cent dithizone until the last portion remains an unchanged green after shaking for 2 or 3 minutes. Finally, to be certain that bismuth has been completely extracted, test the aqueous solution by shaking with 1–2 ml. of 0.001 per cent dithizone for at least 2 minutes. The chloroform should remain an unchanged green. Then add ammonia-cyanide solution and proceed by either of methods described above.

The procedure of Bambach and Burkey (p. 389) may also be followed in separating lead from bismuth. In this case the initial extraction of lead should not be made at a *p*H higher than 9, lest the ammonia remaining in the chloroform (even when washed with two 50 ml. portions of water) raise the *p*H of the buffer above 3.4 and thus lead to loss of lead.[6]

5. Instead of using a chloroform solution of dithizone in the final determination, dithizone can be dissolved in the ammonia-cyanide mixture and clear chloroform added. Solutions of this type are said to remain apparently unchanged for 6 months in a refrigerator (Cholak, Hubbard, and Burkey[11]).

6. For the use of the standard series method in the determination of a few micrograms of lead, see p. 406.

7. Special treatment of the sample is required when tin is present (p. 412).

2. The Mono-Color Method[25]

As already stated this method is less accurate than the mixed-color method, but it lends itself better to the determination of lead in the presence of much bismuth and especially of much thallium.

Reagents

Dithizone solution, 6 mg. of purified dithizone in 100 ml. of redistilled carbon tetrachloride.

Ammonium hydroxide. See p. 395.

Hydroxylamine hydrochloride solution, saturated solution of analytical reagent in cold water. Prepare shortly before use.

Potassium cyanide solution (*A*), 5 or 10 per cent, lead-free.

Potassium cyanide solution (*B*), 0.5 per cent, lead-free.

Ammonium citrate solution, 50 g. in 100 ml. of water. Remove lead from the solution by extracting with dithizone solution. See p. 395.

Standard lead solution. See p. 396.

§ Procedure

If metals precipitated by ammonia are present, treat the solution with a sufficient amount of ammonium citrate to prevent their precipitation, and add enough ammonia to make the solution basic. Then add enough potassium cyanide solution (A) to convert foreign heavy metals into their cyanide complexes. In the usual case 3 to 5 ml. of 5 per cent potassium cyanide per 10 ml. of sample solution will suffice, but when traces of lead are to be

[25] H. Fischer and G. Leopoldi, *Z. anal. Chem.*, 119, 164 (1940).

determined in the presence of much zinc, copper, silver, etc., 10 ml. or more of 10 per cent potassium cyanide may be needed. To prevent the interference of oxidizing substances such as ferric iron, add a milliliter of hydroxylamine hydrochloride solution, heat the solution to boiling, and cool to room temperature. Extract the solution in a separatory funnel with small portions (3–5 ml.) of dithizone until the carbon tetrachloride layer shows no red color. Shake the combined extracts, separated from the aqueous phase, with a few milliliters of potassium cyanide solution (B), and draw off the carbon tetrachloride layer. Again wash the latter with potassium cyanide solution. After the second washing the carbon tetrachloride phase should be virtually free from dithizone and the aqueous phase should be practically, if not entirely, colorless. Finally wash with a few milliliters of water.

The final determination of the lead can naturally be made in a number of ways. After the lead dithizonate solution has been made up to a definite volume with carbon tetrachloride, its transmittancy can be obtained with a spectrophotometer or a filter photometer (a filter giving maximum transmission at 520–530 mμ is suitable), and the lead concentration obtained from a calibration curve. Comparison may be made against a standard lead dithizonate solution with the aid of a Duboscq colorimeter, or the standard series method may be applied (*cf.* the determination of lead in silicate rocks, p. 406).

It may be advantageous to convert lead dithizonate into the equivalent amount of dithizone by shaking the carbon tetrachloride solution with 0.1–0.2 *N* nitric acid, and to measure or compare the color intensity of the resulting green solution (use a filter giving maximum transmission at 610 mμ). To remove water droplets from the carbon tetrachloride it is permissible to filter the latter through a small ashless filter paper which has been washed with dilute nitric acid and then dried at 100°. The dithizone solution for comparison must be obtained from a known amount of lead which has been treated in exactly the same manner as the sample.

Determination of Lead in the Presence of Much Bismuth (1 mg.). The sample solution should contain not more than 25 γ of lead nor more than 5 mg. of bismuth. Add 1 ml. of ammonium citrate solution and then ammonia until slightly basic (litmus paper). For each 10 ml. of solution add 10 ml. of 10 per cent potassium cyanide solution, and shake 3 to 5 minutes with 2 ml. of dithizone solution containing 3 mg. of dithizone in 100 ml. of carbon tetrachloride. A mechanical shaker is convenient; the extraction of lead is slow in the presence of much bismuth. Separate the carbon tetrachloride, extract with another 2 ml. portion of dithizone, and continue in this way until the color of the last extract is pure orange (bismuth dithizonate). To be certain that all of the lead has been extracted, shake the

last portion of carbon tetrachloride extract with three small portions of 1 per cent potassium cyanide solution. The carbon tetrachloride layer should show no pink color. If it does, extract the sample solution with another portion of dithizone. Shake the combined extracts, containing all of the lead and some bismuth, with 5 ml. of 1:100 nitric acid, separate the aqueous phase, adjust its *p*H to 2.8–3 (full yellow color of thymol blue) and shake with small portions of dithizone (6 mg. per 100 ml.) for 3–4 minutes until the dithizone remains pure green. Wash the aqueous solution with carbon tetrachloride, and determine lead according to the directions given above, after making the solution ammoniacal and adding 5 ml. of 5 per cent potassium cyanide and 1 ml. of hydroxylamine hydrochloride solution.

Determination of Lead in the Presence of Thallium. To the sample solution containing up to 500 γ of thallium add 0.5–1 ml. of ammonium citrate, make slightly ammoniacal, and add 10 ml. of 10 per cent potassium cyanide. Extract with about 2 ml. portions of dithizone solution containing 4 mg. dithizone in 100 ml. of carbon tetrachloride. The first extracts contain lead, and the latter ones lead with thallium or thallium alone. Both lead and thallium form red dithizonates and cannot be distinguished by inspection, but can be differentiated as follows. Shake each extract with twice its volume of 0.5 per cent potassium cyanide. Thallium dithizonate but not lead dithizonate is decomposed and the carbon tetrachloride is decolorized if the color is due to thallium alone.

Wash the combined carbon tetrachloride extracts with 0.5 per cent potassium cyanide solution to remove any excess dithizone, dilute to a definite volume with carbon tetrachloride and determine lead by the mono-color method.

Notes. 1. A 0.5 per cent potassium cyanide solution is preferable to 1:200 ammonia as wash solution, because the use of the latter may result in the reaction of heavy metals in droplets of aqueous solution in the drawn-off carbon tetrachloride phase.

The *p*H of 0.5 per cent potassium cyanide solution is about 11.4 and therefore some loss of lead may be expected when a carbon tetrachloride solution of lead dithizonate is washed with cyanide. Fischer and Leopoldi found that 19.6 γ of lead extracted according to the above procedure and the carbon tetrachloride solution washed twice with 5 ml. of 0.5 per cent potassium cyanide (5 seconds shaking) and twice with 5 ml. of water gave an average recovery of 18.5 γ. The error is reduced by compensation when the standard lead solution is treated similarly.

2. Conversion of lead dithizonate to dithizone may in some cases be advantageous because of the possibility of keeping dithizone solutions unchanged for a long time. A dithizone solution in carbon tetrachloride undergoes practically no change in a month if covered with a weakly acid solution of hydroxylamine hydrochloride and kept in a brown bottle in diffuse daylight (Fischer and Leopoldi). Tenth-normal sulfuric acid is nearly as effective as hydroxylamine hydrochloride in stabilizing dithizone solutions. On the other hand a lead dithizonate solution cannot be preserved unchanged for such a long

period of time. If kept in a brown bottle a lead dithizonate solution shows practically no change in 4 days, but decomposes to a considerable extent in 15 days. Covering such a solution with a weakly alkaline cyanide solution increases the rate of decomposition (Fischer and Leopoldi).

3. When metals such as zinc, cadmium, etc. are present the excess of cyanide must be increased. In spite of the high alkalinity of the resulting solution, lead can be extracted quantitatively if excess dithizone is used. In determining percentages of lead of the order of 0.001 in metallic zinc, 40 ml. of 10 per cent potassium cyanide are added to 5 ml. of solution containing 1 g. of zinc.[26]

TABLE 65

DETERMINATION OF LEAD IN THE PRESENCE OF BISMUTH AND THALLIUM BY DITHIZONE[27]

Foreign metal	Pb taken γ	Pb found γ	Error γ
0.1 mg. Bi[a]	9.5	10.0	+0.5
0.1 mg. Bi[a]	9.5	9.0	−0.5
0.5 mg. Bi[a]	18.7	17.7	−1.0
1.0 mg. Bi[a]	7.4	7.1	−0.3
1.0 mg. Bi[a]	7.4	8.3	+0.9
5.0 mg. Bi[b]	9.8	8.3	−1.5
5.0 mg. Bi[b]	7.4	6.9	−0.5
0.15 mg. Tl	9.5	10.6	+1.1
0.3 mg. Tl	4.8	4.2	−0.6
0.75 mg. Tl	9.5	8.2–10.6	−1.3 to +1.1

[a] Bismuth extracted with dithizone at *p*H 2.8–3.0.

[b] Fractional extraction of lead from cyanide medium followed by removal of coextracted bismuth at *p*H 2.8–3.0 (see p. 401).

B. THE TETRAMETHYLDIAMINODIPHENYLMETHANE METHOD

Lead can be determined colorimetrically by electrolytic deposition as dioxide followed by oxidation of tetramethyldiaminodiphenylmethane by the latter to an intensely colored blue diphenylmethane dye.[28]

The following procedure is that of Müller[29] who prefers this method to the dithizone method, especially when foreign metals such as iron, zinc, bismuth, and thallium are present. It may be used for amounts of lead above 5 γ. Chloride and phosphate interfere seriously with the deposition of lead dioxide, and therefore lead must generally first be isolated as the sulfide. The method would appear to have limited use; it is not to be compared with the dithizone method.

[26] H. Fischer, *Metall u. Erz*, **35**, 87 (1938).

[27] Representative values from H. Fisher and F. Leopoldi, *Z. anal. Chem.*, **119**, 183, 185 (1940).

[28] M. A. Trillat, *Compt. rend.*, **136**, 1205 (1903).

[29] H. Müller, *Z. anal. Chem.*, **113**, 161 (1938); M. Fields, *New Zealand J. Sci. Tech.*, **23B**, 224 (1942).

Reagent

Tetramethyldiaminodiphenylmethane solution, 50 mg. in 100 ml. of pure (redistilled) glacial acetic acid. The tetramethyldiaminodiphenylmethane should be recrystallized from hot alcohol containing a few drops of yellow ammonium sulfide, and the purified solid protected from light. The solution is stable for 24 hours.

§ Procedure

The solution of the isolated lead should have a volume not greater than 40 ml. and should contain about 12 mg. of copper and 4 to 6 g. of ammonium nitrate. Add ammonium hydroxide until the blue color of the copper ammonio complex just appears (it should be dischargeable by 1 drop of 20 per cent nitric acid) and then 0.5 ml. of 1 *N* nitric acid. Transfer the solution to the electrolysis vessel, dilute to 100 ml. or sufficiently to cover the electrodes. Use a gauze cylinder as anode and a rotating cathode (500–700 r.p.m.). Bring the temperature of the solution to 30–33° and electrolyze for 20 minutes with *ca.* 0.2 ampere and 2.3 volts. When deposition is complete, wash the electrodes thoroughly with water. Dip the anode in boiling water for 1 second, shake off droplets of water and immerse for one minute in a suitably sized vessel of annular cross section containing 25.0 ml. of freshly prepared tetramethyldiaminodiphenylmethane solution. Compare at once with a standard solution similarly obtained. Use a filter giving maximum transmission at 570 mμ or better at 600 mμ for amounts of lead less than 20 γ.

TABLE 66

DETERMINATION OF LEAD WITH TETRAMETHYLDIAMINODIPHENYLMETHANE AFTER ELECTROLYTIC DEPOSITION AS DIOXIDE ACCORDING TO MÜLLER[29]

Foreign elements γ	Pb taken γ	Pb found γ
	6	7.5
	8	9
	15	15
	17	18.5
	43	42
	63	60
100 Bi	0	1
500 Bi	0	0
50 Bi	15	20
500 Bi	20	18
2000 Zn	12	14
100 Tl	23	24
100 Mn	18	16.5
10000 Fe	10	14
10000 Fe	55	56
5000 Fe	6	8

Notes. 1. According to Müller not more than 1–2 γ of lead will remain in solution after the electrolysis.

2. Although the author claims that good results can be obtained in the presence of foreign metals, especially bismuth, the figures given (*cf.* Table 66) are sometimes erratic. In pure solutions the accuracy is usually within 10 per cent for amounts greater than 8–10 γ. It may be concluded that the method is inferior to the dithizone method properly carried out, especially below 5 γ, when indeed the electrolytic method fails nearly altogether.

III. Applications of the Dithizone Method

A. Silicate Rocks

The following procedure has been shown to give reliable results in the determination of lead in silicate rocks and minerals. The original directions,[30] worked out for the determination of lead by the mono-color standard series method with a carbon tetrachloride solution of dithizone have been retained, but it will be understood that after lead has been isolated it can be determined by other procedures if preferred, *e.g.*, according to the general method given on p. 397 with a chloroform solution of dithizone.

Special Reagents

Dithizone, 0.01 per cent (weight/volume) in carbon tetrachloride. Special purification of the solid dithizone is not necessary if the amount of the diazone (p. 106) present is small.

Dithizone, 0.001 per cent in carbon tetrachloride. Prepare by dilution of the 0.01 per cent solution shortly before use. The diluted solution shaken with a little dilute ammonia solution containing about 0.5 per cent potassium cyanide should give a practically colorless carbon tetrachloride layer.

Perchloric acid, 70 per cent. Redistillation is not necessary if a good grade of acid is used, unless lead contents of some parts per million are to be determined.

Hydrofluoric acid. This is likely to contain comparatively large amounts (1 or 2 p.p.m.) of lead and should be purified either by distillation from platinum or by coprecipitation of the lead with strontium fluoride (Rosenqvist, p. 390). In the latter case, add two 10 ml. portions of 10 per cent strontium chloride solution to 1 liter of concentrated hydrofluoric acid and decant off the supernatant liquid after standing. Care must be taken to see that there are no suspended particles of strontium fluoride in the liquid. In this way the lead content of the acid can be reduced to less than 0.002 p.p.m.

Hydrochloric acid, 1:1. Preferably redistilled.

Hydrochloric acid, 1:500 (*ca.* 0.02 *N*).

Sodium or ammonium citrate, 10 per cent. Make the solution weakly ammoniacal (1:200) and remove lead and other reacting metals by extracting with successive portions of 0.01 per cent dithizone until the carbon tetrachloride phase is colorless or at most shows a pink tinge.

Potassium cyanide, 5 per cent. A milliliter of solution should impart no pink color to the carbon tetrachloride phase when diluted with 2 ml. of water and shaken with a milliliter or two of 0.001 per cent dithizone.

[30] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, 9, 464 (1937). For typical results see Table 67.

Sodium carbonate. If necessary, the salt can be freed from lead by adding 1–2 ml. of 10 per cent strontium chloride dropwise to 100 ml. of nearly saturated solution, filtering off the precipitate, evaporating the filtrate in platinum, and gently igniting the residue.

§ Procedure

Decomposition of Sample. Weigh 0.25 g.[31] of 100-mesh rock powder into a platinum dish, and add a milliliter or two of water, 0.5 ml. of perchloric acid, and 3 ml. of concentrated hydrofluoric acid. Evaporate to dryness, occasionally stirring with a platinum spatula or wire to prevent caking. Repeat the evaporation after adding 2 ml. of hydrofluoric acid. Then heat at a higher temperature to drive off perchloric acid. Add a few milliliters of water and 0.5 ml. of perchloric acid, again evaporate to dryness, and expel the excess of perchloric acid. To the residue add 2 ml. of 1:1 hydrochloric acid and 5 ml. of water, and warm if necessary to bring all soluble material into solution. Next add 5 ml. of ammonium or sodium citrate solution, cool to room temperature, and add ammonium hydroxide until the solution becomes basic to litmus paper and finally an excess of 0.25–0.3 ml. If the solution becomes turbid on the addition of ammonia allow it to stand for 15 minutes, and filter through a small paper (4–5 cm. in diameter) of medium texture, transfer any residue in the dish to the paper and wash with three or four 1 ml. portions of water containing a drop of ammonia and citrate solution. Reserve the filtrate (solution 1).

Ignite the paper and its contents in a platinum crucible, avoiding an unnecessarily high temperature. Mix the residue with 0.1–0.2 g. of sodium carbonate, fuse, and add a few milliliters of water to the melt. Warm to hasten disintegration, and filter the solution through a 4 cm. paper, keeping most of the residue in the crucible. Wash with small portions of water totaling 10 ml. Reserve the filtrate (solution 2), transfer the filter paper to the platinum crucible, and ignite at a low temperature. Add 1 ml. of hydrofluoric acid and 2–3 drops of perchloric acid, evaporate to dryness, and expel the perchloric acid; treat the residue with a few drops of water and 1–2 drops of perchloric acid, and again expel the excess acid. Add 1 ml. 1:1 hydrochloric acid and 2–3 ml. of water and warm to bring the residue into solution. (Any insoluble material should be re-fused with sodium carbonate.) Add 1 ml. of citrate solution and then ammonia in a 3 or 4-drop excess over that required for neutralization (solution 3).

Isolation of Lead and Other Metals Reacting with Dithizone. Transfer the main solution (solution 1) to a small separatory funnel, add 5 ml. of

[31] If it is desired to use a photometer in the final determination it may be necessary to take a 0.5–0.75 g. sample in order that the volume of the carbon tetrachloride solution whose transmittancy is determined will be sufficiently large (5 ml.) to fill the cell used. If a larger sample is taken, increase the volume of the reagents proportionately.

0.01 per cent dithizone solution and shake for one-half minute.[32] If the dithizone is green shake for another half-minute. Allow the phases to separate and draw off the carbon tetrachloride into another separatory funnel. Unless the separated carbon tetrachloride is distinctly green, add another 5 ml. portion of dithizone, shake for one-half to one minute, draw it off, and continue in this manner until the last portion remains green after shaking for at least one-half minute. Next extract the solution of the leached sodium carbonate melt (solution 3) in the same way, except use 1–2 ml. portions of dithizone. Combine these extracts with the others. Finally, extract the filtrate from the sodium carbonate leach (solution 2) with 2 ml. of dithizone, after adding 0.5 ml. of citrate solution and sufficient dilute hydrochloric acid to give the greenish intermediate color of thymol blue.

Wash the combined carbon tetrachloride extracts with 2–3 ml. of water, separate the phases, shake the wash water with a milliliter of dithizone and add this to the washed carbon tetrachloride phase. It is important that the separated carbon tetrachloride be free from droplets of iron-containing solution.

Separation of Lead (and Zinc) from Copper. Shake the combined carbon tetrachloride extracts for 1 minute with 10 ml. of 1:500 hydrochloric acid. If the carbon tetrachloride remains red on shaking add 1–2 ml. of 0.01 per cent dithizone before finishing the shaking. Draw off the carbon tetrachloride into another separatory funnel and shake vigorously for 1 minute with a fresh 10 ml. portion of 1:500 acid. Combine the two acid extracts, add a few drops of carbon tetrachloride and draw off to remove any colored droplets of carbon tetrachloride, transfer to a 25 ml. volumetric flask, and make up to the mark with the dilute acid. This solution contains the lead and zinc of the sample. The carbon tetrachloride contains the copper (see p. 314 for its determination).

Determination of Lead. If the lead is to be determined by the standard series method, transfer 5 ml. of the solution to a color-comparison tube (p. 52), add 0.10 ml. each of citrate solution and concentrated ammonium hydroxide, and 1.0 ml. of potassium cyanide. Prepare a series of standards (containing for example 0, 0.5, 0.75 ... 2 γ of lead) in 5 ml. of the dilute acid and treat with citrate, ammonia, and cyanide. Without delay add 2.0 ml. of 0.001 per cent dithizone solution from a buret to unknown and standards. Shake the tubes well for 10–15 seconds and examine trans-

[32] If copper and zinc are not to be determined simultaneously, add also 1 ml. of potassium cyanide and 1 ml. of 20 per cent hydroxylamine hydrochloride to form cyanide complexes of these metals and prevent their extraction, thus reducing the volume of dithizone required. Add more ammonia if necessary to make the solution basic and proceed as above.

versely against a white background. If desired, adjacent members of the standard series may be mixed for a more precise comparison after the first comparison has been made.

TABLE 67
DETERMINATION OF LEAD IN SILICATE ROCKS

Sample	Pb present %	Pb found %
Granite	0.0004	0.00025
Diabase	0.0008	0.0007
Granite	0.0008	0.0008
Granite	0.0035	0.0035
Gabbro	0.0047	0.0041
Granite	0.0055	0.0057
Granite[a]	0.0055	0.0051
Granite[b]	0.0015	0.0012

[a] Contained 0.4% Cr (III), 0.6% Ba, 0.25% S. Nitric acid used in place of perchloric acid in the decomposition.
[b] Contained 0.01% Tl, 0.02% Ag, 1% Sn.

If a photometer is used, take 5 or 10 ml. of the lead solution and add citrate, ammonia, and cyanide as specified in the preceding paragraph, except use 2 ml. of potassium cyanide for 10 ml. of lead solution. Shake with 2.0–3.0 ml. of 0.001 per cent dithizone. Determine the transmittancy of the carbon tetrachloride at 525 mμ, and refer the reading to a standard curve obtained under the same conditions.

A blank must be run to find the amount of lead contributed by the reagents.

B. STEEL

Sulfide precipitation is used in the following method for the isolation of lead from steels containing much nickel and chromium. The subsequent colorimetric determination is made either photometrically by the monocolor dithizone method, or visually by the mixed color method.[33] Good results have been obtained (Table 68). The following directions are essentially those of the authors except that the sample size has been reduced from 1 g. to 0.5 g.

[33] L. G. Bricker and K. L. Proctor, *Ind. Eng. Chem., Anal. Ed.*, **17**, 511 (1945). According to these authors, photometry of the mixed color of lead dithizonate-dithizone with a filter showing maximum transmittancy at 520 mμ gave irregular results. This is an unexpected finding in view of the success that has been attained in the mixed color measurement at 510–520 mμ (see p. 393 et seq.)

TABLE 68

DETERMINATION OF LEAD IN STEEL[a]

Pb present, %.....	0.0020	0.0040	0.0060	0.0110	0.0213
Pb found, %.....	0.0024	0.0043	0.0060	0.0115	0.0214

[a] Typical results from Bricker and Proctor.[33] Determinations made by photometric technique.

§ Procedure

Dissolve a 0.5 g. sample of steel in 10 ml. of a mixture of equal parts of concentrated hydrochloric and nitric acids. Add 10 ml. of 70 per cent perchloric acid and a few drops of hydrofluoric acid and evaporate to strong fumes of perchloric acid to oxidize chromium. Cool and dilute to 75 ml. with water. Add 1:1 ammonium hydroxide until ferric hydroxide just redissolves. Pass hydrogen sulfide into the flask through a 3-hole stopper, fitted with a small separatory funnel, until the solution is saturated. Add 5 drops of 1:5 ammonium hydroxide through the funnel and pass in hydrogen sulfide for 3 minutes more.

Filter at once through paper (Whatman No. 40) and wash with a little cold water saturated with hydrogen sulfide. Ignite the paper and its contents in a porcelain crucible. Cool and add 5 ml. of hot 1:1 nitric acid. Crush any large particles and digest with stirring for a few minutes. Filter through a small paper into a 60 ml. separatory funnel and wash with 1:100 nitric acid. To the filtrate add 2.5 ml. of citric acid (500 g. in 1 liter of solution) and then concentrated ammonium hydroxide until faintly ammoniacal; cool under the tap. Add 5 ml. of 10 per cent sodium or potassium cyanide followed by ammonia until thymol blue shows a blue color (*p*H 9–9.6).

Extract with 5 ml. portions of dithizone (0.002 per cent *w/v* in chloroform), shaking 30 seconds, until the last portion remains unchanged in color. Allow the layers to separate for 2 minutes before draining off the chloroform. Combine the chloroform extracts in a small separatory funnel. Add to the latter 15 ml. of 1:100 nitric acid and shake thoroughly to bring lead into the aqueous phase. Draw off and discard the chloroform layer. Shake the aqueous solution with a few milliliters of chloroform to collect any small amount of dithizone solution remaining, and draw off. Add 3 ml. of ammonia–cyanide mixture (100 ml. of 10 per cent sodium cyanide and 75 ml. of concentrated ammonium hydroxide diluted to 500 ml. with water) to the nitric acid solution.[34] Measure exactly 15 ml. of dithizone solution (0.002 per cent) into the separatory funnel and shake for 1

[34] If more than 15 ml. of dithizone solution were needed for the extraction, indicating more than 0.02 per cent of lead, dilute the nitric acid extract to a suitable volume with 1:100 nitric acid, take an aliquot, and make it up to 15 ml. if necessary.

minute. Allow the layers to separate for a few minutes and drain off the chloroform into another separatory funnel. Add to the latter 10 ml. of 1:13 ammonium hydroxide and 2.5 ml. of sodium cyanide solution (10 per cent), shake well, and separate the layers. Again shake the chloroform phase with ammonia and cyanide solution. The excess dithizone is usually removed by two shakings with the ammonia-cyanide mixture, but a third may be necessary. Finally run the chloroform layer into a 25 ml. volumetric flask (a glass-stoppered tube graduated at 25 ml. is sufficiently accurate and more convenient) and dilute to the mark with pure chloroform. Mix and obtain the transmittancy of the solution at 510 mμ. The measurement should be made without undue delay. Construct the standard curve by treating known amounts of lead exactly as in the procedure proper. Run a blank on the reagents.

For directions for the visual determination of lead by comparison of mixed colors consult the original.

C. Copper

A dithizone procedure for the determination of 0.01–0.05 per cent of lead in copper metal may be found in the literature.[35]

D. Water

The amount of sample to be taken will depend on the magnitude of the lead concentration and the method of making the final color measurement or comparison. Precautions must be taken to prevent loss of lead by adsorption or by coprecipitation with any insoluble matter formed on standing. The sample should be acidified with hydrochloric acid immediately after collection.

If, as is generally the case, large amounts of metals reacting with dithizone are not present, the following procedure is suitable. Treat the sample with enough lead-free sodium or ammonium citrate to make its concentration about 2 per cent, make slightly ammoniacal (*p*H *ca.* 9), extract the lead and other reacting metals with successive portions of 0.01 per cent dithizone in carbon tetrachloride, and continue as described on p. 406 *et seq.* Should relatively much zinc or copper be present the general procedure given on p. 396 can be applied.

E. Bio Materials

Samples of organic origin may be decomposed by ashing or by digestion with oxidizing acids. The former method is more convenient in some respects but involves possible loss of lead by volatilization (?) and from retention by the surface of the dish, especially if the amount of ash is scanty.

[35] L. Silverman, *Anal. Chem.*, 20, 906 (1948).

The acid digestion method is free from these sources of error, but is open to the objection that the blank may be unpleasantly large unless redistilled acids are used. Directions for both methods of decomposition follow.

1. Ashing

§ Procedure

The amount of sample taken should in general be such that the aliquot of the final solution used for the colorimetric determination will contain 5–10 γ of lead. Transfer the weighed sample to a porcelain casserole or silica dish of suitable size having an unetched smooth glazed interior.[36] If the material is wet, dry it on the steam bath or a low temperature hot plate. If the sample is difficult to ash, or is very low in ash, add a few milliliters of aluminum nitrate-calcium nitrate solution,[37] mix, and dry. Now char the sample by heating carefully with a burner or on a hot plate giving a sufficiently high temperature. Then transfer the casserole to a muffle furnace equipped with a pyrometer and gradually raise the temperature to 500° C. The dish should be placed on an asbestos board or a clay triangle. The sample must not ignite. Continue the heating at 500° (not higher) until the carbon has disappeared. If the material is still dark after some hours, 2–3 ml. of aluminum-calcium nitrate solution may be added and the dried residue reheated for an hour. If the residue is still dark 1–2 ml. of concentrated nitric acid may be added, the mixture dried, and cautiously heated.

Add 10 ml. (or more or less as deemed desirable) of 1:1 hydrochloric acid and heat near the boiling point. If a clear solution is not obtained after heating for 30 minutes, evaporate to dryness on the steam bath and heat the residue for 15 minutes at 100–115° to dehydrate silica. Add 2–5 ml. of hydrochloric acid to the dish, followed by 5 ml. of water. Heat on the steam bath until all soluble material has been brought into solution, then add 3 to 5 ml. of ammonium citrate solution (p. 395) and heat for 10 minutes. If the amount of insoluble material (silica) is very small, filter the solution through a sintered glass or porous porcelain filter crucible and wash with a little dilute hydrochloric acid. If the amount of silica is appreciable, filter the solution through a small ashless paper previously washed with dilute hydrochloric acid and wash the precipitate on the paper with

[36] It is advisable to clean the dish before use by heating for a few minutes with 1 *N* sodium hydroxide solution and then rinsing with dilute nitric acid and water.

[37] 40 g. $Al(NO_3)_3 \cdot 9\,H_2O$ and 20 g. $Ca(NO_3)_2 \cdot 4\,H_2O$ in 100 ml. of water (*Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists*, 5th ed., p. 396).

dilute acid. Transfer the paper to a platinum crucible,[38] ignite, add a milliliter or so of hydrofluoric acid and a few drops of perchloric acid, and evaporate to fumes. Take up the residue in a few milliliters of dilute hydrochloric acid and add the solution to the main portion.

Add enough ammonia to the cold acid-citrate solution to give a *p*H of 9 and allow to stand for about 5 minutes. If no precipitate forms, proceed with the determination of lead as described on p. 396. If a precipitate forms (usually calcium or magnesium phosphate) add enough hydrochloric acid to the cold solution to dissolve it, and adjust the *p*H of the solution to 3–3.5. Add 5 mg. of copper sulfate, pass hydrogen sulfide into the solution for 5–10 minutes, and allow to stand for an hour or longer. Filter, preferably through a sintered glass or porous porcelain filter crucible; do not wash the precipitate. Dissolve the sulfides in a few milliliters of hot nitric acid, wash with water, and boil the solution to expel all hydrogen sulfide. Proceed with the determination of lead according to the directions on p. 396.

Make a note of the volume of all the reagent solutions used in order that the same quantities may be taken in the blank.

2. Acid Digestion

Sulfuric acid is best avoided in the digestion mixture, because, unless redistilled, it may introduce relatively large amounts of lead into the sample, and also it may form slightly soluble calcium sulfate which will occlude lead if not brought completely into solution. Perchloric acid in conjunction with nitric acid may be used to destroy organic matter. Perchloric acid very low in lead is on the market. The following simple digestion procedure is suitable for plant materials[39] and should be applicable to other materials of organic origin, if necessary with some modification in details.

§ Procedure[40]

Transfer 4–5 g. of sample to a 400 ml. Pyrex beaker, add 10 ml. of concentrated nitric acid, cover with a watch glass, and heat gently until any vigorous initial action has subsided. Heat to boiling and boil until the contents are nearly dry. Add 10 ml. of 1:1 nitric acid and 10 ml. of 70 per cent perchloric acid. Heat to gentle boiling and maintain at this

[38] If there is a possibility of tin being present, ignite in a porcelain crucible, transfer the residue to a platinum crucible and hydrofluorize.

[39] J. F. Gieseking, H. J. Snider, and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **7**, 185 (1935); for a similar procedure see H. W. Gerritz, *ibid.*, **7**, 167 (1935).

[40] See also p. 439. Another digestion procedure is described by J. T. L. B. Rameau, J. F. Reith, and W. B. Deys, *Anal. Chim. Acta*, **2**, 823 (1948).

temperature until all organic material has been removed from the sides of the beaker and the liquid has become practically colorless. Remove the beaker from the heat, cool for a few minutes, and wash any salts on the cover glass into the beaker. Evaporate the solution just to dryness, add 5 ml. of 1:1 hydrochloric acid and 10 ml. of water, and warm until all soluble material has been brought into solution. If necessary, filter off the silica, hydrofluorize the ignited residue, etc. as described on p. 410. Determine lead in the solution, or an aliquot of it, according to the general procedure, p. 396. If a clear solution cannot be obtained when the citrate solution is made ammoniacal, isolate lead as the sulfide (see p. 411).

Procedure in the Presence of Tin. If tin is present in more than minute amounts it will be converted into insoluble metastannic acid in the ashing or acid digestion and will cause loss of lead by occlusion. Most of the precipitated tin can be brought into solution and volatilized as follows.[41] Add 15 ml. or more of concentrated hydrobromic acid to the ash or the evaporation residue in the acid digestion (line 4, above) and heat on the steam bath. If nitrates were used in the ashing there will be an evolution of bromine, and the solution should finally be boiled to expel all of it. All the nitrate must be reduced. When the ash or the salts have been dissolved, examine the solution for insoluble metastannic acid. If a residue remains, add 50 to 100 mg. of pure finely granulated tin (*e.g.*, prepared from U. S. Bureau of Standards Sample No. 42B, containing 0.0035 per cent lead) and boil gently until it is dissolved. This treatment should clear the solution. Next add 10 ml. or more of 60 per cent perchloric acid and a few milliliters of hydrobromic acid-bromine mixture (100 ml. redistilled 40 per cent HBr + 15 ml. liquid Br_2). Evaporate to fumes of perchloric acid, adding small portions of hydrobromic acid-bromine totaling 15 ml. in the interval. When complete volatilization of the tin and the bromine has been effected, cool, and dissolve the contents of the vessel in the minimum volume of hot water. Continue with the determination as described above. The quantity of lead introduced from the metallic tin, hydrobromic acid-bromine, and perchloric acid must be found by running a blank.

[41] *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists*, 5th ed., 1940, p. 404.

CHAPTER XXV

LITHIUM

Traces of lithium are best determined by flame photometry or arc spectrography, although amounts greater than 10 γ can be determined fairly satisfactorily by the colorimetric method described below under IIA. Separation from other metals is required.

I. Separations

The solubility of lithium chloride in a variety of organic solvents enables it to be separated without difficulty from the other alkali metal chlorides. The writer has had good success in separating small amounts of lithium by the Palkin method,[1] in which sodium and potassium chlorides are precipitated from a small volume of aqueous solution by the addition of alcohol and ether (see further below, p. 415). Acetone should also be useful in such procedures.[2] From magnesium, lithium is best separated by precipitation of the former with 8-hydroxyquinoline in ammoniacal solution. Many other metals are precipitated at the same time. The separation of calcium is effected by oxalate precipitation, but the coprecipitation of lithium with calcium oxalate necessitates one or more reprecipitations. Whether lithium in small amounts can be determined colorimetrically in silicates remains to be seen. The well-known tendency of lithium to be retained in the residue and the precipitates in the J. Lawrence Smith decomposition method may give rise to difficulties.[3]

Macro quantities of lithium can be volatilized from silicates, sintered with calcium carbonate-chloride, by heating at 1200° in a stream of air[4]; the procedure may have value in isolating smaller amounts of lithium. The other alkali metal chlorides and considerable calcium chloride are also volatilized.

[1] S. Palkin, *J. Am. Chem. Soc.*, **38**, 2326 (1916); R. C. Wells and R. E. Stevens, *Ind. Eng. Chem., Anal. Ed.*, **6**, 440 (1934).

[2] M. H. Brown and J. H. Reedy, *Ind. Eng. Chem., Anal. Ed.*, **2**, 304 (1930). For the use of 2-ethylhexanol see E. R. Caley, *Ind. Eng. Chem., Anal. Ed.*, **14**, 242 (1942), and of dioxane *cf.* Sinka, *Z. anal. Chem.*, **80**, 430 (1930).

[3] For the determination of lithium in its minerals see S. Kallman, *Ind. Eng. Chem., Anal. Ed.*, **16**, 712 (1944). Information in this paper has a bearing on the determination of small amounts of lithium in silicates.

[4] M. H. Fletcher, *Anal. Chem.*, **21**, 173 (1949).

II. Methods of Determination

A. Potassium Ferric Periodate Method

Lithium solutions yield the slightly soluble salt $LiKFeIO_6$ when treated with potassium ferric periodate in potassium hydroxide solution.[5] The precipitate may be washed with potassium hydroxide solution and dis-

Table 69

Colorimetric Determination of Lithium after Precipitation as $LiKFeIO_6$

Lithium calculated from the iron content of the precipitate by use of the theoretical factor Li/Fe = 0.124. The potassium hydroxide used in preparation of precipitant contained 0.25 per cent sodium.

Addition	Li taken γ	Li found γ
	5.0[a]	6.8
	5.0[a]	7.0
	10	13
	10	14
	20	24
	20	22
	50	55
	50	55
	100	107
	100	105
	100	105
0.5 mg. Na	20	26.5
0.5 mg. Na	50	59
0.5 mg. Na	100	108
1.0 mg. Na	0	0
0.2 mg. Ca, 0.2 mg. Mg	50	87
200 mg. Na[b]	20	25
200 mg. Na[b]	50	55
160 mg. Na[b]	100	100
100 mg. Na, 100 mg. K[b]	20	24
100 mg. Na, 100 mg. K[b]	50	50

[a] 0.5 ml. of 1 *N* potassium hydroxide and 1.0 ml. of reagent used instead of double these volumes as in the other determinations.

[b] Ether-alcohol separation of lithium.

solved in dilute acid, in which iron can be determined colorimetrically and lithium found from the Fe:Li ratio. Calcium and magnesium are precipitated by the reagent and give high results even when present in very small

[5] O. Procke and A. Slouf, *Collection Czechoslov. Chem. Commun.*, 11, 273 (1939). These authors describe a volumetric method for the determination of lithium based on this precipitation.

amounts. Sodium forms a sparingly soluble salt with the reagent, although low concentrations of the element do not yield a precipitate. Unfortunately sodium is strongly coprecipitated and difficulty is therefore usually encountered from the sodium present as impurity in the potassium hydroxide used in preparing the precipitant. The results given in Table 69 were obtained by the use of a reagent prepared from potassium hydroxide containing 0.25 per cent sodium (0.43 per cent sodium hydroxide). The positive error, which is relatively great for amounts of lithium of the order 0.01 mg., is believed to be due largely to coprecipitated sodium. If a standard curve is constructed, the presence of a small amount of sodium in the reagent does no great harm.

The iron in the solution of the dissolved triple periodate is conveniently determined by the thiocyanate method, but it is necessary to remember that the ferric thiocyanate color fades with time, especially on exposure to light.

Special Solutions

Potassium ferric periodate reagent. Add slowly with stirring 12 ml. of 0.10 *M* ferric chloride in 0.2 *N* hydrochloric acid to a mixture of 10 ml. of 2 *N* potassium hydroxide (reagent grade containing less than 0.25 per cent sodium) and 40 ml. of water in which has been dissolved 2.3 g. of potassium paraperiodate. Dilute to 100 ml. with 2 *N* potassium hydroxide. Filter the solution if it is not clear and keep it in a paraffin-lined bottle.

Standard iron solution. Prepare a solution containing 0.100 mg. of ferric iron and 0.59 mg. of potassium periodate per milliliter in 0.5 *N* hydrochloric acid.

Standard lithium solution, 0.01 per cent. This may be prepared by dissolving dried lithium carbonate in a slight excess of hydrochloric acid, or ignited lithium sulfate in water ($Li_2CO_3/2$ Li = 5.32, $Li_2SO_4/2$ Li = 7.92).

§ Procedure[6]

Separation of Lithium from Sodium and Potassium. The sample solution may conveniently contain from 20 to 100 γ of lithium. The alkali metals must be present as the chlorides and other metals must be absent. Evaporate the solution to dryness and dissolve the salts in a minimum volume of water (0.5 to 0.6 ml. for 200 mg. of the chlorides). Add 7 or 8 ml. of absolute ethyl alcohol and 20 ml. of anhydrous ether, stir the mixture well, and allow to stand for 5 minutes. Filter the solution through a small dry filter crucible and wash the salts with 5 ml. of a 1:4 alcohol and ether mixture. Evaporate the combined filtrate and washings to dryness in a small beaker.

Precipitation and Determination of Lithium. Dissolve the residue of lithium chloride in a drop or two of water followed by 1 ml. of 1 *N* potas-

[6] E. B. Sandell, unpublished work.

sium hydroxide. Heat the solution to 90–100° and add 2.0 ml. of potassium ferric periodate reagent which has been heated to boiling. Keep the mixture at 90°–100° for 5 minutes with occasional stirring, and then cool to room temperature by immersing the vessel in cold water for about 5 minutes. Filter through a small porous porcelain filter crucible and wash with four 0.75 to 1 ml. portions of 1 *N* potassium hydroxide solution.

Dissolve the precipitate in 10 ml. of cold 1 *N* hydrochloric acid, dilute the solution to exactly 25 ml. with water, transfer 5 ml. of the mixed solution to a 25 ml. volumetric flask, and add water to make the volume approximately 20 ml. Add 3 ml. of 2 *M* potassium thiocyanate solution, make up to 25 ml. with water and obtain the extinction of the solution at once (*cf.* p. 372). Instead of obtaining the amount of lithium from the theoretical factor Li/Fe = 0.124, it is preferable, especially if the sodium content of the potassium hydroxide solution is not known, to obtain it from a standard curve prepared by carrying known amounts of lithium through the procedure. If a Duboscq colorimeter is used, the comparison solution may contain from 0.5 to 1.5 ml. of the standard iron solution together with 2 ml. of 2 *N* hydrochloric acid in a final volume of 25 ml.

B. Stearate Method (Turbidimetric)[7]

An amyl alcohol solution of ammonium stearate added to a solution of lithium chloride in amyl alcohol produces a finely divided precipitate of lithium stearate which may be estimated turbidimetrically. The sensitivity of this method is somewhat smaller than that of the method described under IIA; but the accuracy is comparable. Calcium and magnesium must be absent.

Reagent

Ammonium stearate. Dissolve 2 g. of stearic acid in 100 ml. of ether, and pass dry ammonia into the solution until no further precipitation takes place, adding ether to replace that lost by evaporation. Allow the ether to evaporate and dissolve 2 g. of the residue in 100 ml. of warm (<50°) amyl alcohol. The solution must be prepared fresh because it becomes useless in the course of a few days.

§ Procedure

To 2.0 ml. of amyl alcohol containing 0.05 to 0.5 mg. of lithium as chloride,[8] add 5.0 ml. of ammonium stearate solution. At the same time add

[7] E. R. Caley, *J. Am. Chem. Soc.*, **52**, 2755 (1930).

[8] Lithium chloride may be separated from the other alkali metal chlorides by extraction with amyl alcohol according to the method of Gooch (see W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Wiley, New York, 1929), but better by the alcohol-ether method (p. 415); 2-ethyl hexanol can be substituted for amyl alcohol in the procedure described above.

5.0 ml. of the stearate solution to a series of standards, in identical tubes, containing 0.05, 0.075, ... 0.5 mg. of lithium as chloride in 2.0 ml. of amyl alcohol. The reagent must be added at the same speed to all the solutions. Stopper the tubes, allow to stand for 30 minutes, then shake the contents and compare in the usual way. A filter photometer may be used to advantage in determining the concentration of the suspension from the amount of light transmitted (*cf.* p. 84).

CHAPTER XXVI

MAGNESIUM

I. Separations

Iron (III), aluminum, and similar metals may be separated from magnesium by double ammonia precipitation in the presence of an ammonium salt. Phosphate is separated at the same time if sufficient iron or aluminum is present. Manganese can be removed by precipitation with ammonium sulfide; zinc, nickel, cobalt, and many other metals are also precipitated. The usual double precipitation with oxalate serves to remove calcium if it is present in quantities sufficiently large to interfere (as in the 8-hydroxyquinoline colorimetric method). When traces of magnesium are to be determined in calcium salts, a strong solution of the latter is treated with calcium oxide (about 0.2 g. of freshly ignited CaO for 100 ml. of solution) to precipitate magnesium hydroxide; if necessary the calcium in the precipitate can be separated by the use of oxalate.[1]

The precipitation of magnesium hydroxide by an excess of sodium hydroxide in the presence of aluminum, tin, zinc, and other amphoteric metals is a method for the concentration of magnesium, rather than for its separation, since these metals are coprecipitated with magnesium hydroxide. A method for the separation of magnesium which has been applied in its determination in aluminum alloys is based on the precipitation of magnesium hydroxide by sodium hydroxide in the presence of tartrate and cyanide to keep such metals as iron, manganese, copper, zinc, lead, and nickel in solution.[2]

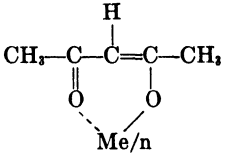
Separations with 8-hydroxyquinoline may be useful at times. For example, in a tartrate-sodium hydroxide solution hydroxyquinoline precipitates magnesium but not aluminum (p. 427).

Electrolysis with a mercury cathode is a useful method for removing many metals at one stroke. Elements left in solution include aluminum, calcium, titanium, zirconium, vanadium, and phosphorus.

[1] J. C. Hostetter, *J. Ind. Eng. Chem.*, **6**, 392 (1914). The solubility of magnesium hydroxide in 100 ml. of 10 per cent calcium chloride under the conditions of the separation is thought to correspond to less than 0.2 mg. of MgO.

[2] H. C. Deterding and R. G. Taylor, *Ind. Eng. Chem., Anal. Ed.*, **18**, 127 (1946). This paper also describes some procedures for separating aluminum from magnesium. *Cf.* A. Robertshaw, *Analyst*, **67**, 259 (1942), for the use of tartrate and cyanide in the precipitation of magnesium as hydroxyquinolate.

An interesting method for removing many metals from a magnesium solution consists in extraction of their acetylacetone complexes by carbon tetrachloride.[3] Aluminum, ferric iron, titanium, manganese, copper, vanadium, uranium, and other metals as well, give complexes of the type



in an approximately neutral (*i.e.*, not too acidic) medium. The separation has not been studied in a systematic way. Abrahamczik gives the following directions for the removal of foreign metals prior to the determination of magnesium with Titan yellow. Make the solution alkaline with sodium bicarbonate and shake with a 1:4 volume mixture of acetylacetone and carbon tetrachloride. The major portion of the metals will be removed by one or two extractions. Then extract with carbon tetrachloride alone to remove remaining traces of metals. Make the aqueous solution slightly acidic (carbon dioxide will be evolved) and extract most of the excess acetylacetone (enol form) with carbon tetrachloride. The remainder can be destroyed with bromine water, and the excess of the latter can then be removed with sulfite.

II. Methods of Determination

The direct colorimetric determination of magnesium is based on the formation of a lake of magnesium hydroxide with a dye such as Titan yellow, and the indirect determination on the precipitation of magnesium 8-hydroxyquinolate, whose amount may be found in various ways from its hydroxyquinoline content. Both methods require the absence of most other metals. The Titan yellow method is in general to be preferred. It is very sensitive, easy to carry out, and may be applied in the presence of relatively much calcium, but it requires the absence of any appreciable amount of ammonium salts.

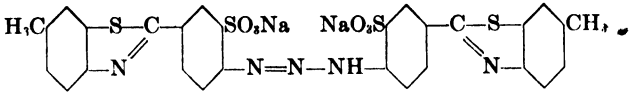
A. Titan Yellow Method[4]

When magnesium hydroxide is precipitated with sodium hydroxide in

[3] E. Abrahamczik, *Mikrochemie ver. Mikrochim. Acta*, **33**, 209 (1947).

[4] Among papers on the determination of magnesium by this method may be mentioned: W. S. Gillam, *Ind. Eng. Chem., Anal. Ed.*, **13**, 499 (1941); E. E. Ludwig and C. R. Johnson, *ibid.*, **14**, 895 (1942); A. D. Hirschfelder and E. R. Serles, *J. Biol. Chem.*, **104**, 635 (1934); C. Urbach and R. Baril, *Mikrochemie*, **14**, 343 (1934); V. G. Haury, *J. Lab. Clin. Med.*, **23**, 1079 (1938); R. J. Gardner, *Biochem. J.*, **40**, 828 (1946); W. Stross, *Analyst*, **67**, 317 (1942); E. B. Kidson, *New Zealand J. Sci. Tech.*, **27A**, 411 (1946). See Abrahamczik, *loc. cit.*, for a more complete list.

the presence of various organic dyestuffs, the latter are adsorbed on the precipitate with a change in color. Since magnesium hydroxide is very slightly soluble in an excess of sodium hydroxide and the color intensity of the lake or the adsorption body is great, a very sensitive reaction can be obtained in this way. Titan yellow,[5] the sodium salt of methylbenzothiazole (1,3)-4,4′-diazoaminobenzene-(2,2′)-disulfonic acid



is a suitable color reagent.[6] It gives a red color with magnesium in sodium hydroxide solution (pH > 12) and a yellow-brown color in the absence

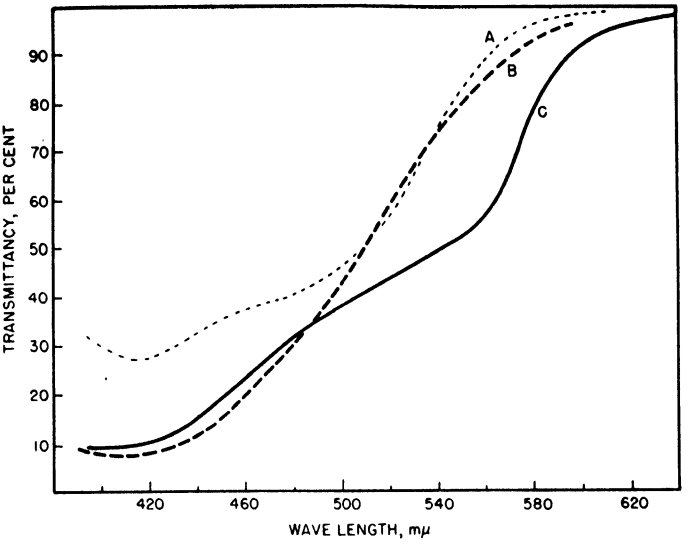


Fig. 48. Transmission curves of Grübler Titan yellow (A), Eastman Titan yellow (B), and magnesium lake from 3 p.p.m. magnesium and Eastman Titan yellow (C). (Data of J. Neumayer.)

of magnesium. Fairly stable colloidal suspensions of the lake can be obtained if the magnesium concentration is kept below 4 parts per million. An equilibrium exists between the dyestuff and the lake, and the lake formation follows the simple laws of adsorption.[7] The initial portion of the concentration-extinction curve is a straight line, but at higher magnesium

[5] This dye is known under a variety of trade names such as Titan yellow A, Titan yellow G, and Clayton yellow, all said to be the same substance.

[6] I. M. Kolthoff, *Biochem. Z.*, **185**, 344 (1927).

[7] H. Ginsberg, *Z. Elektrochem.*, **45**, 829 (1939).

concentrations the curve runs almost parallel to the concentration axis. Addition of a protective colloid is usually not necessary in trace analysis. When relatively much magnesium is to be determined, addition of a suitable protective colloid is of advantage since the linear portion of the curve can then be extended to rather high magnesium concentrations. It appears that the best colloid for the purpose is starch-glycerin,[8] which under the proper conditions permits a linear relation between extinction and concentration up to 20 p.p.m. of magnesium.

The reaction is subject to interference from many metals. Some metal hydroxides (*e.g.*, cadmium, nickel, and cobalt) adsorb Titan yellow and produce more or less of a color change. Certain metals giving hydroxides soluble in an excess of sodium hydroxide, particularly aluminum, zinc, and tin, interfere seriously by diminishing the intensity of the magnesium color. Even as little as 1 or 2 parts per million of aluminum will reduce the color strength. This interference is thought to result from the adsorption of aluminate, zincate, or stannate on the magnesium hydroxide, with a resultant diminution in the adsorption of Titan yellow. On the other hand, aluminum in small amounts is found to intensify the color of the lake formed by the dye Brilliant yellow with magnesium hydroxide (p. 425).

A number of studies have been made of the effect of various factors on the determination of magnesium by the Titan yellow method. There is considerable inconsistency in the findings. Some claim that hydroxylamine hydrochloride must be present to give a stable color, whereas others have found its presence unnecessary. Some state that the extinction-concentration curve is linear up to 6 p.p.m., others that it is linear to only 2 p.p.m., etc. In part these contradictions are due to differences in the Titan yellow used. Products of different manufacturers (and sometimes different batches from the same company) differ widely in appearance and show great differences in behavior. Thus a product of Grübler (Titan yellow A) was found by Beguet[9] to give a very stable lake in the absence of hydroxylamine hydrochloride and protective colloid. An Eastman product, on the other hand, produced a lake whose color intensity decreased with time unless hydroxylamine hydrochloride was present.

Variation in the concentration of excess sodium hydroxide has but a

[8] H. A. J. Pieters, W. J. Hanssen, and J. J. Geurts, *Anal. Chim. Acta*, 2, 241 (1948). These authors determine magnesium in water by treating a suitable volume of sample (magnesium up to 2 mg.) with calcium chloride (10 mg. calcium), 10 ml. starch solution (20 g. per liter), 10 ml. glycerin, 10.0 ml. 0.10 per cent Titan yellow, 10.0 ml. of 2 *N* sodium hydroxide, diluting to 100 ml. and determining the transmittancy after 1 hour. The following must not be present in amounts greater than indicated: Al, 0.05 mg.; Fe (III), 0.05 mg.; PO_4, 5 mg.; SiO_2, 0.5 mg.; electrolytes, 300 mg. The same paper contains directions for magnesium in silicates.

[9] A. J. L. Beguet, M.S. Thesis, University of Minnesota, 1947.

slight effect on the intensity of the magnesium color.[10] A final concentration of 0.1 *N* is satisfactory. The length of the linear part of the concentration–extinction curve is increased as the Titan yellow concentration is increased from 0.001 per cent (in the final solution) to 0.003 per cent (Eastman product).[11] At the latter dye concentration the curve is linear up to 3 p.p.m. and almost so to 4 p.p.m., in the absence of a protective colloid. The limit of the useful range is about 5 p.p.m., above which the curve approaches horizontality with the concentration axis. The excess of dye (Eastman) has little effect on the color intensity in the linear portion of the curve. Temperature variation has little effect, if the extinction of the blank is measured at the same temperature as that of the lake; identical results were obtained at 25 and 35°. The stability was found to be excellent with Grübler Titan yellow. At a concentration of 3 p.p.m. of magnesium, no change could be detected in a period of 2 hours (no protective colloid present). Almost as good stability was found when Eastman's reagent was used, provided hydroxylamine hydrochloride was present. A 3 p.p.m. suspension showed no change after 1 hour, and a 4 p.p.m. suspension faded about 5 per cent in this period of time.

Sodium chloride and sulfate were found by Beguet to have a slight effect in comparatively high concentrations (Grübler Titan yellow). In 2 per cent sodium chloride solution, 2 p.p.m. of magnesium gave a color intensity about 8 per cent less than in the absence of sodium chloride; in 2 per cent sodium sulfate solution the same concentration of magnesium showed a color approximately 15 per cent weaker than in pure solution.

Calcium intensifies the color of the magnesium lake. The magnitude of the effect depends on the purity of the reagent and other factors. Under the conditions of the procedure given below, with an Eastman product, 100 p.p.m. of calcium in the solution increases the color intensity by about

	Extinction (1 cm., green filter)		
P.p.m. Mg	No Ca	100 p.p.m. Ca	250 p.p.m. Ca
0	0 000	0 002	0.006
1	0.056	0.066	0.076
2	0.107	0.129	0.149
3	0.164	0.192	0.218
4	0.213	0.249	0.277

[10] P. N. Richardson, University of Minnesota, 1948, found that an increase in the sodium hydroxide concentration from 0.1 to 0.2 *N* decreased the color strength of the magnesium lake by less than 10 per cent (Eastman Titan yellow).

[11] A Grübler product did not show this behavior.[9] The length of the linear portion of the curve was substantially independent of the dye concentration in the range mentioned.

20 per cent, and 250 p.p.m. by 35 per cent, as shown by the figures on page 422.[12]

The intensifying effect of calcium becomes weaker as its concentration increases (Fig. 49). Error due to calcium in the sample solution can be reduced to a small value in many cases by adding the same amount of calcium salt to the sample and standard solutions. For example, if the sample solution originally contains 250 p.p.m. of calcium (weight ratio

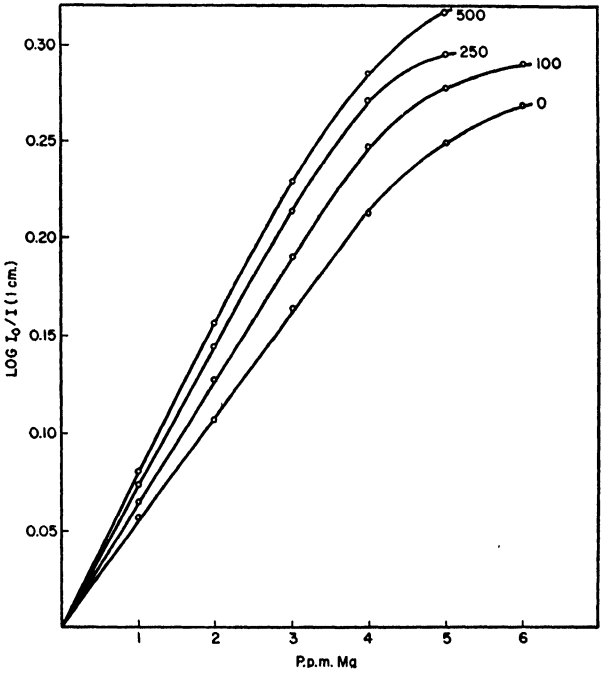


Fig. 49. Effect of calcium on determination of magnesium with Titan yellow. The concentration of calcium in p.p.m. is indicated on the curves. (Data of J. Neumayer.)

Ca/Mg about 100) and the same amount is added to the standard magnesium solutions used to prepare the standard curve, the error will amount to about 8 per cent. The total amount of calcium present in the final solution should preferably not exceed 500 p.p.m., else the precipitation of calcium carbonate takes place too rapidly. At low calcium concentrations it does not matter whether the sodium hydroxide solution is carbonate-free (prepared by dilution of a filtered saturated solution) or contains such amounts of carbonate as are ordinarily found in reagent-grade material.

[12] Experiments of J. J. Neumayer, University of Minnesota, 1948.

Special Solutions

Titan yellow, 0.15 per cent aqueous solution. Prepare fresh weekly.[13]

Sodium hydroxide, 1 *N*. The absence of an appreciable amount of carbonate is desirable.

Calcium chloride, 1.0 per cent calcium, in 0.01 *N* hydrochloric acid. The solution should not contain appreciable amounts of magnesium. To remove magnesium, make

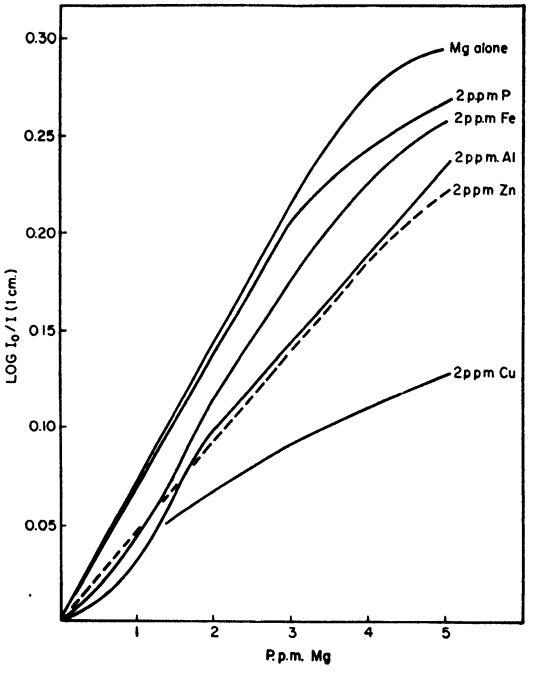


Fig. 50. Effect of aluminum, zinc, iron, copper, and phosphorus on the determination of magnesium with Titan yellow in the presence of 250 p.p.m. of calcium in each case. (Data of J. Neumayer.)

a 2.0 per cent calcium solution about 0.1 *N* in sodium hydroxide, filter off the precipitate, make the filtrate slightly acidic, and dilute to 1.0 per cent calcium concentration.

Hydroxylamine hydrochloride, 5 per cent aqueous solution.

Standard magnesium solution, 0.01 per cent. This is most conveniently prepared by dissolving pure magnesium metal in a slight excess of hydrochloric acid and diluting to volume. The acidity of the solution may be about 0.01 *N*.

[13] The color strength of Titan yellow remains constant or almost so on long standing; a slight decrease is sometimes noticeable, which is possibly accelerated on exposure to light. In spite of this seeming constancy, a change does occur (at least with some products) such that weaker colors are produced with magnesium. For example, a reagent solution which had been kept for 2 months gave a lake whose color intensity was only half that produced by a fresh reagent.

§ Procedure

Separate iron, aluminum, phosphate, etc. in the usual way by double precipitation with ammonium hydroxide. It is usually not necessary to separate calcium. (If other metals such as manganese, copper, zinc, and nickel are present in more than traces they must be removed by appropriate methods.) Evaporate the filtrate to dryness if ammonia precipitation was made and ignite the residue gently to expel ammonium salts; alternatively destroy ammonium salts by evaporation to dryness with nitric acid. Moisten the residue with a few drops of 1:1 hydrochloric acid, warm, add water, and dilute to volume in a volumetric flask of suitable size.

Pipet into a 50 ml. volumetric flask an aliquot of such size that the final magnesium concentration will not exceed 5 p.p.m. and will preferably be greater than 0.5 p.p.m. Almost neutralize any acid present by the addition of dilute sodium hydroxide solution. Dilute the solution to approximately 35 ml. and add 1.0 ml. of hydroxylamine hydrochloride, 1.00 ml. of calcium solution,[14] and 1.00 ml. of Titan yellow solution. Then add 5.0 ml. of sodium hydroxide solution while swirling the flask. Make up to the mark with water, mix, and transfer the suspension to a suitable cell (depth preferably greater than 1 cm. for magnesium concentrations below 1 p.p.m.). Use a green filter with transmission maximum near 535 mμ. It is preferable to determine the extinction soon after the lake has been formed.

To establish the reference curve take 0, 1, 2, 3, 4, and 5 γ of magnesium and treat each solution in the same manner as the sample solution.

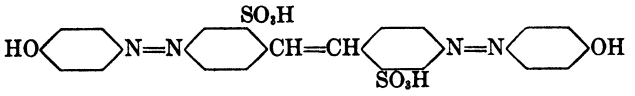
B. Other Lake Methods

Thiazole yellow (the sodium salt of methylbenzolthiazole 2,2-disulfonic acid) has been reported as the most selective of 140 dyestuffs tested as magnesium reagents.[15] It appears to be very similar to Titan yellow; a scarlet lake is formed with magnesium hydroxide in sodium hydroxide medium. Among interfering elements may be mentioned calcium, iron, aluminum, manganese, and phosphorus. The interfering metals are removed by precipitation with sodium tungstate (optimum *p*H range 5.0–6.0). The procedure has been applied in the determination of magnesium in plant material and soil solutions.

Brilliant yellow (diaminostilbene-diphenylsulfonic acid) has been proposed as a reagent possessing an advantage over Titan yellow for the determination of magnesium in the presence of small amounts of alumi-

[14] If the amount of calcium in the sample is known approximately, a like amount may be added to the standards (and none to the sample) for a more accurate determination.

[15] D. S. Mikkelsen and S. J. Toth, *J. Am. Soc. Agron.*, **39**, 165 (1947); D. S. Mikkelsen, S. J. Toth, and A. L. Prince, *Soil Sci.*, **66**, 385 (1948).



num.[16] Whereas aluminum in very low concentrations decreases the color intensity of the magnesium-Titan yellow lake it increases that of the Brilliant yellow lake. In the range 1 to 10 p.p.m. of aluminum the intensifying effect is virtually constant. The effect of small amounts of aluminum can thus be eliminated by treating both sample and standards with a suitable amount of aluminum to keep its concentration in this range. At higher aluminum concentrations the color intensity of the red magnesium lake is decreased. Calcium also increases the color strength of the Brilliant yellow lake. Less than 2.5 p.p.m. of iron is reported to be without effect on the magnesium determination. The use of "Colloresin" as protective colloid is recommended. It is preferred to starch because it gives a stronger color and more stable suspensions. The color intensity is proportional to the magnesium concentration up to about 5 p.p.m. The sensitivity of this method is about the same as with Titan yellow as reagent.

Other lake reagents for magnesium include quinalizarin[17] and curcumin.[18]

C. The 8-Hydroxyquinoline Method

Many procedures have been described for the colorimetric determination of magnesium after precipitation as 8-hydroxyquinolate in ammoniacal solution. The precipitate is very slightly soluble in basic medium. The solubility has been reported as 1.9×10^{-6} mole per liter in an ammonium hydroxide-ammonium chloride buffer of *p*H 10, which corresponds to 46 γ of magnesium per liter.[19] The hydroxyquinoline in the precipitate can be determined with Folin's phenol reagent, with ferric iron in acetic acid or very dilute hydrochloric acid (green color due to $FeOx^{++}$),[20] or by conversion into an azo dye by the use of diazobenzene sulfonic acid.[21] A simpler method, and one which is to be preferred when a suitable photometer is

[16] M. Taras, *Anal. Chem.*, **20**, 1157 (1948).

[17] A. Thiel and E. van Hengel, *Ber.*, **71B**, 1157 (1938). The excess dye is unstable in basic medium and its color fades rapidly.

[18] W. E. Thrun, *Ind. Eng. Chem., Anal. Ed.*, **4**, 426 (1932). For the use of *p*-nitrobenzeneazoresorcinol as photometric magnesium reagent, consult Y. Rusconi, D. Monnier, and P. E. Wenger, *Helv. Chim. Acta*, **31**, 1549 (1948).

[19] K. G. Stone and N. H. Furman, *Ind. Eng. Chem., Anal. Ed.*, **16**, 596 (1944).

[20] See, for example, W. S. Hoffman, *J. Biol. Chem.*, **118**, 37 (1937); L. Gerber, R. I. Claassen, and C. S. Boruff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 658 (1942); M. E. Weeks and J. R. Todd, *ibid.*, **15**, 297 (1943); C. P. Sideris, *ibid.*, **12**, 232 (1940). The latter author extracts the ferric quinolate with chloroform and dilutes to volume with butyl alcohol.

[21] F. Alten, H. Weiland, and H. Loofman, *Angew. Chem.*, **46**, 668 (1933).

available, consists in the measurement of the absorption in the near ultraviolet after dissolving the precipitate in hydrochloric acid; hydroxyquinolinium ion absorbs strongly in the region near 365 mμ.

Since 8-hydroxyquinoline gives precipitates with most metals in ammoniacal solution, these must be completely separated before the method can be applied. Small amounts of aluminum, ferric iron, copper, and various other metals can first be precipitated with 8-hydroxyquinoline in acetic acid-acetate medium. Calcium, unless present in very low concentrations, must be separated as the oxalate, for calcium quinolate is not very soluble and is likely to come down with the magnesium precipitate. According to Sideris (*loc. cit.*) it is possible to separate magnesium from aluminum, iron, manganese, lead, and zinc by precipitating the hydroxyquinolates of all these metals in ammoniacal solution and then extracting the last named quinolates with chloroform; the undissolved magnesium quinolate may be filtered off. This separation procedure appears promising, but there are not sufficient data available to demonstrate its reliability for traces of magnesium.

General directions for the determination of magnesium by the 8-hydroxyquinoline method follow.[22] The washed quinolate precipitate is dissolved in dilute hydrochloric acid and the concentration of the hydroxyquinoline is found from the intensity of the color produced by the addition of ferric chloride, essentially according to the procedure of Hoffman (*loc. cit.*).

Reagents

8-Hydroxyquinoline, 5 per cent solution in 2 *N* acetic acid. This solution is stable for months.

Ammonium hydroxide wash solution, 1:25. When very small amounts of magnesium are to be determined it is preferable to saturate this solution with magnesium hydroxyquinolate.

Ferric chloride solution, 5 per cent $FeCl_3.6H_2O$ in 0.1 *N* hydrochloric acid.

Hydrochloric acid, 0.01 *N*.

§ Procedure

The sample solution, containing up to about 100 γ of magnesium, should have a volume in the neighborhood of 5 ml. A small beaker (10 or 15 ml.) is a convenient precipitation vessel. To the neutral or slightly acid solution add 0.2 ml. of 8-hydroxyquinoline and heat to 70° or 80°. While stirring, add 1:1 ammonium hydroxide until the solution is basic and then an excess of 5 or 10 drops. Set the solution aside for an hour without fur-

[22] A procedure for the determination of magnesium in aluminum alloys by 8-hydroxyquinoline precipitation followed by measurement of the ultraviolet absorption of the acid solution of the precipitate has been described by Deterding and Taylor.[3] The amounts of magnesium involved were above the trace range, but possibly this procedure can be applied to smaller quantities with such modifications as may be necessary.

ther heating. Filter, preferably using a filter stick (see p. 500), and wash carefully with about four small (0.5 ml.) portions of the ammonia wash solution.

Dissolve the precipitate in 1 ml. of hot 0.01 *N* hydrochloric acid and wash the beaker and filter stick with small portions of warm water. Cool the solution and transfer it to a 10 or 25 ml. volumetric flask (see Note). Add 0.10 ml. of the ferric chloride solution and dilute to volume with water. Obtain the extinction of the solution with an orange filter or light of 650 mμ wave length. The standard curve is obtained by carrying appropriate amounts of magnesium through the whole procedure. The relationship between magnesium concentration and color intensity is linear or nearly so.

Note. If a suitable filter photometer or spectrophotometer is available, measure the transmittancy of the diluted solution at 365 mμ, instead of proceeding further as described above. In this case stronger acid (*e.g.*, 0.1 *N*) can be used to dissolve the precipitate.

D. Miscellaneous Methods

Precipitation of magnesium as magnesium ammonium phosphate followed by determination of phosphate in the precipitate by one of the numerous colorimetric methods for phosphorus has been applied for the determineration of small amounts, but it has now been supplanted by the 8-hydroxyquinoline method. Another indirect method for magnesium is based on its precipitation by tropeoline OO.[23] Nephelometric and turbidimetric methods based on the formation of suspensions of the phosphate and oleate have been described.

[23] E. Havinga and A. F. K. Buys Ballot, *Rec. trav. chim.*, 61, 849 (1942).

CHAPTER XXVII

MANGANESE

I. Separations

For isolating manganese from very dilute solutions or for separating it from substances such as chloride which interfere in the colorimetric determination, precipitation with sodium hydroxide is useful (Table 70). There will generally be sufficient oxygen present in the solution to oxidize the precipitate to hydrous manganese dioxide which is highly insoluble. A few milligrams of ferric salt may be added to give ferric hydroxide which will gather the manganese.[1] The sodium hydroxide should be added to the sample solution at room temperature, the mixture stirred for a minute or two, and then heated to boiling to coagulate the precipitate. The latter,

TABLE 70

ISOLATION OF MANGANESE BY PRECIPITATION WITH SODIUM HYDROXIDE IN THE PRESENCE OF FERRIC IRON[a]

(The volume of the solution was 200 ml. in each case and 10 mg. of ferric ion were present. The cold solution was treated with 5 ml. of 10 per cent sodium hydroxide and then heated to boiling to coagulate the precipitate. Ten to 20 ml. of 0.1 per cent sodium hydroxide solution were used for washing the precipitate.)

Mn taken, γ	Mn found, γ	Percentage recovery
51	46	90
51	48	94
102	98	96
102	88	86
102	104	102
102	100	98
204	203	99
204	204	100
102[b]	100	98
102[b]	100	98

[a] Data obtained by R. W. De Net, University of Minnesota, 1945.
[b] Contained 20 g. of sodium chloride.

[1] Magnesium hydroxide has been used as a collector for manganese in its determination in sodium hydroxide; see C. G. Ethrington and J. W. Hughes, *Analyst*, **72**, 472 (1947). F. Koroleff, *Acta Chem. Scand.*, **1**, 503 (1947), precipitates manganese from sea water by the use of potassium hydroxide; the precipitate (largely magnesium hydroxide) contains all the manganese to within 1 γ per liter.

after being washed, is dissolved in dilute sulfuric or nitric acid to which a little sulfite has been added, and the permanganate method applied.

From chromium, as well as from vanadium, molybdenum, and tungsten, manganese can be separated by treatment with sodium peroxide in alkaline solution (or by fusion with sodium peroxide or carbonate, followed by heating with alcohol to reduce manganate).

The separation of manganese from iron (rarely required) can be accomplished by extracting ferric chloride with ether from 1:1 hydrochloric acid. Before manganese can be determined colorimetrically in the aqueous phase, it must be separated from the chloride as already described, or chloride removed by evaporation with sulfuric acid.

Manganous hydroxyquinolate can be extracted by chloroform from solutions having a *p*H of approximately 9.[2]

II. Methods of Determination

A. The Permanganate Method

The colorimetric determination of manganese by oxidation to permanganate in acid solution is so sensitive and specific that it leaves little to be desired. Two oxidizing agents come into consideration for the purpose: potassium (or sodium) periodate and ammonium persulfate (peroxydisulfate). The latter reagent, with silver ion as catalyst, has been in disrepute because of the supposed difficulty of transforming manganous ion into permanganate without obtaining a precipitate or colloidal solution of manganese dioxide. Periodate oxidizes manganous salts smoothly to permanganate, and for many years it has been considered the standard oxidizing agent for the colorimetric method. However, the persulfate method has recently been studied in detail by Nydahl[3] who has established the conditions under which satisfactory results can be obtained. It appears that persulfate may even have an advantage over periodate as an oxidizing agent when the manganese concentration is very low, since complete oxidation by periodate then takes place slowly.

1. Periodate as Oxidizing Agent[4]

The reaction $2\,Mn^{++} + 5\,IO_4^- + 3\,H_2O \rightarrow 2\,MnO_4^- + 5\,IO_3^- + 6\,H^+$ proceeds fairly rapidly in a hot solution containing nitric or sulfuric acid.[5] Since ferric periodate is slightly soluble in nitric acid, either sulfuric or phosphoric acid must be present if the solution contains much iron. Phosphoric

[2] D. Williams and R. V. Andes, *Ind. Eng. Chem., Anal. Ed.*, **17**, 28 (1945).

[3] F. Nydahl, *Anal. Chim. Acta*, **3**, 144 (1949).

[4] H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, **39**, 2366 (1917).

[5] Koroleff[1] adds silver salt to speed up the reaction and permit the use of less periodate in the oxidation.

acid decolorizes ferric iron by complex formation, and its presence is desirable in any case since it prevents possible precipitation of periodates or iodates of manganese. Unless the amount of manganese is very small the concentration of acid can be increased considerably over the minimum required to prevent precipitation without ill effect, and as a matter of fact the speed of oxidation of manganese is increased when the sulfuric acid concentration is increased above 3.5 *N*. It has been shown,[6] however, that with low concentrations of manganese (a few micrograms in 10 ml.) the acidity should be less than that corresponding to 15 ml. of concentrated sulfuric acid per 100 ml. of solution, for above this the full color does not develop, or it fades and a yellow tint is developed. Richards[6] recommends an acidity of 2 *N* (5–6 per cent by volume of sulfuric acid) for small amounts of manganese, because at this acidity the oxidation is more rapid than at 3.5 *N* (10 per cent sulfuric acid by volume).

Reducing substances reacting with periodate or permanganate must be removed or destroyed before the periodate oxidation is attempted. Although chloride in small amount can be oxidized by periodate, it is safer to remove it by evaporation with sulfuric acid, especially if the sample contains only a small amount of manganese.[7] Ferrous iron, sulfite, nitrite, bromide, iodide, etc., and oxalate and other oxidizable organic anions may be removed or destroyed by evaporating the solution of the sample with nitric acid or a mixture of nitric and sulfuric acids.[8] Among the anions not interfering may be mentioned arsenate, borate, fluoride, perchlorate, and pyrophosphate.

Foreign metals, with a few exceptions, do not interfere except when they are colored. The effect of copper, nickel, cobalt, etc. can be compensated by the use of an aliquot portion of the sample solution in the photometer reference cell or by the addition of a like amount to the comparison solution. For example, the determination can in the latter case be made by

[6] M. B. Richards, *Analyst*, **55**, 554 (1930). According to Nydahl,[3] oxidation of about 5 γ of manganese in 100 ml. of solution is only 50 per cent complete after heating for 1 hour on the steam bath under the conditions of Richards. In the presence of 17 mg. of silver nitrate the oxidation was 86 per cent complete in 1 hour and 91 per cent complete in 2 hours.

[7] Williams and Andes,[2] in determining manganese in caustic soda, add phosphoric acid to produce a *p*H of 2 and then oxidize with periodate. They state that the permanganate color develops and is stable in presence of small amounts of chloride ion.

[8] In determining manganese in sea water, T. G. Thompson and T. L. Wilson, *J. Am. Chem. Soc.*, **57**, 233 (1935), remove chloride and organic matter by treating the evaporation residue with concentrated sulfuric acid, heating to expel the acid, and fusing the salts. In Koroleff's procedure for manganese in sea water, the chloride in the precipitate produced by potassium hydroxide is removed either by precipitation with excess silver ion or by fuming with sulfuric acid.

colorimetric titration (p. 53), the standard permanganate solution being added to a comparison solution containing the same amount of sample as the oxidized sample solution. Chromium (III) is oxidized to a greater or less extent by periodate; increasing the acidity decreases the amount of chromium oxidized. Cerium (III) is also oxidized by periodate in acid solution. Silver, lead, and mercury give no precipitates if sufficient acid is present, but bismuth and tin give turbidities even in strongly acid solutions.[9]

Beer's law holds closely for concentrations of manganese up to 150 mg. per liter at least. Variation in acid concentration and periodate excess do not affect the color intensity.

Standard Manganese Solution

This is most easily prepared by dissolving pure (99.9+ per cent) electrolytic manganese metal in dilute nitric acid, boiling out oxides of nitrogen, and diluting to give a 0.01 per cent solution. If manganese metal is not available, the standard solution can be obtained by reducing potassium permanganate solution, standardized in the usual way, with a little sulfite after the addition of sulfuric acid, and then boiling out the sulfur dioxide.[10] The standard permanganate solution is obtained by suitably diluting the manganous solution and oxidizing with potassium periodate in the same way that the sample solution is oxidized.

§ General Procedure

If the solution of the sample contains chloride, add sulfuric acid and evaporate to fumes of the latter. If ferrous iron and other oxidizable substances are present, boil with nitric acid, or add the latter before evaporation with sulfuric acid.

The solution, ready for analysis, should in the usual case (0.1–1 mg. of manganese present) contain 10 ml. of concentrated sulfuric acid or 15 to 20 ml. of nitric acid, and in addition 5 to 10 ml. of 85 per cent phosphoric acid, in a volume of 100 ml. However, if the amount of manganese present is of the order of a few micrograms make the solution 2 *N* in sulfuric acid and add 20 mg. of silver nitrate. Add 0.3 g. of potassium metaperiodate,[11] or an equivalent amount of any other alkali metal periodate, for each 100 ml. of solution, heat to boiling with stirring, and keep at or slightly below the boiling point for 10 minutes (or at least 1 hour for very small amounts of manganese).[3] Cool, dilute to volume if the comparison method requires,

[9] J. P. Mehlig, *Ind. Eng. Chem., Anal. Ed.*, 11, 274 (1939).

[10] In many cases a standard solution obtained by weighing out a good grade of potassium permanganate crystals and reducing will serve the purpose. 2.88 mg. of $KMnO_4$ is equivalent to 1.00 mg. of manganese.

[11] According to J. H. High, *Analyst*, 68, 368 (1943), 50 mg. of potassium periodate suffices for the oxidation of 2.3 mg. of manganese in 100 ml. of solution.

and make the color comparison or measurement in any convenient way. Permanganate solutions show maximum absorption at about 525 mμ.[12]

The oxidized solution containing an excess of periodate is stable and may be kept many months without change, at least if stored in the dark.

2. Persulfate as Oxidizing Agent[3]

The oxidation is carried out at the boiling point in a phosphoric-nitric acid medium in the presence of very little silver nitrate. The concentration of silver can be kept so low (10^{-5} *M*) that visible precipitation by small amounts of chloride that may be present is not produced. Phosphoric acid must be present to prevent precipitation of manganese dioxide and assure smooth oxidation to permanganate; its concentration should be at least 0.1 *M*. The concentration of nitric acid should be about 0.3 *M*; a higher concentration is undesirable. The interference of chlorides can be prevented by addition of mercuric sulfate to form slightly dissociated complexes. As much as 0.1 g. of sodium chloride in 100 ml. of solution is readily prevented from interfering. Only minute amounts of bromide and iodide may be present.

The determination of manganese can be made in the presence of reasonable amounts of most forms of organic matter if the period of heating is increased and more persulfate is added. Soil extracts containing much humic acid may be turbid after oxidation. In such a case the extinction of the solution can be found after destruction of permanganate by addition of hydroquinone and a correction thus obtained.

The oxidized permanganate solution is stable for at least 24 hours at room temperature if excess persulfate is present and organic matter is absent. The relative error in the determination of 0.05–5 mg. of manganese in the absence of interfering substances is usually not more than 1 per cent.

Special Solution

Dissolve 75 g. of mercuric sulfate in 400 ml. of concentrated nitric acid and 200 ml. of water. Add 200 ml. of 85 per cent phosphoric acid and 0.035 g. of silver nitrate, and dilute the cooled solution to 1 liter.

§ Procedure

Add 5 ml. of the preceding special solution to the sample solution (0.005 to 5 mg. of manganese). As much as 0.1 g. of sodium chloride may be present. Dilute the mixture to about 90 ml., add 1 g. of ammonium persulfate, and bring to boiling in about 2 minutes over a flame (do not heat on a water bath). Remove the vessel (flask) from the flame, allow to stand

[12] In the presence of Cr (VI) determine the transmittancy at 575 mμ; at and above this wave length dichromate ion absorbs very slightly.

for 1 minute, and then cool under the tap. Dilute to 100 ml. with water free from reducing substances and obtain the extinction of the solution at 525 mμ.

Notes. 1. If the amount of manganese is greater than about 2 mg., a small amount of manganese dioxide may precipitate. In such a case add 2 ml. of 85 per cent phosphoric acid, reduce manganese with 1 or 2 drops of hydroxylamine sulfate solution (10 per cent) and then reheat to convert manganese completely into permanganate.

2. When organic matter is present, boil for a longer period (5 minutes or more) and add more ammonium persulfate (total of 2 to 5 grams) at intervals. If the solution is turbid after the oxidation (presence of relatively much humic acid), add 1 drop of 1 per cent hydroquinone solution to the absorption cell after the extinction of the solution has been measured, stir, and again obtain the extinction. The difference in the two readings is the extinction due to permanganate.

B. Other Methods

Manganese in higher states of oxidation (IV and VII) reacts with various organic compounds to give strongly colored oxidation products. *o*-Tolidine,[13] tetramethyldiaminodiphenylmethane,[14] tetramethyldiaminotriphenylmethane, and benzidine[15] are some of the reagents that have been used. These methods are unspecific since other strong oxidizing agents react similarly. The colorations produced are not stable, although very intense so that as little as 0.1 γ of manganese can be determined.

4,4′-Tetramethyldiaminotriphenylmethane[16] gives a more sensitive reaction than the diphenyl compound. It has been applied in the determination of manganese in bio material (see procedure on p. 438), after oxidation with periodate. The reagent is converted into the yellow oxidation product at 75–85°; in this temperature range periodate does not react appreciably with the compound. The method is inferior to the permanganate method in all respects except sensitivity, which is so great (0.0001 γ Mn per square cm. for 0.001 extinction at 475 mμ) that the procedure is of value when the quantity of sample is limited. Recoveries of 0.05 to 0.2 γ of manganese added to bio material ranged from 96 to 112 per cent. It may be possible to increase the sensitivity still further by extracting the colored oxidation product with immiscible organic solvents. Chromium, vanadium, and cerium in their highest valences also produce a yellow color. Copper, iron, lead, and silver are without effect. Chloride must be absent.

[13] L. Forman, *J. Am. Water Works Assoc.*, **21**, 1212 (1929).

[14] R. G. Harry, *J. Soc. Chem. Ind.*, **50**, 434T (1931); D. J. D. Nicholas, *Nature*, **157**, 696 (1946).

[15] R. C. Stratton, J. B. Ficklen, and W. A. Hough, *Ind. Eng. Chem., Anal. Ed.*, **4**, 2 (1932); N. A. Clark, *ibid.*, **5**, 241 (1933); A. C. Wiese and B. C. Johnson, *J. Biol. Chem.*, **127**, 203 (1939).

[16] E. M. Gates and G. H. Ellis, *J. Biol. Chem.*, **168**, 537 (1947).

Manganese in alkaline medium gives a reddish brown soluble product with formaldoxime. The colored compound is said to be $(CH_2NO)_3Mn$, with manganese present in the trivalent state.[17] Various workers have based a colorimetric method on this reaction.[18] The coloration is indeed strong and the method a sensitive one, but it suffers from the defects of requiring a basic milieu and the complete absence of iron. Kniphorst removes iron with zinc oxide and reports good results, at least when iron and manganese are present in comparable amounts as in food materials.

Manganese has been determined colorimetrically as pyrophosphatomanganic acid (violet color); the sensitivity is not great.[19]

III. Applications of the Permanganate Method

A. Silicate Rocks

In silicate rocks manganese usually occurs in more than trace amounts (>0.01 per cent), and the following directions are intended for such quantities as are generally encountered.

§ Procedure

Transfer 0.5 g. of finely powdered sample to a large platinum crucible or a small platinum dish and add 5 ml. of 1:1 sulfuric acid and 3–4 ml. of hydrofluoric acid. Mix, and heat the vessel in a "radiator" or on a hot plate, carefully at first and then more strongly until fumes of sulfuric acid are given off. Cool, wash down the sides of the vessel with a little water, and add 2–3 ml. of dilute sulfuric acid and a few drops of nitric acid. Evaporate again to strong fumes of sulfuric acid. Add 10–15 ml. of water and warm until all soluble material has been brought into solution. Filter through a small filter paper and wash with hot water, keeping the total volume of the filtrate and washings below 50 ml. Add to the solution 3 ml. of concentrated sulfuric acid, 2 ml. of 85 per cent phosphoric acid and 0.3 g. of potassium periodate. Heat to boiling, keep at or just below the boiling point for 10 minutes, cool, and dilute the solution to 100 ml. or to a larger volume if the color intensity is strong. After mixing, determine the transmittancy of the solution or compare against a similar standard.

[17] K A. Hofmann and U. Ehrhardt, *Ber.*, **46**, 1457 (1913). If manganese is originally present in the manganous form it is air-oxidized to the trivalent state.

[18] L. C. E. Kniphorst, *Chem. Weekblad*, **42**, 328 (1946); C. P. Sideris, *Ind. Eng. Chem., Anal. Ed.*, **9**, 445 (1937) and **12**, 307 (1940); G. H. Wagenaar, *Pharm. Weekblad*, **75**, 641 (1938); E. Kahane, *Ann. chim. anal.*, **17**, 175 (1935).

[19] E. S. Tomula and V. Aho, *Ann. Acad. Sci. Fennicae*, **A 52**, No. 4 (1939); **A 55**, No. 1 (1940).

B. Iron Ore

§ Procedure

Decompose a suitable weight of sample (containing not more than 5 mg. of manganese) with hydrochloric acid. Filter off any residue on paper, ignite and heat with hydrofluoric and sulfuric acids; evaporate the mixture to fumes of sulfuric acid. Dissolve the residue in hydrochloric acid and add to the main solution.

Add 5–10 ml. of sulfuric acid and 20 ml. of nitric acid to the solution of the sample and evaporate until fumes of sulfuric acid appear; all chloride should thus be removed. Then add approximately 50 ml. of water, and heat until all ferric sulfate has been brought into solution. Filter off any suspended material, add 5 to 10 ml. of 85 per cent phosphoric acid to the filtrate and mix. The solution should be practically colorless. Add 0.3 g. potassium or sodium paraperiodate, heat to boiling and keep at or near this temperature for 10 minutes. If there is any delay in the appearance of the permanganate color the presence of chloride is indicated and more periodate should be added to oxidize any small amounts of the latter. Dilute the solution to a suitable volume (usually 250 ml.) depending upon the color intensity, and compare against a standard solution or determine the transmittancy.

C. Steel

§ Procedure

Dissolve 0.5–1 g. of sample in 50 ml. of 1:3 nitric acid and boil for a few minutes to expel oxides of nitrogen. Cautiously add 1 g. of ammonium persulfate, and boil 10–15 minutes to oxidize carbon compounds and destroy the excess of persulfate. If a color of permanganate is visible or oxides of manganese separate, add a few drops of sulfur dioxide solution or dilute sodium sulfite solution to destroy the color and to clear the solution. Then boil for 5 minutes to expel sulfur dioxide. Dilute to about 100 ml., add 10 ml. of 85 per cent phosphoric acid and 0.5 g. of potassium periodate, heat to boiling, and keep at the boiling point for 5 minutes. Cool the solution and dilute to 250 ml. (or a smaller or larger volume as the color intensity may demand). Determine the transmittancy of the solution or compare against a standard solution. The standards for comparison or for the construction of the reference curve should preferably contain about the same amount of iron as the sample solution itself. When a photometer is used, any color due to nickel, cobalt, etc. as well as any faint color of iron may be compensated by using an aliquot of the sample solution, not oxidized with periodate but otherwise treated the same as the sample, in the

reference cell of the instrument. When chromium is present, the extinction of the solution should be obtained at 575 mμ as already mentioned.

D. Non-Ferrous Alloys

Attention may be called to procedures for the colorimetric determination of manganese in aluminum and copper-base alloys, in which oxidation is effected with persulfate at room temperature in the presence of silver as catalyst.[20] The brown color of silver peroxide is destroyed by the addition of urea.

E. Water

§ Procedure

The persulfate procedure is very suitable (p. 433). Alternatively acidify 50–100 ml. of water with 3–4 drops each of sulfuric and nitric acids and evaporate to dryness (a Pyrex beaker may be used). Then determine manganese by the periodate procedure (p. 432), keeping the volumes small.

For isolating very small amounts of manganese in water (as little as 10 γ per liter) use the sodium hydroxide precipitation method with a little ferric iron as a collector (p. 429). The precipitate of ferric hydroxide, calcium carbonate, etc. may be dissolved in dilute nitric acid containing a little sulfite to reduce higher oxides of manganese. By applying the general periodate procedure in a volume of 5–10 ml. a few micrograms of manganese can easily be determined.

Consult the paper of Thompson and Wilson[8] for the determination of manganese in sea water.

F. Bio Materials

Organic matter can be destroyed either by wet oxidation or by ashing. Ashing by ignition has some advantages when very low percentages of manganese are to be determined, since the volume of the final solution can be kept small and high sensitivity thus obtained. Under proper ashing conditions there is but little retention of manganese by silica remaining after treatment with acid (*cf.* Table 5 for some values for siliceous samples). A muffle furnace, not a burner, should be used for the ignition and the temperature should preferably be kept below 600° to preclude or minimize the formation of acid insoluble manganese silicates. Any manganese in the acid-insoluble material can be recovered by hydrofluorization or fusion with sodium carbonate.

[20] G. H. Osborn and W. Stross, *Light Metals*, August, p. 1 (1943); J. H. High, *Analyst*, 70, 18 (1945).

Wet oxidation can be carried out by the usual methods. Directions are given below for oxidation with nitric and perchloric acids, and (for those wishing to avoid the use of perchloric acid) with nitric and sulfuric acids.

The permanganate method as described under II A is usually the most suitable one for determining manganese in the final solution. However, if only a small weight of sample is available a more sensitive indirect method based on the oxidation of tetramethyldiaminotriphenylmethane by permanganate in acid solution may be applied.

§ Procedures

1. Ashing by Ignition.[21] Transfer 1 to 5 g. of sample (the latter amount for manganese contents of 10 p.p.m.) to a platinum or, less preferably, to a silica or porcelain dish. Char at a low temperature and then heat in a muffle furnace at 550–600° until a white ash is obtained. Moisten the ash with a few drops of concentrated hydrochloric acid, add a milliliter or two of water, warm, and rinse the solution together with any insoluble material into a small Pyrex beaker. Add 1–2 ml. of 1:1 sulfuric acid and evaporate to thick fumes of sulfuric acid. (If much calcium is present omit the addition of sulfuric acid and evaporate to dryness two or three times with small portions of nitric acid.) Dilute with water to about 25 ml., warm, and if the solution contains suspended material filter through a small paper previously washed with hot 0.1 *N* sulfuric acid. Wash with a little dilute sulfuric acid. If the quantity of insoluble material is relatively large, or for the greatest accuracy in any case, ignite the paper and its contents in a platinum crucible. Add 1–2 ml. of hydrofluoric acid and a few drops of sulfuric acid and evaporate to fumes of the latter. Take up the residue in a little dilute sulfuric acid and add the clear solution to the main solution. Add 3 ml. each of concentrated sulfuric acid and 85 per cent phosphoric acid and dilute to about 75 ml. Then add 0.3 g. of potassium periodate, heat to boiling, and keep just below the boiling point for 30 minutes.[22] Dilute to 100 ml. (or more if the color is strong) and find the extinction of the solution, or compare in a colorimeter against a suitable standard.

Determination of manganese with 4,4'-tetramethyldiaminotriphenylmethane.[16] Dissolve the ash (first evaporated with nitric acid to remove chloride) in the smallest possible volume of nitric acid-phosphoric acid mixture

[21] Among others, ashing by ignition has been used by D. R. K. Coleman and F. C. Gilbert, *Analyst*, **64**, 726 (1939); T. W. Ray, *J. Biol. Chem.*, **134**, 677 (1940); F. E. Read, *Analyst*, **64**, 586 (1939); and M. B. Richards, *Analyst*, **55**, 554 (1930).

[22] When the amount of manganese is very small (5–10 γ), add 20 mg. of silver nitrate and heat for 1 hour. Oxidation to permanganate may also be made by the persulfate method (p. 433).

(600 ml. redistilled 1 *N* nitric acid and 75 ml. low-manganese 85 per cent phosphoric acid diluted to 1 liter with water), warming gently to hasten solution. Transfer an aliquot of this solution, containing 0.05 to 0.5 γ of manganese, to a 20 ml. glass-stoppered test tube, dilute to 10 ml. with the acid mixture, and add 50 mg. of sodium or potassium periodate. Heat for $1^1/_2$ hours in a boiling water bath. Transfer two 3 ml. aliquots of solution to colorimeter tubes, cover with small beakers, and heat for at least 10 minutes in a water bath kept at 80 ± 1° C. Remove the tube from the bath, immediately add 3 drops of reagent solution (0.1 per cent 4,4′-tetramethyldiaminotriphenylmethane in 5 per cent by weight of phosphoric acid, prepared fresh daily), shake gently for 5 seconds, place in the photometer, and obtain the minimum transmittancy reading. (With 0.5 γ of manganese the maximum color intensity is attained in about 30 seconds, after which it remains constant for about 45 seconds; the maximum color of a blank is developed in 3 minutes.) Make the reading at 575 mμ or use the filter combination Corning 3387 and 3962 (standard thickness) and 5113 (half-standard thickness). Run a complete set of standards simultaneously (Beer's law is not followed). Reagent blanks should give a transmittancy greater than 90 per cent.

2. Nitric-perchloric Acid Digestion.[23] Transfer 1 to 4 g. of sample to a 500 ml. Kjeldahl flask. Add 40 ml. of concentrated nitric acid and boil gently so that nearly all of the acid is evaporated in one-half hour; avoid charring the sample. Then add 13 ml. of 60 per cent perchloric acid and boil gently until white fumes appear. Reduce the heat and continue the digestion barely at the boiling point for 10–15 minutes. Cool, dilute with an equal volume of water, and filter through a sintered glass crucible or funnel. Wash with water and dilute the filtrate to about 75 ml. if necessary. Add 3 ml. of phosphoric acid and 0.3 g. of sodium or potassium periodate, heat to boiling, and keep slightly below the boiling point for 30 minutes.[22] Cool and dilute to 100 ml. (or a larger volume if the color is strong). Obtain the extinction of the solution or compare against a standard solution in a colorimeter.

3. Nitric-sulfuric Acid Digestion.[24] Transfer 1 to 5 g. of sample to a 500 ml. Kjeldahl flask, moisten with concentrated nitric acid, and add 5 to 10 ml. of concentrated sulfuric acid. After subsidence of any initial vigorous reaction, heat gently and cautiously add nitric acid in small (*ca.* 1 ml.) portions. When the color of the mixture begins to lighten, increase the heat and continue the addition of nitric acid until on evaporation to fumes

[23] J. W. Cook, *Ind. Eng. Chem., Anal. Ed.*, **13**, 48 (1941). For digestion with sulfuric-nitric-perchloric acid see p. 386.

[24] D. R. K. Coleman and F. C. Gilbert, *Analyst*, **64**, 726 (1939).

of sulfuric acid a practically colorless solution is obtained. Add 1 g. of potassium persulfate, and dilute with an equal volume of water. Evaporate until fumes of sulfuric acid appear. Cool and transfer the solution to a 250 ml. Erlenmeyer flask with about 75 ml. of water. Boil for 5 minutes. If the solution is not entirely clear, filter it. If necessary dilute to 100–125 ml., then add 3 ml. of 85 per cent phosphoric acid and 0.3 g. of potassium periodate, and heat to boiling. Keep at or slightly below the boiling point for 30 minutes.[22] Cool, dilute to a suitable volume, and obtain the transmittancy of the solution or compare against a suitable standard solution in a colorimeter.

CHAPTER XXVIII

MERCURY

I. Separations

A. Sulfide Precipitation

In the absence of large quantities of metals yielding slightly soluble sulfides in acid solution, mercury may be advantageously isolated by precipitation with hydrogen sulfide. The sulfides of copper (p. 21), arsenic (V), and cadmium[1] have been used successfully as collectors. Arsenic and cadmium have the advantage that they do not interfere subsequently in the dithizone method. Cadmium would seem to be especially suitable because it forms mixed crystals with mercuric sulfide. One microgram of mercury can be recovered satisfactorily from 100 ml. of solution in this way. The sulfide precipitate is dissolved in chlorine water or hydrochloric acid containing a little potassium chlorate, most of the excess chlorine is removed by aeration at room temperature, and the remainder by the addition of a reducing agent such as hydroxylamine hydrochloride.

Mercury can also be isolated by allowing the sample solution (*p*H 5–7) to flow slowly through an asbestos pad impregnated with cadmium sulfide.[2] In this way more than 98 per cent of the mercury in 200 ml. of solution containing 0.5 γ can be recovered.

B. Dithizone Extraction

By the use of an excess of dithizone in carbon tetrachloride solution it is possible to extract mercury from a mineral acid solution (*ca.* 1 *N*) and separate it from such metals as lead, cadmium, zinc, nickel, cobalt, and iron, which do not react appreciably with the reagent under these conditions. At high acidities much chloride hinders the extraction of mercury; complete extraction can still be effected in 1 *N* acid solutions which are 0.2 *N* in chloride ion. It is even possible to obtain a separation from copper, if the copper-mercury ratio is not too unfavorable, by making use of fractional

[1] R. Vesterberg and O. Sjöblom, *Arkiv Kemi Mineral. Geol.*, **A22**, No. 22 (1946). The sulfide precipitation is made at *p*H 5–6 (determination of mercury in bio material). Cadmium sulfide has likewise been used as collector by W. L. C. van Zwet and J. C. Duran, *Chem. Weekblad*, **38**, 186 (1941).

[2] A. E. Ballard and C. D. W. Thornton, *Ind. Eng. Chem., Anal. Ed.*, **13**, 893 (1941).

extraction, *i.e.*, shaking the acid solution with successive small portions of dilute dithizone solution until the color of the last extract remains green or shows the red-violet color of cupric dithizonate. A chloroform solution of dithizone is preferable to a carbon tetrachloride solution for separation from copper because the former extracts copper with greater difficulty from mineral acid medium.[3] According to Milton and Hoskins[4] small quantities of mercury (10 to 50 γ) can be separated satisfactorily from 500 γ of copper by shaking 25 ml. of aqueous solution which is 0.075–0.1 N in hydrochloric acid with 1 ml. portions of 0.005 per cent dithizone solution in chloroform. If the solution is less acid than 0.075 N, copper is extracted also; above 0.15 N the extraction of mercury is incomplete.

It has been suggested that copper be extracted from an acid medium containing bromide or iodide (together with a reducing agent such as sulfurous acid in the latter case), which prevent the reaction of mercury by forming stable complexes with it.[5] In a variant procedure the carbon tetrachloride solution of copper and mercuric dithizonates is shaken with an acid bromide or iodide solution; copper remains in the organic solvent, mercury enters the aqueous phase.[6] If the aqueous solution is now made basic (or adjusted to *p*H 6 if bromide is the complex-forming agent), mercury can be extracted with dithizone.

Copper and mercury can also be separated by shaking a chloroform (and doubtless a carbon tetrachloride) solution of their dithizonates or dinaphthylthiocarbazonates with a dilute sulfuric acid solution containing sodium thiosulfate (p. 451).[7] Mercury passes into the aqueous phase, copper remains in the organic solvent. The thiosulfate and sulfur must then be destroyed with an oxidizing agent before mercury can be determined.

Still another method for the separation (and concomitant determination) of mercury from copper is based on the extraction of the former with a chloroform solution of dithizone in the presence of potassium cobalticya-

[3] The rate of reaction of copper is perhaps as important as the ultimate equilibrium. Barnes, *Analyst*, **72**, 469 (1947) states that the reaction of copper is so slow that an error of only 0.3 γ of mercury results when 100 ml. of solution having a *p*H of 1.2 containing 70 γ copper and 5.5 γ mercury is shaken with 10 ml. 0.002 per cent dithizone in chloroform for 1 minute (all the mercury reacts).

[4] R. F. Milton and J. L. Hoskins, *Analyst*, **72**, 6 (1947).

[5] Milton and Hoskins, *loc. cit.*, had no success with iodide as complex former when using a chloroform solution of dithizone. A *p*H of 5 was required for the complete extraction of copper; at this *p*H appreciable amounts of mercury were also extracted.

[6] E. P. Laug and K. W. Nelson, *J. Assoc. Official Agr. Chem.*, **25**, 399 (1942), use bromide as complex-former.

[7] W. O. Winkler, *J. Assoc. Official Agr. Chem.*, **21**, 220 (1938).

nide as complexing agent for copper.[8] A chloroform solution of dithizone is used. Cobalticyanide is not an ideal complex former because it produces a precipitate with copper in concentrations greater than 1 p.p.m. However, the precipitate formation does not appear to have much effect on the results (see p. 448) if the chloroform layer is carefully drawn off.

Attempts to complex copper with rubeanic acid have been unsuccessful (Milton and Hoskins).

Mercury can be separated from small amounts of silver by first extracting both metals with dithizone and then shaking the extract with a dilute solution of chloride or thiocyanate to decompose silver dithizonate while leaving mercury unaffected in the organic solvent.

C. Other Methods

A method for the isolation of traces of mercury, which has been used extensively by Stock[9] and coworkers involves electrolytic deposition of the metal on a gold or copper wire, followed by volatilization by heating in a capillary tube.

Certain types of inorganic material may simply be heated at a high temperature to expel the mercury present. Thus, to isolate mercury in rocks and minerals, a 20–100 g. sample is heated for several hours at 800° C. in a porcelain tube, while air is passed through it. The mercury in the issuing stream is condensed in a U-tube cooled with liquid air.[10]

II. Methods of Determination

The analyst engaged in the separation and determination of traces of mercury must bear in mind several sources of error that may vitiate the results. In the first place, mercury is by no means an infrequent contaminant of some reagents, in which however it occurs only in minute amounts. Attention may be called to its frequent presence in hydrochloric acid.[11] Mercury may also be present in filter paper, rubber stoppers, etc., espe-

[8] H. Barnes, *J. Marine Biol. Assoc. United Kingdom*, **26**, 303 (1946); *Analyst*, **71**, 578 (1946).

[9] A great deal of work has been done by A. Stock on the trace analysis of mercury, mostly by the micrometric method in which the diameter of the globule of the isolated mercury is measured. A list of the papers of Stock may be found in *Ber.*, **71**, 550 (1938). For the methods used see especially *Z. angew. Chem.*, **39**, 466, 791 (1926); **41**, 546 (1928); **42**, 429 (1929); **44**, 200 (1931); **46**, 62, 187 (1933); **47**, 641 (1934). *Ber.*, **67**, 122 (1934); **71**, 550 (1938); **72**, 1844 (1939).

[10] A. Stock and F. Cucuel, *Naturwissenschaften*, **22**, 390 (1934). For a similar method see A. A. Saukov and N. Kh. Aĭdin'yan, *Compt. rend. acad. sci. U. R. S. S.*, **32**, 358 (1941); *Chem. Abst.*, **37**, 1960.

[11] The mercury in synthetic hydrochloric acid has its origin in the chlorine which has been obtained by electrolysis of sodium chloride with amalgam electrodes.

cially if these have long been exposed to the atmosphere of the laboratory which may contain mercury vapor. Glassware should be well-rinsed with nitric acid and water before use. Mercury shows a great tendency to be adsorbed on glass. The adsorption is strongest from neutral solutions. Even acidified solutions of mercury are stated to undergo an appreciable change in concentration on standing, especially if they are very dilute. However, a 0.001 per cent mercury (II) solution in *ca.* 0.01 *N* sulfuric acid has been reported to remain unchanged in strength for 6 months. Adsorption is weakest on silica, but Pyrex ware is suitable for all but the most refined work.

The volatility of mercury and its compounds often complicates the decomposition and preparation of the sample for analysis. Suitable precautions to prevent volatilization losses must be taken.

A. The Dithizone Method

Divalent mercury reacts readily with excess dithizone in fairly acid medium (1 *N* in mineral acid) to yield the keto complex which is soluble in carbon tetrachloride or chloroform (orange color).[12] The mixed color method (p. 101) is the most suitable one for the determination of mercury with dithizone.[13] By obtaining the transmittancy of the organic solvent phase at suitable wave lengths one can find either the concentration of the mercuric dithizonate formed or of the dithizone remaining after shaking with an excess of reagent.[14]

A carbon tetrachloride or chloroform solution of mercuric dithizonate is markedly sensitive to light; the orange color changes to greenish orange and eventually to green or bluish purple when the solution is exposed to strong light. Since the reaction is reversible the original color of mercuric

[12] Mercurous mercury gives a yellow solution under the same conditions.

[13] Milton and Hoskins, *loc. cit.*, apply the mono color method by removing the excess dithizone by shaking with dilute ammonia, which at the same time converts the keto complex into the enol. The reversion principle (p. 104) is applied by H. Irving, G. Andrew, and E. J. Risdon, *J. Chem. Soc.*, **1949**, 541, who extract mercury (with some copper) with a chloroform solution of dithizone from sulfuric acid medium of *p*H 1, and then revert mercuric dithizonate to dithizone with 6 per cent potassium iodide at *p*H 4. This procedure gives good results in the presence of at least 20 times as much copper, as well as 20 mg. of bismuth, lead, or ferrous iron, and 100 mg. of ferric iron.

[14] Another possibility is the measurement of the transmittancy at the two wave lengths corresponding to maximum absorption by mercuric dithizonate and dithizone. The advantage of this procedure is that the concentration of the dithizone solution need not be exactly known once the preliminary data (p. 104) have been obtained and the same solid reagent is used. On the other hand, more preliminary work is required than in the single wave length method. This method has been applied by J. F. Reith and K. W. Gerritsma, *Rec. trav. chim.*, **64**, 41 (1945), who were able to determine 2.5 to 100 γ of mercury with a maximum error of less than 2 per cent for the larger quantities.

dithizonate is restored in the dark and also by shaking the organic solvent with acid. Reith and Gerritsma[14] found that the photochemical decomposition is prevented if acetic acid is added to the aqueous mercury solution before it is shaken with a chloroform solution of dithizone. Some of the acetic acid is extracted by the chloroform and inhibits the decomposition in this phase.

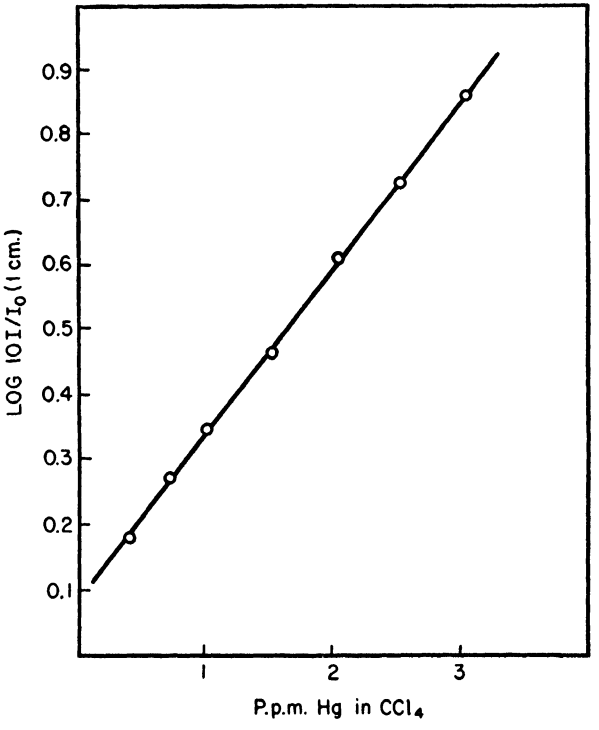


Fig. 51. Determination of mercury (II) by the mixed color method; yellow filter (*ca.* 590 mμ). (From data of P. G. Johnson.)

Other metals reacting with dithizone in acid solution are copper, silver, gold, palladium, and divalent platinum. Small amounts of silver do not interfere if a sufficient concentration of chloride is present, but copper must be separated. Lead, zinc, nickel, cobalt, etc., do not interfere unless they are present in high concentrations, since the dithizonates of these metals have equilibrium constants that are much smaller than that of the mercuric complex. Bismuth in appreciable amounts may be expected to interfere to some extent since its dithizonate is stable in dilute acid solutions.

Special Solutions

Dithizone, 0.001 per cent (*w/v*) in analytical-reagent chloroform.

Standard mercury solution, 0.100 per cent. Dissolve 0.1354 g. of mercuric chloride in 100 ml. of 1 *N* sulfuric acid. From this solution prepare by dilution a 0.001 or 0.002 per cent solution in 1 *N* sulfuric acid. The latter solution should preferably be prepared fresh every few days.

§ Procedure

The sample solution may contain up to 15 γ of mercury (II) and should be about 1 *N* in sulfuric acid after dilution to 20 ml. or other convenient constant volume. Add 2 ml. of 6 *N* acetic acid and a few milliliters of chloroform and shake for a minute to saturate the aqueous solution with the latter. Allow the phases to separate and carefully draw off the chloroform. Add exactly 5 ml. of dithizone and shake vigorously for 1 minute. A mixed color should be obtained. Dry the stem of the funnel with a roll of filter paper if necessary and transfer the chloroform (which should be entirely clear) to a suitable cell. Determine the transmittancy of the solution at 500 mμ (absorption by mercuric dithizonate) or at 610 mμ absorption by excess dithizone). See Fig. 51.

B. The Di-β-naphthylthiocarbazone Method

The naphthyl analog of diphenylthiocarbazone reacts with mercury in mineral acid medium to give a red complex in chloroform solution. This reagent has been applied principally in the determination of mercury in bio materials and the procedure will be found under that heading (p. 450). The chief advantage in the use of napththylthiocarbazone is said to lie in the stability of its mercury compound when exposed to light. However, now that it is known that acetic acid stabilizes mercuric dithizonate, there appears to be no marked advantage in using the naphthyl compound.

C. The Diphenylcarbazone Method

Diphenylcarbazone gives a slightly soluble blue-violet product with mercury salts, which under suitable conditions forms a colloidal suspension and makes a colorimetric determination possible. The nature of the blue product is not definitely known, but it may be a complex salt analogous to the compound that mercury (II) forms with dithizone. Diphenylcarbazide gives the same reaction as diphenylcarbazone because of its easy oxidizability to the carbazone by the oxygen of the air. The reaction is very sensitive, but is subject to many interferences. Diphenylcarbazone was used by Stock and others in determining minute amounts of mercury separated by distillation.

The use of diphenylcarbazide as a reagent for mercury was studied by

Laird and Smith.[15] Since the dithizone method is much to be preferred to the diphenylcarbazide method, only a summary of the findings of these authors will be given here. The *p*H of the sample solution should be adjusted to 4 ± 0.3 (acetic acid-sodium acetate buffer is suitable). The reagent is added in the form of a freshly-prepared 1 per cent solution in absolute alcohol. The intensity of color is independent of the amount of reagent added provided the ratio of reagent to mercury is 2:1 or greater. Beer's law is not strictly obeyed. Maximum color intensity is attained within 15 minutes, and no appreciable fading occurs in a period of several hours.

Electrolytes tend to flocculate the colored product. Nitrates and sulfates of the alkali metals and ammonium cause precipitation in less than an hour if the concentration of the salt is greater than 0.003 to 0.004 *N*. Flocculation is more rapid the higher the *p*H. At a *p*H greater than 6, flocculation occurs in a short time even in the absence of an electrolyte. Chloride reduces the color intensity seriously; a chloride concentration as low as 0.0001 *N* causes destruction of the color. Ammonium ion shows a slight tendency to reduce the color intensity. Many heavy metals, including iron and copper, interfere by giving colored products. Zinc interferes if present in an amount five times greater than that of mercury.

The mercury compound may be extracted by carbon tetrachloride or chloroform.

D. Other Methods

Procedures for the determination of small amounts of mercury have been based on the formation of colloidal mercuric sulfide, colloidal iodomercurates of alkaloids such as strychnine (nephelometric), and a brown color with potassium iodide and ammonia. These methods are of slight importance in trace analysis.

p-Dimethylaminobenzylidenerhodanine is a mercury reagent (p. 128).

Mercury (II) forms a very slightly soluble salt with $[Cr(CNS)_4(NH_3)_2]^-$ in mineral acid medium. A nephelometric method has been based on this property. The precipitate can also be brought into solution in methyl ethyl ketone by treatment with thiourea; a red solution is thus obtained which serves for colorimetry or photometry.[16]

Another method is based on the orange coloration imparted to cuprous iodide by mercury. It is applied in the determination of mercury in air after absorption in potassium iodide-iodine solution.[17]

[15] F. W. Laird and Sister Alonza Smith, *Ind. Eng. Chem., Anal. Ed.*, **10**, 576 (1938).
[16] C. Mahr, *Angew. Chem.*, **53**, 257 (1940).
[17] Method of Polejaeff. See E. C. Barnes, *J. Ind. Hygiene Toxicol.*, **28**, 257 (1946).

A very sensitive physical method may be based on the absorption of radiation of 253.7 mμ wave length by mercury vapor.[18] This principle has been applied not only in the determination of mercury vapor in air (p. 449), but also in the determination of traces of mercury which have been isolated as the sulfide. In the latter case the sulfide (collected on cadmium sulfide, p. 441) is volatilized into an absorption cell with quartz windows by heating at 550° and the absorption then measured.[19] Less than 0.1 γ of mercury can be determined in this way.

III. Applications of the Dithiocarbazone Methods

A. Metals

Procedures have been described by Fischer and Leopoldi for the determination of as little as 0.001 per cent mercury in zinc, lead, cadmium, or bismuth, of 0.001 per cent in copper and 0.1 per cent in silver.[20]

B. Sea Water Leachates

The following procedure was devised for the determination of 5–100 γ mercury per liter of sea water leachates of anti-fouling compositions.[21] Reference has already been made to the principle of this method for mercury in the presence of copper (p. 442). From 11 to 55 γ of mercury per liter, in the presence of 50 to 500 times as much copper, could be determined within ±2 γ.

§ Procedure

Add 2 ml. of 1:3 nitric acid to 92 ml. of sample containing 1 to 10 γ of mercury, followed by 1 ml. of 4 per cent hydroxylamine hydrochloride solution and 5 ml. of freshly prepared 10 per cent potassium cobalticyanide solution. After mixing, allow to stand 10 minutes. Then add 10 ml. of chloroform dithizone solution (20 mg. per liter) and shake vigorously in a separatory funnel for 1 minute. Draw off the chloroform layer, free from water droplets, into a 1 cm. cell. Obtain the extinction of the solution with a blue-green filter (see p. 446). Precautions must be taken to prevent error due to photo-decomposition of mercuric dithizonate (p. 444).

[18] K. Müller, *Z. Physik*, **65**, 739 (1930); K. Müller and P. Pringsheim, *Naturwissenschaften*, **18**, 364 (1930); M. W. Zemansky, *Phys. Rev.*, **36**, 919 (1930).

[19] A. E. Ballard and C. D. W. Thornton, *Ind. Eng. Chem., Anal. Ed.*, **13**, 893 (1941).

[20] H. Fischer and G. Leopoldi, *Metall u. Erz*, **38**, 154 (1941). This paper has not been available to the writer.

[21] H. Barnes, *J. Marine Biol. Assoc. United Kingdom*, **26**, 303 (1946). For a similar method for the determination of mercury (and copper) in the anti-fouling compositions themselves see *Analyst*, **71**, 578 (1946).

C. Air

The determination of mercury vapor in air is best made by measuring the absorption of radiation of 253.7 mμ wave length. Special instruments for the purpose are available.[22] As little as 5 γ of mercury per cubic meter of air can be detected. Less satisfactory are the chemical methods, of which the following is typical.[23]

§ Procedure[24]

Pass the air, at a rate of 60–80 liters per hour, through two absorption tubes containing a mixture of 5 ml. of 0.1 *N* potassium permanganate and 5 ml. of 10 per cent sulfuric acid. Reduce the permanganate at room temperature with a slight excess of hydroxylamine hydrochloride. Make up the solution to 25 ml. and take an aliquot (*e.g.*, 10/25) for analysis. Shake the solution with 0.5–1 ml. of 0.001 per cent dithizone in cabon tetrachloride or chloroform and compare against standards similarly obtained, or use the photometric method (p. 446). In the latter case, the whole solution can be used.

D. Bio Materials

A number of procedures have been described for the determination of mercury in samples of organic origin by the dithizone[25] and di-β-naphthylthiocarbazone methods. The chief problems involved are the complete decomposition of the sample without loss of mercury, the extraction of mercury by the dithiocarbazone without destruction of reagent by residual oxidizing agents, and the separation of mercury from copper. The following procedure meets the requirements.[26] Potassium permanganate is used as the final oxidizing agent in the destruction of organic matter. Traces of mercury are stated to be present in permanganate, and since relatively large amounts of the latter are needed, the blank is rather high (0.6–0.9 γ

[22] For descriptions and use see T. T. Woodson, *Rev. Sci. Instruments*, **10**, 308 (1939); V. F. Hanson, *Ind. Eng. Chem., Anal. Ed.*, **13**, 119 (1941); M. Shepherd, S. Schuhmann, R. H. Flinn, J. W. Hough, and P. A. Neal, *J. Research Natl. Bur. Standards*, **26**, 357 (1941).

[23] If mercury compounds may be present as a dust, special collection apparatus must be used to assure trapping all the element, whether in vapor or particulate form. See, for example, R. F. Milton and W. D. Duffield, *Analyst*, **72**, 11 (1947); E. C. Barnes.[17]

[24] N. S. Kuzyatina, *Zavodskaya Lab.*, **8**, 174 (1939). See also Cholak and Hubbard, *loc. cit.*

[25] E. P. Laug and K. W. Nelson, *J. Assoc. Official Agr. Chem.*, **25**, 399 (1942); J. F. Reith and C. P. van Dijk, *Chem. Weekblad*, **37**, 186 (1940); Milton and Hoskins, *loc. cit.*; F. L. Kozelka, *Anal. Chem.*, **19**, 494 (1947).

[26] J. Cholak and D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, **18**, 149 (1946); Hubbard, *ibid.*, **12**, 768 (1940).

mercury). The reagent used is di-β-naphthylthiocarbazone, a substance not readily obtainable in pure form. A commercial product (Eastman) is reported by Cholak and Hubbard to have a molar extinction coefficient of 10,000 at 645 mμ, compared to 45,700 for a product synthesized by Hubbard. After one purification the commercial product had an extinction coefficient of 25,000.

It seems likely that dithizone can be substituted for the naphthyl compound in the procedure. In this case the final determination should be made in the presence of acetic acid to prevent photo-decomposition of mercuric dithizonate (p. 445).

The separation of copper from mercury is effected by the use of thiosulfate (p. 442). The authors state that silver and bismuth do not interfere, since they are not extracted in the presence of chloride.

Special Solutions

Sulfuric-nitric acid mixture. Equal volumes of the concentrated acids.
Hydroxylamine hydrochloride, 50 and 5 per cent (*w/v*) solutions.
Potassium permanganate, 5-grain (0.325 g.) tablets and a saturated solution.
Sodium thiosulfate, 1.5 g. in 100 ml. of water.
Di-β-naphthylthiocarbazone (adequate purity). (*a*) Initial extraction solution: 20 mg. in 1 liter pure chloroform (p. 108). (*b*) Final extraction solution: 6 mg. per liter of chloroform for the range 0–5 γ of mercury.

§ Procedure

Preparation of sample. Urine and aqueous solutions of most organic materials are treated as follows. Transfer 50 ml. of sample to a 200 ml. boiling flask provided with a water-cooled finger condenser and add 10 ml. of 1:1 sulfuric acid and one tablet (5-grain) of potassium permanganate. Drop a few small pieces of Carborundum into the flask and boil gently. When the solution clears, quickly add another tablet of potassium permanganate. Repeat until the permanganate discoloration persists. Cool to room temperature and decolorize the solution with strong hydroxylamine solution added dropwise, followed by an excess of 2 ml. Heat the solution just to boiling, keeping the condenser in place. Then transfer the solution to a 150 ml. separatory funnel.

Decompose solid tissue and blood as follows. Transfer 1 to 50 g. of material to a 1 liter digestion flask (Fig. 52) and add 40 ml. of sulfuric–nitric acid mixture. Boil for 2 hours, cool in an ice bath, and remove any fats or fatty acids by filtering through a plug of glass wool in a funnel. Collect the filtrate in a similar 1 liter digestion flask, add 2 tablets of potassium permanganate, and heat to boiling. Add permanganate tablets, two at the time, until a precipitate of manganese dioxide persists or 8–10 tablets

have been used for each 10 g. of sample. Cool the solution in an ice bath and add 5 ml. of strong hydroxylamine hydrochloride solution. If there is a separation of fats on cooling remove them by filtration as before.

Initial extraction. In the case of digested urine samples, dilute the solution in the separatory funnel to 100 ml. and shake with 2 ml. of di-β-naphthylthiocarbazone solution (*a*) for 1 minute. Continue the extraction with, first, a 2 or 3 ml. portion and then with 5 ml. portions of the reagent if necessary. Combine the chloroform extracts.

In the case of tissue and blood samples, transfer the prepared sample to a 500 ml. separatory funnel, dilute to 400 ml. with water, add 5 ml. of hydroxylamine hydrochloride solution (50 per cent), and extract with 5 ml. portions of naphthylthiocarbazone solution (*a*), shaking for 1 minute each time.

Each 5 ml. portion of reagent extracts approximately 25 γ of mercury.

Separation of mercury from copper. To the combined chloroform extracts or an aliquot containing not more than 50 γ of mercury, add 50 ml. of 1:50 sulfuric acid and 4 ml. of sodium thiosulfate solution, and shake for 1 minute in a separatory funnel. Discard the chloroform layer which contains the copper. Wash the aqueous solution twice with 5 ml. portions of chloroform and transfer the former to a 200 ml. boiling flask. Add 5 ml. of saturated potassium permanganate, insert a water-cooled finger condenser in the flask and heat for 10 minutes. Cool the solution, decolorize it with 5 per cent hydroxylamine hydrochloride added dropwise, and add 1 ml. in excess. Re-insert the condenser and heat the solution just to boiling. Cool and transfer to a 150 ml. separatory funnel.

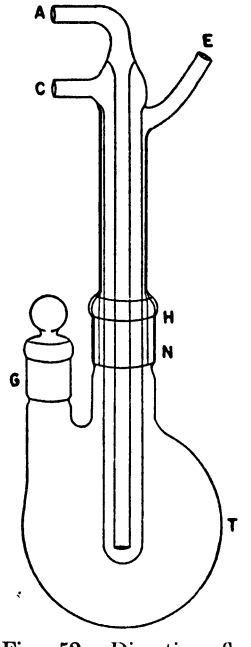


Fig. 52. Digestion flask for determination of mercury in organic material. (According to Cholak and Hubbard.) Height of apparatus, 40 cm. *A*. Water inlet. *C*. Water outlet. *E*. Gas outlet. *G*. 24/40 ⅀. *H*. 34/45 ⅀. *N*. 1.5- to 2-mm. gas gap. *T*. 1-liter Pyrex flask.

Photometric determination. Dilute the solution to 100 ml. and extract mercury with excess di-β-naphthylthiocarbazone, using 20 ml. of solution (*a*) for the range 0 to 50 γ and 10 ml. of solution (*b*) for 0 to 5 γ of mercury. Shake for 1 minute. Obtain the extinction of the clear chloroform solution at 515 mμ. For readings in the lower range of concentrations a 5 cm. cell is to be preferred (alternatively extract with less than 10 ml. of solution and

use a shorter cell); at higher concentrations a 1 cm. cell is suitable. A blank must be run through the procedure.

Prepare the standard curves from known amounts of mercury in 50 ml. of 1:50 sulfuric acid containing 1 ml. of 5 per cent hydroxylamine hydrochloride and diluted to 100 ml. as in the actual determination.

TABLE 71

RECOVERIES OF MERCURY FROM MATERIALS OF BIO ORIGIN[26]
(50 g. of sample in each case)

Sample	Mercury added, γ	Mercury found, γ
Blood.....	0	1.0, 0.8
Blood.....	0.5	1.4, 1.4
Blood.....	1.0	1.6, 2.0
Blood.....	5.0	5.9, 5.3
Blood.....	10.0	11, 11
Blood.....	20.0	21, 20
Liver.....	0	3.8, 2.6
Liver.....	5 0	8.4, 8.4
Liver.....	100	101, 102.5

CHAPTER XXIX

MOLYBDENUM

The colorimetric determination of minute amounts of molybdenum in complex materials is easily carried out. There are a number of good methods available. Because of its great sensitivity and general freedom from interferences, the thiocyanate-stannous chloride method (IIA below) is usually superior to the others.

I. Separations

A. Precipitation Methods

Precipitation of molybdenum as the sulfide is a useful method of separation from metals not forming acid-insoluble sulfides. In the presence of tartaric acid a separation from tungsten can be effected in this way. Copper sulfide has been recommended as a collector for molybdenum sulfide, but in the writer's experience it is not a satisfactory one. Antimony (V) sulfide is much better for the purpose. It forms mixed crystals with molybdenum (VI) sulfide. A relatively small fraction of the molybdenum remains unprecipitated, possibly because of reduction to a lower valence state by hydrogen sulfide. The remaining molybdenum can be recovered by boiling the filtrate to remove hydrogen sulfide, adding bromine water and a small amount of antimony (V), and again precipitating with hydrogen sulfide. See Table 72 for some results obtained by this method under conditions existing in the separation of molybdenum from tungsten in the determination of the latter in silicates.[1]

α-Benzoinoxime has been used as a precipitant for small amounts of molybdenum in connection with its polarographic determination.[2] The solution (50 ml.), containing 5 per cent hydrochloric acid, was cooled below 10° C. and treated with 2 ml. of 2 per cent alcoholic benzoinoxime solution and a few drops of bromine water. After 10–15 minutes, with occasional stirring during the interval, the precipitate was filtered off, ignited at 450°, and then dissolved in dilute sodium hydroxide solution. Seventy per

[1] The colorimetric determination of molybdenum in the antimonic sulfide precipitate by the thiocyanate method has not been investigated, but presumably it can be carried out by dissolving the precipitate in dilute sodium hydroxide, oxidizing the sulfur with a slight xcess of bromine, and proceeding as described on p. 458.

[2] M. L. Nichols and L. H. Rogers, *Ind. Eng. Chem., Anal. Ed.*, **16**, 137 (1944).

cent of the molybdenum was recovered with 1 γ, 90 per cent with 5 γ, and approximately 99 per cent with 100 γ. Benzoinoxime precipitation has been applied in separating molybdenum from rhenium.[3]

TABLE 72

ISOLATION OF MOLYBDENUM AS THE SULFIDE

A solution (20 ml.) containing molybdate, 10 ml. of 2.5 *N* sodium hydroxide, and 50–90 mg. of aluminum was treated with 6 *N* sulfuric acid until a slight permanent precipitate of aluminum hydroxide was obtained. Then were added 0.5 g. of tartaric acid, 0.75 ml. of 6 *N* sulfuric acid and antimony pentachloride (0.2 ml. 4 *N* HCl solution) as collector. The solution was heated to boiling and hydrogen sulfide passed in for 5–10 minutes. After 30 to 60 minutes' standing without further heating, the precipitate was filtered off on a fine-grained paper and washed with hydrogen sulfide water slightly acidified with sulfuric acid. The molybdenum in the filtrate and washings was determined by the thiocyanate-stannous chloride method with ethyl acetate extraction after expulsion of hydrogen sulfide.

Collector	Mo present, γ	Mo unprecipitated, γ
1 mg. Sb (III)	20	*ca.* 7
1 mg. Sb (V)	20	0.3
1 mg. Sb (V)	20	0.15
1 mg. Sb (V)	20	0.3
1 mg. Sb (V)	20	0.3[a]
1 mg. Sb (V)	10	0 15
2.5 mg. Sb (V)	10	0.2
1 mg. Sb (V)	25	0.05 or less[b]

[a] Precipitation at room temperature (difficulty with colloidal precipitate).
[b] H_2S boiled out of filtrate, 1 mg. Sb (V) added, and H_2S precipitation repeated.

Certain metals, such as iron, can be precipitated with sodium hydroxide[4] and molybdate left in solution, but there are few data to show the extent of coprecipitation of molybdenum. A sodium carbonate fusion of a siliceous sample serves to bring molybdenum into solution without any significant retention by the residue.

Under the proper conditions, molybdenum can be quantitatively coprecipitated with manganese dioxide, and a separation made from much copper.[5]

[3] A. D. Melaven and K. B. Whetsel, *Anal. Chem.*, **20**, 1209 (1948).

[4] Depending on conditions, molybdenum (VI) may or may not be carried down in an ammonium hydroxide precipitate. According to Lundell and Hoffman, *Outlines of Methods of Chemical Analysis*, p. 58, much of it is coprecipitated if a slight excess of ammonia is added to the sample solution, whereas very little is carried down if the solution is poured into an excess of ammonium hydroxide. Molybdenum has been isolated from sea water by ammonia precipitation after the addition of about 0.1 g. of ferrous ammonium sulfate per liter of sample (T. Ernst and H. Hörman, *Nach. Ges. Wissen. Göttingen*, N. F., **1**, 205 (1936)).

[5] B. Park, *Ind. Eng. Chem., Anal. Ed.*, **6**, 189 (1934).

B. Extraction Methods

Molybdenum (VI) can be extracted from 6 *N* hydrochloric acid by ethyl ether. According to Perrin (see p. 465) the partition coefficient increases rapidly as the hydrochloric acid concentration is increased to about 6 *N* (density 1.10), after which it rapidly decreases. Approximately 70 per cent of the molybdenum is extracted at the optimum acidity when an equal volume of ether is used. Molybdenum can be recovered from the ether extracts by shaking with water. Ferric iron is coextracted; it has been reported that the presence of much iron makes the extraction of molybdenum more complete. By the use of ether, a good separation can be obtained from all elements that interfere in the stannous chloride-thiocyanate method, with the exception of tungsten, vanadium, and possibly rhenium. If citric acid is added before the extraction is made, the amount of vanadium extracted is reduced to a level at which there is no interference. See p. 465 for the procedure.

Molybdenum cupferrate can be extracted by chloroform. By extraction at a *p*H of about 1.6, as little as 5 γ Mo per liter has been satisfactorily recovered.[6] Neutral salts up to 5 per cent do not interfere with the extraction. The organic matter in the residue from the evaporation of the chloroform can be destroyed by heating with sulfuric and nitric acids. Other metals that will be extracted under the conditions include ferric iron, titanium, vanadium (V), stannic tin, and probably copper.

For the separation of molybdenum from rhenium by extraction see p. 512.

Molybdenum can be separated from tungsten by extraction of the dithiol complex of molybdenum with butyl acetate from a mineral acid medium containing citric acid (p. 460).

Dithizone extraction is of considerable value in separating a number of heavy metals from molybdenum (VI), if these are not present in large amounts.

II. Methods of Determination

A. The Thiocyanate-Stannous Chloride Method

In acid solution in the presence of a suitable reducing agent such as stannous chloride, thiocyanate gives an amber to orange-red color with molybdenum. The colored compound is a thiocyanate complex of quin-

[6] D. Bertrand, *Bull. soc. chim.*, 6, 1676 (1939). Immiscible solvent extraction of molybdenum cupferrate has also been applied by Piper and Beckwith[34] and Robinson,[29] who show that the extraction is complete in more strongly acid solutions.

quevalent molybdenum, which can be extracted by such solvents as ethyl ether, butyl acetate, or cyclohexanol.

According to Babko[7] various complexes can be formed between quinquevalent molybdenum and thiocyanate:

$$Mo^{+5} + m CNS^- \rightleftharpoons [Mo(CNS)_m]^{5-m} \text{ (colorless)}$$

$$[Mo(CNS)_m]^{5-m} + (5 - m)\, CNS^- \rightleftharpoons Mo(CNS)_5 \text{ (red)}.$$

The two transitions are believed to occur at about 0.005 and 0.08 *M* thiocyanate concentration respectively. Above a thiocyanate concentration

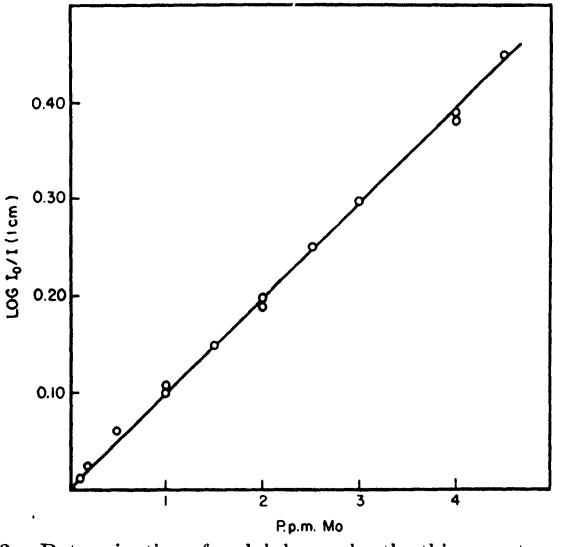


Fig. 53. Determination of molybdenum by the thiocyanate method of Perrin (470 mμ filter). (Data of L. W. Murray.)

of 0.2 to 0.4 *M* a weakening of the red color takes place, presumably because of the formation of less strongly colored $[Mo(CNS)_6]^-$.

The color intensity given by a constant quantity of molybdenum depends upon a number of factors such as the acidity, the concentration of thiocyanate, and the time of standing. The effect of these variables has been studied by Hurd and Allen.[8] They found that the acidity of the solution in hydrochloric acid should be 5 per cent. At this acidity the color intensity remains very nearly constant for an hour, after showing a slight decrease for the first 5 minutes after mixing the reagents (1 per cent potassium thiocyanate present). Acidities higher and lower than this give less color and greater fading. Fading is especially marked in strongly

[7] A. K. Babko, *J. Gen. Chem.* (*U. S. S. R.*), **17**, 642 (1947); *Chem. Abst.*, **42**, 476. See also C. F. Hiskey and V. W. Meloche, *J. Am. Chem. Soc.*, **62**, 1565 (1940).

[8] L. C. Hurd and H. O. Allen, *Ind. Eng. Chem., Anal. Ed.*, **7**, 396 (1935).

acid solutions. The potassium thiocyanate concentration should be 0.6 per cent or greater; below this concentration, fading is marked. The concentration of stannous chloride plays a minor role; 0.04 and 0.8 per cent concentrations give practically the same results. Stannic chloride (formed when ferric iron is present in the sample) shows a slight tendency to cause fading of the color.

In various organic solvents, miscible and immiscible with water, the molybdenum thiocyanate complex is more stable than in aqueous medium. Ethyl ether was commonly used for the extraction of the complex in the earlier procedures; it separates cleanly from the aqueous phase after shaking, but its volatility is a disadvantage. Moreover, it seems that the color of the complex in ether slowly becomes stronger on standing, at least under some conditions. Other immiscible solvents which have been used are isopropyl ether, cyclohexanol, butyl acetate, ethyl acetate, and isoamyl alcohol. Acetone[9] and ethylene glycol monobutyl ether (butyl Cellosolve) and diethylene glycol monobutyl ether (butyl Carbitol)[10] are miscible solvents which have been recommended for the same purpose.

The use of isoamyl alcohol as an extractant in the determination of molybdenum (with special reference to bio material) has been studied in detail by Perrin.[11] He found the optimum hydrochloric acid concentration to be approximately 1 N. The color intensity is less at lower and higher concentrations of acid, the difference being more pronounced for 20 γ than for 10 γ of molybdenum. The concentration of acid should not vary by more than ± 0.2 N if the error is not to exceed 3 per cent. The concentration of potassium thiocyanate should not be less than 1 per cent. Variation in the excess of stannous chloride has but little effect, aside from the effect caused by the acid introduced at the same time. Indifferent salts such as sodium sulfate and potassium perchlorate do not affect the color intensity, even in 2 per cent concentration. The effect of iron is remarkable. With more than 4 γ of molybdenum the full color intensity is not developed unless 0.5–1 mg. of iron is present; more iron (up to 10–30 mg.) causes no further change. The enhancing effect of iron is greater the larger the concentration of molybdenum. The peculiar influence of iron has also been noted by others. Temperature variation from 15 to 30° has no significant effect. The volume of the aqueous phase should be held approximately constant because of the appreciable solubility of amyl alcohol in water. It is reported that the maximum variation in the color intensity of the alcohol extract is 3 per cent in the course of two days.

[9] F. S. Grimaldi and R. C. Wells, *Ind. Eng. Chem., Anal. Ed.*, **15**, 315 (1943). See p. 466.

[10] M. Kapron and P. L. Hehman, *Ind. Eng. Chem., Anal. Ed.*, **17**, 573 (1945).

[11] D. D. Perrin, *New Zealand J. Sci. Tech.*, **27A**, 396 (1946).

Delaying the extraction for 90 minutes after the addition of stannous chloride was found to give the normal color strength, even though the color of the aqueous phase had faded in the interval.

Under the conditions of the determination of molybdenum in bio material (p. 468), Perrin lists the following elements among those interfering in the amount specified when the amount of molybdenum is 10 γ (error greater than 3 per cent): Ti (III), 0.7 mg., yellow color; V, 0.4 mg., yellow color; Cr (VI), 2 mg., purple color; W (VI), 0.15 mg., yellow color at high levels, low Mo values in middle range; U (VI), 11 mg., yellow color; Co, 12 mg., slight green color; Cu, 5 mg., low values; Pb, 10 mg., low values; F, 20 mg., low values. Platinum, rhodium, and rhenium also give colored products which are extracted by the alcohol. Certain metal salts give insoluble products under the conditions (Ag, Hg, Au, Se, Te, as well as Cu). Several hundred milligrams of phosphoric acid are without effect. These observations are in general in accord with the experience of the writer, using ethyl ether as extractant.

Directions are given below for the determination of molybdenum with and without extraction. Extraction is recommended for the greatest sensitivity and accuracy. The simpler procedure without extraction can be applied when colored substances are not present and when the amount of molybdenum is not too small.

Special Solutions

Potassium thiocyanate, 10 per cent.

Stannous chloride, 10 g. of the dihydrate in 100 ml. of 1 *N* hydrochloric acid. Filter the solution if not entirely clear. Prepare fresh weekly.

Ferrous ammonium sulfate, 1 g. in 100 ml. of 0.2 *N* sulfuric acid.

Isoamyl alcohol. Redistil and collect the fraction boiling between 128 and 131°. After use the alcohol can be recovered by heating over lime and redistilling.

Standard molybdenum solution, 0.010 per cent Mo. Dissolve 0.075 g. of pure MoO_3 in a few milliliters of dilute sodium hydroxide, dilute with water to about 50 ml., make slightly acidic with hydrochloric acid, and make up to 500 ml. with water. This solution is conveniently diluted to 0.001 per cent in 0.1 *N* hydrochloric acid, preferably weekly. The standard solution may also be prepared from ammonium molybdate, in which case the molybdenum content should be obtained by a standard method.

§ Procedure

Without Extraction.[12] The sample solution may conveniently have a volume in the neighborhood of 25 ml. and may contain up to 300 γ of molybdenum. Add 5 ml. of concentrated hydrochloric acid, 1 ml. of ferrous ammonium sulfate solution, and 4 ml. of potassium thiocyanate

[12] When much tungsten is present, follow the procedure on p. 465. For the determination of molybdenum in the presence of much rhenium consult J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **23**, 497 (1939).

solution. After mixing, add 2 ml. (or more if iron and other reducible substances are present) of stannous chloride, and dilute with water to 50 ml. in a volumetric flask. Determine the transmittancy of the solution within 15 minutes, preferably less, at approximately 475 mμ. Prepare the standards in the same way as the sample. If the sample contains relatively much iron it is desirable to add roughly the same amount to the standards.

Extraction with Isoamyl Alcohol. To 10–15 ml. of sample solution (1–50 γ Mo) in a separatory funnel add 2.0 ml. of concentrated hydrochloric acid, 1 ml. of ferrous ammonium sulfate solution (unless iron is already present in amounts greater than 1 mg.), and 3.0 ml. of potassium thiocyanate solution. After mixing, add 3 ml. of stannous chloride solution (or more if much iron is present), dilute with water to 25 ml.,[13] and again mix. Add exactly 5 ml. (or 10 ml.) of isoamyl alcohol and shake vigorously for one-half minute. Allow the phases to separate and draw off the water layer. Filter the amyl alcohol through a small plug of glass wool in a small funnel to remove water droplets and any insoluble matter that may be present. A few milligrams of stannous chloride may be placed on the plug to hinder the oxidation of ferrous iron and the appearance of a red color due to ferric thiocyanate in the filtrate. Obtain the transmittancy of the alcohol solution at 475 mμ, using a 1 or 2 cm. cell. Prepare the standard extracts in the same manner as the extract of the sample.

If the concentration of the molybdenum complex is very low, it may be better to transfer the alcohol extract to a narrow tube (p. 52) and compare visually against standards (*cf.* p. 463).

B. The Dithiol Method

4-Methyl-1,2-dimercaptobenzene (dithiol) yields a slightly soluble product with molybdenum (VI) in dilute mineral acid medium.[14] This complex can be extracted with butyl acetate, to which it imparts a strong yellow-green color. A sensitive colorimetric method has been based on this behavior.[15] Many other metals are precipitated by the reagent. Most of these precipitates (including those of ferric iron and copper) are insoluble in butyl acetate; a few (stannous tin) are soluble. It appears that small amounts (0.1 mg.) of iron, copper, and tin do not interfere in the procedure. Many heavy metals can be removed by dithizone extraction.

[13] The funnel should be marked for this volume. A variation of 1 ml. is insignificant. If desired, the subsequent extraction can be made with two portions of amyl alcohol, in which case practically all of the molybdenum complex will be extracted from the water layer and the volume of the latter need not be so accurately controlled.

[14] J. H. Hamence, *Analyst*, **65**, 152 (1940).

[15] C. F. Bickford, W. S. Jones, and J. S. Keene, *J. Am. Pharm. Assoc.*, **37**, 255 (1948).

Tungsten (VI) also gives a slightly soluble product with dithiol, soluble in butyl acetate with a blue-green color. The reaction of tungsten can be prevented by the addition of citric acid. Under the conditions of the

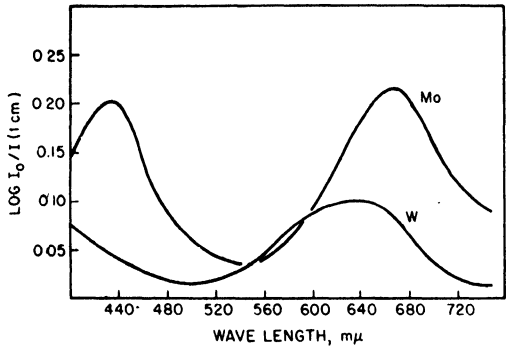


Fig. 54. Extinction curves of the dithiol complexes of molybdenum and tungsten. (According to Bickford, Jones, and Keene.)

procedure below, approximately 0.3 per cent of the tungsten (1 to 10 mg.) in the aqueous phase is extracted by the butyl acetate.

Special Reagents

Dithiol solution. Add 0.1 to 0.2 g. of dithiol to 100 ml. of 0.25 *N* sodium hydroxide solution, followed by 0.5 ml. of thioglycolic acid (to inhibit oxidation of dithiol). Keep the solution in a refrigerator. Prepare fresh daily.

Butyl acetate. Redistilled commercial material may be used.

§ Procedure[16]

Add 4 ml. of 1:3 sulfuric acid, 3 drops of 85 per cent phosphoric acid, and 0.5 g. of citric acid to the sample solution (1 to 25 γ of Mo). Dilute with water to 20 ml. and add 2 ml. of dithiol solution. Allow to stand at room temperature for 2 hours. Extract the molybdenum complex with 14–15 and 9–10 ml. portions respectively of butyl acetate. Make up to 25 ml. with butyl acetate. Filter the solution if it is not entirely clear. Obtain the extinction of the solution at 670 mμ. Beer's law is valid.

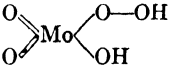
[16] Directions of Bickford, Jones, and Keene.[15] Attention is called to a micro (but not trace) procedure developed by J. E. Wells and R. Pemberton, *Analyst*, **72**, 185 (1947), for the colorimetric determination of molybdenum in steel. A 4 mg. sample is taken and the dithiol compound is formed in *ca.* 4.5 *N* hydrochloric acid solution. Amyl acetate is used for extraction. Small amounts of tungsten do not interfere under the specified conditions.

C. Other Methods

In hot mineral acid solution, phenylhydrazine gives a red-colored product with molybdate.[17] The color is stable. The sensitivity of the reaction is fairly high. Tungsten gives no color, vanadium a green color. The reaction has been applied in the determination of molybdenum in silicate rocks[18] and in manganese ores.[19]

Potassium ethyl xanthate reacts with molybdenum in faintly acid solution to give a red-colored compound[20] which may be extracted with chloroform.[21] Various heavy metals (copper, iron, etc.) also give colored products with xanthate.

Other reagents that have been used for the colorimetric determination of molybdenum include hydrogen sulfide[22] (colloidal MoS_3 formed), tannic acid,[23] hydrogen peroxide[24] which forms permolybdic acid and sodium



thiosulfate[25] (lilac-colored reduction product in acid medium, extractable by ether or ethyl acetate).

[17] L. Spiegel and T. Maas, *Ber.*, **36**, 512 (1903); E. Montignie, *Bull. soc. chim.*, [4], **47**, 128 (1930). It is stated that phenylhydrazine is oxidized by molybdate to diazonium salt which couples with the excess phenylhydrazine and molybdate.

[18] G. von Hevesy and R. Hobbie, *Z. anorg. allgem. Chem.*, **212**, 134 (1933).

[19] H. Hauptmann and M. Balconi, *Z. anorg. allgem. Chem.*, **214**, 380 (1933).

[20] Perhaps $MoO_3 \cdot [SC(SX)(OC_2H_5)]_2$ according to Feigl.

[21] S. L. Malowan, *Z. anorg. allgem. Chem.*, **108**, 73 (1919); *Z. anal. Chem.*, **79**, 202 (1929). According to F. Pavelka and A. Laghi, *Mikrochemie ver. Mikrochim. Acta*, **31**, 138 (1943), the best *p*H for the reaction is 1.8–1.9. They were able to determine 20 γ of molybdenum within ± 5 per cent (chloroform extraction).

[22] E. Wendehorst, *Z. anorg. allgem. Chem.*, **144**, 319 (1925); J. M. McCandless and J. I. Burton, *Ind. Eng. Chem.*, **19**, 406 (1927); H. ter Meulen, *Rec. trav. chim.*, **51**, 549 (1932); D. Bertrand, *Bull. soc. chim.*, **6**, 1676 (1939).

[23] O. Steiner, *Z. anal. Chem.*, **81**, 389 (1930).

[24] A. D. Funck, *Z. anal. Chem.*, **68**, 283 (1926). The sensitivity is low. Better results are obtained by photometry in the ultraviolet (maximum absorption at 330 mμ in perchloric acid solution). Even here, however, the sensitivity is only 0.1 γ of molybdenum per square cm. for 0.001 extinction. See A. Weissler, *Ind. Eng. Chem., Anal. Ed.*, **17**, 695 (1945). The color is intensified in phosphoric acid medium according to G. Thanheiser and P. Goebbels, *Mitt. Kaiser Wilhelm Inst. Eisenforschung Düsseldorf*, **23**, 187 (1941).

[25] P. Falciola, *Ann. chim. applicata*, **17**, 261 (1927).

III. Special Applications of the Thiocyanate-Stannous Chloride Method

A. Silicate Rocks

The following procedure permits the determination of as little as 0.0001 per cent of molybdenum. The sample is fused with sodium carbonate, the melt leached, and the thiocyanate complex extracted from the acidified filtrate with ethyl ether.[26] No interference by the elements of igneous rocks in their usual amounts has been found. Much tungsten alters the hue of the ether solution to greenish yellow, but the effect of small amounts (50 W/1 Mo) is not serious. Relatively large quantities of vanadium may color the ether slightly (*cf.* p. 589). It has been observed by Hoffman and Lundell that under similar conditions vanadium gives a color about $^1/_{200}$ as strong as molybdenum. Titanium cannot give a coloration, for it is removed at the beginning. Such quantities of platinum as are introduced in the sodium carbonate fusion are too small to have any significant effect. No appreciable retention of molybdenum by the leached residue, whether of a silicic or sub-silicic rock, has been found.

There appears to be no reason[27] why the procedure for molybdenum in soils, given in the next section, cannot be applied to silicate rocks as well. This procedure may even have advantages, since a larger sample can be handled more conveniently than in the sodium carbonate fusion procedure. In addition comparatively large amounts of vanadium and tungsten are without effect.

§ Procedure[28]

Fuse 1 g. of rock powder with sodium carbonate and leach the melt as described on p. 265. Transfer 50 ml. of the filtrate which has been made up to 100 ml. to a separatory funnel and add slowly, while swirling, 8 ml. of concentrated hydrochloric acid. Shake the solution carefully to liberate carbon dioxide in supersaturated solution and cool to 15–20°. Add 3 ml. of 5 per cent potassium thiocyanate solution, mix, and then add 3 ml. of 10 per cent stannous chloride solution in 2 *N* hydrochloric acid. Mix and allow to stand for 0.5–0.75 minute. Add 6 to 7 ml. of ether which has been shaken with $^1/_{10}$ its volume of equal parts of thiocyanate and stannous chloride, shake well for $^1/_2$ minute, allow the two liquids to separate, draw off the aqueous layer into a beaker, and run the ether into a color

[26] Isopropyl ether or isoamyl alcohol would be preferable as extractant, because of their lower volatility, but it is not known whether they can be safely substituted in this case.

[27] Difficulty may be encountered in obtaining complete solution of much calcium sulfate, but perhaps the excess can be filtered off without loss of molybdenum.

[28] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 336 (1936).

comparison tube having a diameter of 10 mm. and preferably provided with a glass stopper (p. 52). Return the aqueous solution to the separatory funnel, extract with 2 to 3 ml. of ether, and combine the latter with the first extract. Usually two extractions will suffice, but as a precaution extract once more with 2 ml. of ether and add this extract to the others if it shows any significant amount of color.

Compare the combined ether extracts against a series of standards which have been obtained by extracting known molybdenum solutions having about the same volume and composition as the sample, or use a photometer which permits measurements with *ca.* 5 ml. of solution. Alternatively use the colorimetric titration technique as follows. Prepare a standard solution of molybdenum thiocyanate in ether by adding to 50 ml. of aqueous solution containing 0.25 mg. of molybdenum and 2.5 g. of sodium carbonate, 8 ml. of concentrated hydrochloric acid, 3 ml. of potassium thiocyanate, and 3 ml. of stannous chloride, and extracting the cold mixture with 10, 5, 5, 5, and 5 ml. portions of ether (the last extract should be colorless or very nearly so). Deliver the extracts into a 25 ml. volumetric flask and make up to the mark with ether. Using gentle suction draw the ether solution into a dry microburet, which has been cooled to 15–20° if necessary, and cover well. Add the ether solution to a color comparison tube containing approximately the same volume of ether as the sample tube until

TABLE 73

DETERMINATION OF MOLYBDENUM IN ROCKS BY THE THIOCYANATE-STANNOUS CHLORIDE METHOD WITH ETHER EXTRACTION

Sample	MoO_3 present, %	MoO_3 found, %
Granite (0 1 g.) + 10% P_2O_5	0.007	0.008
Granite (0.1 g.) + 0 5% F	0 007	0.007
Granite + 0 5% U + 1% Ta	0 0073	0.0075
Diorite (0 5 g.)	0.0003	0.00035
Diorite (0.5 g.)	0.0003	0.00025
Synthetic acid rock (0.5 g.)	0.0007	0.00075
Synthetic acid rock (0 5 g.) + 0.05% WO_3	0.0007	0.0009

the colors match when the tubes are viewed axially. The standard ethereal molybdenum thiocyanate solution must be prepared fresh each 3–4 hours because its color intensity slowly increases on standing. In all the operations care must be taken to prevent any significant evaporation of ether from the standard solution. The room temperature should be 20° or less if possible.

Run a blank through the whole procedure.

B. Phosphate Rock

The following method[29] has been shown to give good recoveries of molybdenum. It appears that the molybdenum content of phosphate rock may run from about 1 p.p.m. to several hundred p.p.m.

§ Procedure

Mix 5 g. of finely ground sample with 15 g. of sodium carbonate and heat uncovered in a large platinum crucible for 15 minutes over a Meker burner to burn off organic matter in an oxidizing atmosphere (the bottom of the crucible is preferably covered with a few tenths of a gram of sodium carbonate before addition of the mixture). Then cover the crucible and gradually increase the temperature to about 1050°. Remove the cover of the crucible and swirl the molten contents every five minutes. When the fusion becomes quiet (in about 20 minutes), distribute the melt over the sides of the crucible while cooling.

Detach the cake from the crucible and leach near the boiling point with 100 ml. of water in a beaker for 2 hours or more, while breaking up the cake with a stirring rod. When the mass has been broken up into small pieces, pour off the liquid into another beaker, transfer the solid to a small mortar and grind to a fine slurry. Combine the slurry with the reserved solution and digest further for 15 minutes near the boiling point. Then filter the solution into a large platinum dish. Add a moderate excess of hydrochloric acid, evaporate to dryness, and take up the residue in 7.5 ml. of concentrated hydrochloric acid and water. Filter off the silica and wash with water to give about 120 ml. of filtrate.

Transfer the solution to a 200 ml. separatory funnel and add 5 ml. of 5 per cent potassium thiocyanate. Mix, add 5 ml. of 10 per cent stannous chloride in 1:9 hydrochloric acid, and again mix. After one-half minute add 10 ml. of isopropyl ether and shake vigorously for one-half minute. Allow to stand until the ether layer is clear, draw off the water layer, and transfer the ether to a 25 ml. volumetric flask. Extract again with 10 ml. of ether and add the extract to the first portion. Make up to the mark with ether and compare at once in a colorimeter against a standard prepared as follows: Transfer 125 ml. of 5 per cent sodium carbonate solution to a separatory funnel and add from 0.005 to 0.5 mg. of MoO_3 (as ammonium molybdate), 25 ml. of hydrochloric acid, swirl to liberate carbon diox-

[29] W. O. Robinson, *Soil Sci.*, 66, 317 (1948). The author reports that molybdenum can be isolated from relatively strong solutions of hydrochloric acid by extracting its cupferron compound by ethyl nitrate. Fusion of the evaporation residue with sodium carbonate and determination of molybdenum in the extract gave results in satisfactory agreement with those obtained by the above method.

ide, cool under the tap, and develop the molybdenum-thiocyanate color as already described.

Alternatively make the color comparison in the separatory funnels. This may be done by adding increments of standard molybdenum solution with thorough shaking after each addition. A cylindrical rather than pear-shaped separatory funnel is to be preferred for such comparison.

C. Soils

In the following method,[30] the sample is ignited and then decomposed with sulfuric and hydrofluoric acids. Molybdenum is isolated by ether extraction from hydrochloric acid solution as described on p. 455, and finally determined by isoamyl alcohol extraction of the thiocyanate complex. An error of less than 0.3 γ of molybdenum is caused by as much as 0.5 g. of TiO_2, 25 mg. of V_2O_5, 5 mg. of Ag, 0.25 g. of Cr_2O_3, and 5 mg. of WO_3. Much iron is without effect except insofar as it requires more stannous chloride solution for reduction, the addition of which increases the acidity of the solution and slightly affects the color strength of the molybdenum complex; a correction can be applied for this effect. One-fourth gram of P_2O_5 does not cause any error. Five and 10 microgram quantities of molybdenum added to 5 g. soil samples were recovered satisfactorily, the largest error being about 10 per cent. The average molybdenum content of soils appears to be 0.5–1 p.p.m.

§ Procedure

Weigh into a silica dish 10 to 20 g. of soil which has been dried at 100° and ground to pass a screen of $^1/_{64}$-inch mesh. Heat at 400–450° for 3 hours to destroy organic matter. (For peats, larger samples and a longer period of ashing are necessary.) Transfer 5 g. of ash to a platinum dish and add 10 ml. of water, 2 ml. of concentrated sulfuric acid, and 10 ml. of concentrated hydrofluoric acid. Heat gently until most of the liquid has evaporated, and then more strongly to expel the residual sulfuric acid. Take up the residue in 6 *N* hydrochloric acid and transfer to a 100 ml. beaker. Evaporate to a volume of 5 ml., filter through paper into a separatory funnel, and wash the residue with more hydrochloric acid until the volume of the filtrate is 20 ml.

Add 4 ml. of 40 per cent citric acid in 6 *N* hydrochloric acid, and extract the solution with four 25 ml. portions of reagent-quality ethyl ether. Shake the combined ether extracts with three 10 ml. portions of water to transfer the molybdenum to the aqueous phase, and discard the ether. Evaporate the aqueous solution to about 3 ml. and add 4 ml. of 6 *N* hydro-

[30] D. D. Perrin, *New Zealand J. Sci. Tech.*, **28A**, 183 (1946).

chloric acid, 3 ml. of 10 per cent potassium thiocyanate solution, and sufficient 40 per cent stannous chloride in 1:9 hydrochloric acid to destroy the color of ferric thiocyanate. Make a note of the volume of stannous chloride added, since a correction is to be applied. Bring the volume of the solution to 25 ml. with water and extract the molybdenum complex with isoamyl alcohol as described on p. 459. If much iron is present, the stannic tin produced may have a stabilizing effect on the water-alcohol emulsion; in such a case transfer the mixture to a centrifuge-tube and centrifuge for 10 minutes at 2000 r.p.m. to separate the phases. There is no adsorption of molybdenum on a hydrous stannic oxide precipitate.

Apply a correction for the decrease in color produced by much iron after estimating its amount from the volume of stannous chloride used:

Grams Fe_2O_3 in sample	0.5	1.0	1.5	2.0	3.0	4.0
Percentage decrease in color	1	2	3	4	7	10

Add approximately 2 mg. of iron to each standard solution and blank (p. 457).

D. Tungsten Ores

Grimaldi and Wells[9] have described a procedure for the determination of small amounts of molybdenum in tungsten and molybdenum ores. The thiocyanate color is developed in water-acetone solution and citrate is used to prevent the interference of tungsten. Iron is stated to interfere in the method by giving a slight color and it must be removed. When tungsten is present, phosphorus in more than small amounts (about 30 mg.) interferes by causing the molybdenum color to fade and slowly giving a blue color. Large quantities of vanadium impart a blue-green color. A few hundredths of a milligram of molybdenum can be accurately determined in the presence of 0.2 g. or more of tungstic oxide.

§ Procedure[31]

With substances such as scheelite containing up to 40 per cent of tungstic oxide and as much as 1 per cent of molybdenum oxide, fuse a 0.5 g. sample with 2.5 g. of sodium carbonate and, if thought necessary, 0.05 g. of sodium nitrate. Extract the melt with water containing a drop or two of alcohol to reduce manganate, filter, and wash with 1 per cent sodium carbonate solution. Make the filtrate just acid with hydrochloric acid. If any chromate is present, reduce it with sulfurous acid. Evaporate the solution to a volume of about 25 ml. to remove carbon dioxide. Disregard any

[31] The directions of Grimaldi and Wells, given here, call for color comparison by colorimetric titration. It will be understood that a photometer can advantageously be used instead.

silica that may separate. Neutralize with 10 per cent sodium hydroxide and add an excess of 10 ml., digest on the steam bath for ten minutes, filter hot, and wash with dilute sodium hydroxide. Make the filtrate barely acid with hydrochloric acid (phenolphthalein as indicator) and dilute to exactly 100 ml. (Molybdenite and wulfenite ores are best brought into solution by acid treatment according to the usual procedures.)

Transfer a 15 ml. aliquot of the sample solution to a 100 ml. beaker and add 1.5 g. of ammonium citrate. When the latter has dissolved add 5 ml. of 10 per cent ammonium thiocyanate and 25 ml. of acetone, cool, and add dropwise exactly 7 ml. of 10 per cent stannous chloride in 1:1 hydrochloric acid. In another 100 ml. beaker prepare a similar blank solution and add to it standard molybdenum solution (1 ml. $\equiv$ 0.1 mg. MoO_3) until the color matches that of the sample solution.

E. Steel

§ Procedure[32]

Dissolve 0.2 g. (for less than 0.2 per cent Mo) of sample in 10 ml. of 1:4 sulfuric acid, warming to hasten solution. When action has ceased, add 1 ml. of 30 per cent hydrogen peroxide and boil for 5 minutes. If any insoluble material remains filter it off on paper and wash with water. Boil the solution down to 5 ml. to destroy excess hydrogen peroxide. If tungstic acid has separated add 0.5 g. of tartaric or citric acid followed by sodium hydroxide solution (2 to 4 *N*) until the solution is slightly basic. Then add 15 ml. of 1:4 sulfuric acid, transfer to a separatory funnel and dilute to 40–50 ml. with water. Cool the solution if necessary and add 5 ml. of potassium thiocyanate solution (5 per cent). Mix and add 5 ml. of stannous chloride solution (300 g. $SnCl_2 \cdot 2H_2O$ in 1 liter 1:9 hydrochloric acid). Cool the solution to room temperature under the tap, add 30 ml. of ethyl ether[33] (previously shaken with stannous chloride and thiocyanate, p. 462) and shake well for $^1/_2$ minute. Allow the layers to separate, draw off the aqueous solution and transfer the ether layer, without any appreciable amount of aqueous phase, to a 50 or 100 ml. volumetric flask. Extract the aqueous phase with a 20 ml. portion of ether, combine the latter with the first portion, and make up to 50 or 100 ml. with ether. Transfer the mixed solution to the cell of a photometer, cover, and determine the extinction (p. 459).

[32] Essentially the directions given by T. R. Cunningham and H. L. Hanmer, *Ind. Eng. Chem., Anal. Ed.*, **13**, 106 (1941). Kapron and Hehman[10] give detailed directions for the determination of molybdenum in various kinds of steel without extraction by an immiscible solvent.

[33] Isopropyl ether very likely can be substituted for ethyl ether.

Construct the reference curve by extracting with ether ferric sulfate solutions which contain the equivalent of 0.2 g. of iron and various amounts of molybdenum, and which have been treated in the same manner as the sample solution.

F. Bio Materials

In the following method, due to Perrin,[34] organic matter is destroyed by an oxidizing acid attack and molybdenum is determined directly in the digest, after neutralization of the acids, by the isoamyl alcohol extraction procedure (p. 459). It appears that the only element in bio material that may interfere is copper, which in amounts above 5 mg. causes low values. The presence of much copper is revealed by the appearance of a strong blue color when the digest is treated with ammonia. Copper can be removed, when necessary, by extracting with a carbon tetrachloride solution of dithizone after removal of the excess ammonia by boiling. Any dithizone in the aqueous phase can be destroyed by evaporating the solution with nitric acid.

Satisfactory recoveries of 2.5 to 20 γ of added molybdenum were obtained by Perrin.

§ Procedure

Digest 2 g. of finely ground solid or 10 ml. of whole blood with 1 ml. of concentrated sulfuric acid, 1 ml. of 60–70 per cent perchloric acid, and nitric acid (5 ml. of the latter being added at first and then more as required to prevent charring). If desired, the digestion and subsequent steps may all be carried out in 1 × 8 inch Pyrex test tubes graduated at 25 ml. When digestion is complete, boil off most of the perchloric acid. Variation in the amount of acid left at the end of the digestion has no significant effect on the final result.

Dilute the digest to 10 ml. with water and make alkaline with concentrated ammonia (phenolphthalein as indicator). Evaporate to near-dryness on the water bath to remove excess ammonia. Add 4 ml. of 6 *N* hydrochloric to the cold residue, dilute to 15 ml. with water and continue as described on p. 459 under "Extraction with Isoamyl Alcohol."

[34] D. D. Perrin.[30] Procedures for the determination of molybdenum in plant materials have also been given by Nichols and Rogers[2]; F. B. Marmoy, *J. Soc. Chem. Ind.*, **58**, 275 (1939); K. E. Stanfield, *Ind. Eng. Chem., Anal. Ed.*, **7**, 273 (1935). In a method recently described by C. S. Piper and R. S. Beckwith, *J. Soc. Chem. Ind.*, **67**, 374 (1948), molybdenum is isolated by chloroform extraction of its cupferrate at *p*H 0–0.5 and finally determined with dithiol. Lately, a simple procedure without extraction has been described by I. Barshad, *Anal. Chem.*, **21**, 1148 (1949). Ferric iron and nitrate are added to produce maximum color intensity without fading; an explanation of the beneficial effect of these is offered. Organic matter is destroyed by ignition.

CHAPTER XXX

NICKEL

I. Separations

A. The Dimethylglyoxime Extraction Method

The solubility of nickel (II) dimethylglyoxime in chloroform[1] (pale yellow solution) provides an easy means of separation of minute amounts of nickel in the analysis of silicate rocks, biological material, water, etc.[2] From a faintly ammoniacal solution containing citrate, nickel may thus be separated by extraction from ferric iron, aluminum, cobalt, etc. Copper accompanies nickel to a greater or less extent in the extraction, but much of the copper is removed from the chloroform extract when it is shaken with dilute ammonia (*cf.* p. 475), whereas nickel remains in the chloroform. The cobalt compound of dimethylglyoxime (brown) is not extracted by chloroform to any significant extent since the latter remains colorless, but much cobalt naturally interferes by consuming the reagent. Nevertheless a satisfactory separation of nickel from a thousand times as much cobalt can be effected (see Table 75).[3]

Much manganese interferes in the extraction of nickel, probably by oxidizing the latter to the nickelic condition in the ammoniacal solution; nickelic dimethylglyoxime is not extracted by chloroform. This interference can be prevented by adding hydroxylamine hydrochloride to keep manganese in the divalent state.

The nickel dimethylglyoxime in the chloroform may be decomposed and nickel transferred to the aqueous phase by shaking with dilute hydrochloric acid; most of the dimethylglyoxime remains in the chloroform. The nickel in the acid solution may then be determined most conveniently by the dimethylglyoxime method (IIA).

B. Precipitation Methods

In some instances, when the most minute amounts of nickel are not involved and when the sample solution can be reduced to a small volume,

[1] The solubility of nickel dimethylglyoxime in chloroform at room temperature corresponds to approximately 0.03 mg. of nickel per milliliter.

[2] E. B. Sandell and R. W. Perlich, *Ind. Eng. Chem., Anal. Ed.*, 11, 309 (1939).

[3] At more unfavorable ratios cobalt can be complexed with cyanide. For directions see the paper cited in footnote 17.

isolation of nickel by precipitation with dimethylglyoxime can be of use. This method of separation has been applied with satisfactory results for amounts of nickel ranging from a few micrograms up to 50 micrograms in the presence of 16 mg. of ferric iron, about 1 mg. of copper and manganese, 0.6 mg. of zinc, and 0.06 mg. of cobalt.[4]

Nickel has been isolated from sea water by precipitation with ammonium sulfide after addition of ferrous ion (approximately 100 mg. ferrous ammonium sulfate per liter).[5]

Ferricyanide has been used for precipitation of small quantities of nickel with zinc as collector.[6]

Separation of nickel from various heavy metals by precipitation of the latter with excess ammonia is best avoided because of the tendency of nickel to be carried down in such hydroxide precipitates.

II. Methods of Determination

A. The Dimethylglyoxime Method

A very satisfactory method for the determination of small quantities of nickel is based on the strong wine-red or brown color obtained when dimethylglyoxime is added to a basic solution of a nickel salt which has been treated with an oxidizing agent such as bromine.[7] The identity of the colored product has not been established. Feigl[7] presented results tending to show that it is a complex of quadrivalent nickel with dimethylglyoxime. Later workers have not been able to verify this finding.[8] The suggestion has been made that dimethylglyoxime is oxidized in the reaction and that the oxidation product forms the colored complex with nickel.[9]

The hue and color intensity of the nickelic dimethylglyoxime solution depend upon the original acidity of the nickel solution. If bromine water is added to an acid solution followed by ammonia and glyoxime, a brownish solution is obtained, while if bromine is added to a faintly ammoniacal

[4] E. Passamaneck, *Ind. Eng. Chem., Anal. Ed.*, **17**, 257 (1945). The volume of the solution must be reduced to about 2 ml. The solubility of nickel dimethylglyoxime in water is reported to correspond to 0.08 γ of nickel per milliliter.

[5] T. Ernst and H. Hörman, *Nach. Ges. Wissen. Göttingen*, N. F. **1**, 205 (1936); *Z anal. Chem.*, **111**, 425 (1937/38).

[6] E. Reichel and L. Stuzin, *Z. anal. Chem.*, **113**, 389 (1938).

[7] This reaction was discovered by F. Feigl, *Ber.*, **57**, 758 (1924), and applied quantitatively by A. Rollet, *Compt. rend.*, **183**, 212 (1926). Oxidizing agents which have been used include hypochlorite (Jones[21]), chlorite (Wulff and Lundberg[9]), persulfate (K. ter Haar and W. Westerveld, *Rec. trav. chim.*, **67**, 71 (1948)), and iodine. These do not possess any advantages over bromine, and some are definitely inferior.

[8] A. Okac and M. Polster, *Coll. Czech. Chem. Comm.*, **13**, 561, 572 (1948). See also Wulff and Lundberg.[9]

[9] P. Wulff and A. Lundberg, *Z. Ver. deut. Chem., Beih.*, No. **48**, 76 (1944).

or neutral solution (followed by ammonia in the latter case) a wine-red color is produced.

The procedure given below calls for an initially acid solution of the sample, such as is usually encountered in practice. Under constant conditions highly reproducible values are obtained. The full color intensity develops nearly immediately after the addition of the glyoxime. In

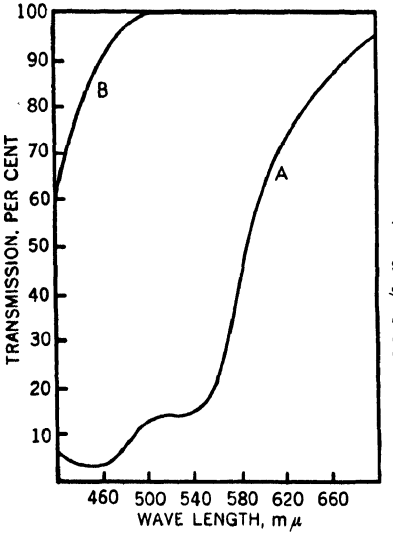


Fig. 55. Transmission curves of (*A*) nickelic dimethylglyoxime solution (5 minutes after preparation) and (*B*) ammoniacal solution of ferric iron containing citrate. (From Murray and Ashley, *Ind. Eng. Chem., Anal. Ed.*, **10**, 1 (1938).)

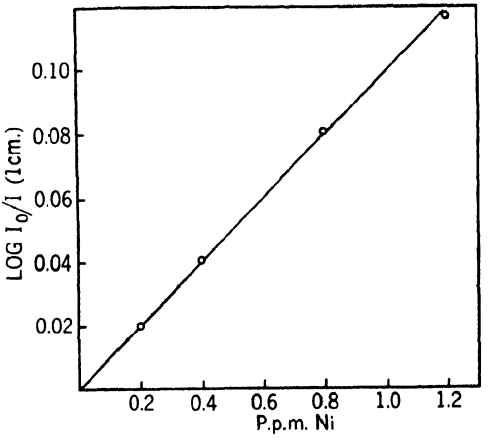


Fig. 56. Determination of nickel by the dimethylglyoxime method according to the directions in the text (green filter).

aqueous solutions containing no more alcohol than that introduced by the dimethylglyoxime reagent solution the color intensity increases with time. Under conditions similar to those prescribed in the procedure below, the transmittancy in the wave length range 455 to 700 mμ or higher decreases progressively for several hours at least, whereas between 455 and 415 mμ it increases.[10] When the solution contains much alcohol the transmittancy increases over the whole range on standing but the rate of change is less on

[10] A. M. Mitchell and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **17**, 380 (1945). According to B. McDuffie (private communication) the stability of the color depends markedly upon the alkalinity of the solution. At sufficiently high alkalinities the color intensity remains constant for days.

the whole than in aqueous solution. Therefore Mitchell and Mellon[10] propose to carry out the reaction in alcoholic medium (27.5 ml. of 95 per cent ethyl alcohol in a total volume of 50 ml. is stated to be the optimum concentration). The fading of the color in the first half hour after mixing is then very small.[11] The addition of alcohol is superfluous if the transmittancy of the aqueous solution is determined within 5 minutes after mixing. The apparent rate of change with time depends upon the wave length of measurement. With a suitable filter there may be no significant change in transmittancy of the aqueous solution for some time. Thus under the conditions of the procedure on p. 473, a solution containing 10.0 γ of nickel in 25 ml. showed an apparent content of 10.0 γ 20 minutes after mixing, 10.5 γ after 1 hour, 10.9 γ after 2.5 hours, and 7.4 γ after 23 hours; a solution containing 5.0 γ of nickel gave 5.5 γ after 1.5 hours. Beer's law is followed (Fig. 56) up to 5 p.p.m. of nickel under the conditions of the procedure given below.

TABLE 74

DETERMINATION OF NICKEL WITH DIMETHYLGLYOXIME (EFFECT OF VARIATIONS IN PROCEDURE AND OF SOME FOREIGN METALS)

Except as indicated, 10.0 γ Ni in 10 ml. 0.5 *N* hydrochloric acid, 0.3 ml. bromine water, 2–3 drops ammonia in excess, 0.5 ml. 1% dimethylglyoxime; final volume 25 ml. Green filter.

Variation in procedure	Ni found γ
Neutral nickel solutions	13.1
10 ml. 0.25 *N* HCl	10.0
1.0 ml. bromine water	9.3
0.50 g. NaCl	10.0
0.50 g. sodium citrate	Weak color
0.50 g. sodium citrate, 1 ml. bromine water	9.1
1.0 mg. Fe^{III}, 0.50 g. sodium citrate, 1 ml. bromine water (compared against similar standard)	11.5
0.2 mg. Cu	15.3
0.2 mg. Co	11.7

[11] Mitchell and Mellon state that the following ions (among others) do not interfere in the alcohol method when present in quantities 300 times that of nickel: acetate, arsenate, benzoate, bromide, chloride, citrate, fluoride, molybdate, nitrate, nitrite, oxalate, perchlorate, orthophosphate, pyrophosphate, sulfate, tartrate, tungstate, and the alkali metals. Many ions give precipitates under the conditions, among which may be mentioned: chlorostannate, iodide, vanadate, barium, iron, and other heavy metals giving precipitates with ammonia (but citrate should aid in keeping these in solution). Certain colorless ions (chlorate, selenate, thiocyanate, cadmium, calcium, zinc) interfere in large amounts. Auric, cobalt, and dichromate ions may not be present.

Copper and cobalt also give colors with dimethylglyoxime but these are so much weaker than the nickel color that these metals do not interfere if their amount is equal to, or less than, that of nickel. Citrate or tartrate is added to prevent the precipitation of iron, aluminum, and other metals. The light yellow solution of ferric iron in basic citrate or tartrate medium absorbs but slightly above 500 mμ (Fig. 55; see further, p. 477). Small amounts of manganese, molybdenum, vanadium, titanium do not interfere. Chromium leads to high results if present in appreciable amounts. The following procedure includes directions for the separation of nickel by chloroform extraction of nickelous dimethylglyoxime; this separation had best be used when minute amounts of nickel are to be determined in the presence of iron as well as other metals such as chromium which are likely to cause difficulty.

TABLE 75

DETERMINATION OF NICKEL WITH DIMETHYLGLYOXIME AFTER SEPARATION BY CHLOROFORM EXTRACTION OF THE DIMETHYLGLYOXIME COMPOUND

Foreign metals	Ni taken γ	Ni found γ
17.5 mg. Fe^{III}	5.0	4.8
		4.5
17.5 mg. Fe^{III}, 0.08 mg. Cu	2.5	2.5
17.5 mg. Fe^{III}, 0.25 mg. Cu, 0.13 mg. Co	2.5	2.7
17.5 mg. Fe^{III}, 2.5 mg. Mn^{II}	2.5	2.5
17.5 mg. Fe, 0.5 mg. Cr^{VI}, 0.13 mg. V^{V}	5.0	5.0
5 mg. Co[a]	5.0	4.5

[a] 3.5 ml. 1% dimethylglyoxime used in chloroform extraction.

Special Solutions

Dimethylglyoxime solution, 1 per cent in ethyl alcohol. The solution is stable.

Sodium citrate, 10 per cent in water.

Bromine water, saturated.

Chloroform, reagent quality.

Standard nickel solution, 0.00100 per cent in 0.1 *N* hydrochloric acid. It may be prepared from uneffloresced crystals of nickel chloride ($NiCl_2 \cdot 6H_2O/Ni = 4.05$) or from pure nickel metal.

§ Procedure

Extraction of Nickel. To 5–20 ml. of slightly acid solution, preferably containing 5 γ or more nickel, add 5 ml.[12] of sodium citrate and make slightly ammoniacal (a few drops of concentrated ammonia in excess). Add 2 ml. (or more if much cobalt is present) of dimethylglyoxime solution

[12] Or enough to keep iron (III), aluminum, etc. from precipitating.

and extract in a small separatory funnel with three 2 to 3 ml. portions of chloroform, shaking for one-half minute each time. Shake the combined chloroform extracts with 5 ml. of 1:50 ammonia, and run the chloroform into another separatory funnel; shake the water layer with a milliliter or two of chloroform and combine the latter with the washed extract.

Shake the chloroform solution vigorously for 1 minute with two portions of 0.5 *N* hydrochloric acid, each having a volume of 5 ml. (or slightly less if the solution is finally made up to 10 ml.). Transfer the hydrochloric acid solutions to a volumetric flask of suitable size (*cf.* Fig. 56), or to a color comparison tube if the standard series method is to be used. If a Duboscq colorimeter is to be used the nickel concentration should be greater than 1 γ per ml. Not more than 6 γ nickel should be present in 1 ml. of solution because above this concentration a precipitate may form.

Colorimetric Determination. Add 10 drops of bromine water[13] to the acid sample solution or an aliquot of it, and then concentrated ammonium hydroxide until the color of bromine is destroyed,[14] followed by an excess of 1 ml. Cool the solution below 30° if necessary and add 1 ml. of dimethylglyoxime solution. (The volumes specified are sufficient for final dilution to 25 ml.) Dilute to volume and determine the transmittancy within 5 minutes. The analyst has a choice of several possibilities in the selection of a wave length (Fig. 55). The minimum at *ca.* 540 mμ may be utilized; at 560 mμ the transmittancy changes less rapidly with time. Greater sensitivity can be had by making the measurement at 450 mμ. When a filter photometer is used, choose a green filter such as Corning No. 440 Signal Green. The standard nickel solutions for the establishment of the standard curve should have approximately the same original acidity as the sample solution. Run a reagent blank.

Alternative procedure with alcohol to stabilize color.[10] Transfer the slightly acidic solution (10 to 500 γ of nickel) to a 100 ml. volumetric flask, add 1 ml. of saturated bromine water, 4 ml. of concentrated ammonia, 35 ml. of 95 per cent ethyl alcohol, and 20 ml. of 0.1 per cent dimethylglyoxime in 95 per cent ethyl alcohol. Dilute to volume with water and obtain the transmittancy at 450 mμ within one-half hour. A Corning No. 440 Signal Green filter may be used with a filter photometer. Beer's law is valid up to 5 p.p.m. of nickel at least.

[13] If the amount of nickel present is greater than 1 γ per ml., add 1 ml. of saturated bromine water and allow to stand for 15 minutes before addition of ammonia (Eugene Ayres and Ralph O. Clark, private communication). Satisfactory results can then be obtained with as much as 5 γ of nickel per ml. If sufficient bromine is not present, nickelous dimethylglyoxime is precipitated.

[14] Sometimes the solution does not become entirely colorless because enough dimethylglyoxime may be present to give a visible reaction with the nickel.

B. The Diethyldithiocarbamate Method

Nickel diethyldithiocarbamate can be extracted with isoamyl alcohol (and other immiscible organic solvents) in which it shows a yellow-green coloration. Since the strongest absorption occurs at the edge of the ultraviolet, a spectrophotometer should be used in obtaining the transmittancy of the solution. The reaction is sensitive but not at all selective since copper, bismuth, and cobalt also yield extractable carbamates which are strongly colored. It is therefore necessary to separate nickel sharply from these metals before applying this method. The separation can be made by the dimethylglyoxime-chloroform extraction already described (p. 469). Detailed directions for carrying out this procedure have been published.[15] The authors state that copper, which is partially extracted in the preliminary dimethylglyoxime separation, is removed by washing the chloroform-nickel dimethylglyoxime extract with 1:50 ammonium hydroxide.

The final determination of the isolated nickel is made by adding 5 ml. of citrate buffer (20 per cent diammonium citrate containing sufficient ammonia to give a *p*H of 9–9.5 and then extracted with carbamate-carbon tetrachloride to remove traces of reacting metals) to 25 ml. of 0.5 *N* hydrochloric acid solution containing the nickel, making slightly alkaline with ammonia (10 drops in excess), adding 5 ml. of 0.2 per cent aqueous sodium diethyldithiocarbamate solution, and shaking for 2 minutes with 10 ml. of isoamyl alcohol. The extinction is measured at 385 mμ.

C. Other Methods

A photometric method for nickel may be based on the formation of a stable colloidal dispersion of nickelous dimethylglyoxime by the use of a protective colloid.[16] A similar method involves the use of 1:2 cyclohexanedione-dioxime.[17]

Nickelous dimethylglyoxime dissolves in pyridine to give a solution of yellow or orange-red color. It has been proposed to determine nickel in this way after drying the washed precipitate at 100°.[4]

Potassium dithiooxalate imparts a deep red coloration to neutral or slightly acid nickel solutions.[18] The reaction is highly sensitive and Beer's

[15] O. R. Alexander, E. M. Godar, and N. J. Linde, *Ind. Eng. Chem., Anal. Ed.*, **18**, 206 (1946).

[16] Wulff and Lundberg[9] improved the procedure of Juza and Langheim (p. 85), but do not consider the precision satisfactory.

[17] W. C. Johnson and M. Simmons, *Analyst*, **71**, 554 (1946). This paper contains procedures for the determination of nickel in steel and cobalt salts with this reagent. The nickel complex can be extracted by benzene (separation from much cobalt if the latter is converted into cobalticyanide and the excess cyanide is removed with formaldehyde).

[18] J. H. Yoe and F. H. Wirsing, *J. Am. Chem. Soc.*, **54**, 1866 (1932).

law is followed, but unfortunately the majority of the cations interfere by giving more or less strong colors. Among the noninterfering ions may be mentioned the alkali and alkaline earth metals, aluminum, phosphate and manganese, the latter in amounts less than 300 p.p.m. Both iron and cobalt give strong colors.

Potassium dithiocarbonate produces a red to brown color in ammoniacal nickel solution.[19] This reagent is inferior to potassium dithiooxalate.

Formaldoxime has also been used as a nickel reagent but has little to recommend it for general purposes.[20]

III. Applications of the Dimethylglyoxime Method

A. Silicate Rocks

§ Procedure

Weigh 0.25 gram of finely powdered basic rock (0.01 to 0.05 per cent nickel), or 0.5 gram or more of acidic rock, into a platinum dish, add a few milliliters of water, 0.5 ml. of 70 per cent perchloric acid, and 2.5 ml. of hydrofluoric acid (for a sample greater than 0.25 gram these amounts should be correspondingly increased). Evaporate the mixture almost to dryness, add another milliliter or two of hydrofluoric acid, evaporate to dryness, take up the residue in 0.5 ml. of perchloric acid and 2 or 3 ml. of water, and again evaporate to dryness. To the residue add 0.5 to 1 ml. of concentrated hydrochloric acid and 5 ml. of water. Heat to bring all soluble material into solution, add 5 ml. of 10 per cent sodium citrate solution, neutralize the cold solution with concentrated ammonium hydroxide using litmus paper, and add a few drops in excess. If there is an appreciable amount of precipitate or residue in the solution at this point, filter through a small paper, wash with small portions of water, and ignite the paper and its contents. Fuse the residue with approximately 0.1 gram of sodium carbonate, add an excess of dilute hydrochloric acid to the cooled melt, and heat to effect as complete solution as possible. Add 2 or 3 ml. of 10 per cent sodium citrate solution, make slightly ammoniacal, and reserve the solution.

To the main solution (filtrate from any insoluble material) add 2 ml. of 1 per cent alcoholic dimethylglyoxime solution, and shake vigorously for one-half minute with two or three portions of reagent-quality chloroform, each having a volume of 2 or 3 ml. In a similar manner extract the ammoniacal solution of the sodium carbonate melt. Combine all the chloroform extracts and shake vigorously with 5 ml. of 1 to 50 ammonium hydroxide solution. Draw off the chloroform, taking care that no drops of

[19] I. V. Lindt, *Z. anal. Chem.*, **53**, 165 (1914).

[20] G. Denigès, *Bull. soc. pharm. Bordeaux*, **70**, 101 (1932).

the aqueous phase accompany it, and shake the water layer with a milliliter or two of chloroform to recover any suspended drops of chloroform solution. Then proceed as described on p. 474.

B. Steel

The following method was developed primarily for the determination of relatively large amounts of nickel in steels.[21] It is stated that for nickel contents below 1 per cent the error does not exceed 0.02 per cent. The interference of iron is reduced to a minimum by adding tartrate and sufficient sodium hydroxide to give a pale yellow solution which absorbs but slightly above 500 mμ. Tartrate is superior to citrate as complex former because it permits the *p*H of the solution to be raised high enough to reduce the color of ferric iron without fear of precipitation of ferric hydroxide. Under the conditions of the procedure below, nickel gives a color which develops rapidly and is stable for 24 hours; minimum transmittancy is shown at 470 mμ. With a spectrophotometer giving a band width of 35 mμ, it is recommended that readings be made at a wave length of 530 mμ to minimize the effect of iron. Copper is stated to give a color intensity $^1/_{25}$ that of nickel, and cobalt slightly greater than $^1/_{100}$ that of nickel. Chromium, in amounts encountered in chromium-nickel stainless steels, was found not to interfere. Tungsten, vanadium, and molybdenum may be present.

§ Procedure

Decompose a 0.25 g. sample with 20 ml. of an acid mixture containing 135 ml. of concentrated sulfuric acid and 165 ml. of 85 per cent phosphoric acid per liter. (Samples containing little chromium may be dissolved in 1:1 nitric acid; stainless steels may require the use of hydrochloric acid.) Carefully add 10 ml. of 1:1 nitric acid and boil out oxides of nitrogen. Transfer the solution to a volumetric flask of suitable size and dilute to the mark with water. Transfer to a 100 ml. volumetric flask an aliquot containing 0.05 to 0.3 mg. of nickel. Add, with mixing after each addition, 5 ml. of 20 per cent tartaric acid, 5 ml. of saturated bromine water, 10 ml. of concentrated ammonium hydroxide, and 5 ml. of 1 per cent alcoholic dimethylglyoxime solution. After 1 minute add 10 ml. of 6 *N* sodium hydroxide solution and dilute to the mark. Determine the transmittancy at 530 mμ (or at 480–490 mμ if a spectrophotometer furnishing a narrow

[21] G. R. Makepeace and C. H. Craft, *Ind. Eng. Chem., Anal. Ed.*, **16**, 375 (1944). This method is a modification of an earlier procedure worked out by W. M. Murray and S. E. Q. Ashley, *Ind. Eng. Chem., Anal. Ed.*, **10**, 1 (1938). See further Wulff and Lundberg[9]; B. Jones, *Analyst*, **54**, 582 (1929); Alexander et al.[18] (final determination with diethyldithiocarbamate).

band of wave lengths is used) after 5 minutes. Construct the standard curve by treating similarly steel samples of known nickel content.

Notes. 1. The tartaric acid and dimethylglyoxime used must be pure. Not all C.P. products are satisfactory. Difficulties due to impure tartaric acid may be overcome by adding a second 5 ml. portion of bromine water, after introduction of dimethylglyoxime, to furnish the full color intensity. Impure dimethylglyoxime solutions, which cause fading of the nickel color, should be slightly acidified with sulfuric acid and treated with enough bromine water to impart a yellow color 15 or 30 minutes before use. The treated reagent is usable for a few hours only.

2. The amounts of tartaric acid, bromine water and dimethylglyoxime may be increased 100 per cent or decreased 25 per cent without affecting the results. Variations of 50 to 20 per cent in the quantity of ammonium hydroxide and sodium hydroxide are without significant effect.

3. The time elapsing between the addition of dimethylglyoxime and of sodium hydroxide (which arrests color development) is not critical if it exceeds 1 minute.

C. Bronze

After removal of metastannic acid by filtration and copper and lead by electrolysis, nickel can readily be determined by the dimethylglyoxime method of IIA.[22] A procedure based on the one given on p. 474 may be followed. In the absence of appreciable amounts of iron the transmittancy may be determined at 475 mμ (a blue filter such as Corning No. 556 is suitable).

D. Bio Materials[23]

The quantity of sample taken should preferably be such that 5 γ or more of nickel are present. The organic material is destroyed by acid digestion (see p. 385) or by ignition. The latter procedure will be satisfactory if the ash can be brought completely into solution with hydrochloric acid (*cf.* p. 15), but the digestion method is perhaps to be preferred. The acid solution is then treated with sodium citrate and excess ammonia, dimethylglyoxime is added, the nickel compound of the latter is extracted with chloroform as described on p. 473 and nickel is finally determined according to the general procedure on p. 474. The effect of copper can be disregarded if its amount is not greater than 50 to 100 times that of nickel.

[22] H. Seaman, *Ind. Eng. Chem., Anal. Ed.*, **16**, 354 (1944). See also G. Haim and B. Tarrant, *ibid.*, **18**, 51 (1946), who remove most of the copper by reduction to metal by hypophosphite.

[23] Detailed directions for the determination of traces of nickel in food products have been given by Alexander, Godar, and Linde.[15] Their procedure involves isolation of nickel by chloroform extraction of nickel dimethylglyoxime and final determination as the diethyldithiocarbamate (p. 475). The sample is decomposed by acid digestion. A procedure for nickel in organs of molluscs has been described by R. Paulais, *Compt. rend.*, **203**, 685 (1936).

CHAPTER XXXI

OSMIUM

I. Separations

The volatility of osmium tetroxide provides the best method for the separation of osmium from the platinum metals as well as other metals. The procedures that have been described for the distillation of decigram[1] and centigram-milligram[2] quantities of osmium and the recovery of osmium from the distillate do not work well when applied to microgram quantities, and modifications must be introduced. Experiments by the writer have shown that microgram amounts of osmium in the form of the tetroxide or as osmate can be distilled with satisfactory recovery by simply boiling off one-fifth of the original solution (5 *N* in nitric acid).[3] An all-glass distilling apparatus with a water-cooled condenser is used. The distillate is collected in 1:1 hydrochloric acid saturated with sulfur dioxide. Five or ten milliliters of this solution suffice for the collection of the distillate from 50 ml. of the original solution. The evaporation of the hydrochloric acid—sulfur dioxide solution has been found to lead to a loss of osmium, and the element must therefore be determined in this solution without concentration. The presence of sulfur dioxide does not cause interference in the subsequent photometric determination of osmium with thiourea. Although the latter reagent develops a yellow color with sulfurous acid, the transmittancy of the solution is hardly affected if a suitable green filter is used. Reducing substances in the solution from which osmium is to be distilled are destroyed by oxidation in sulfuric acid solution with a slight excess of potassium permanganate. The remaining permanganate and any higher manganese oxides formed are destroyed with a small excess of ferrous ammonium sulfate (about 50 mg. of the hydrated salt). If these are not destroyed, ruthenium will distil with the osmium. By

[1] R. Gilchrist, *Bur. Standards J. Research*, **6**, 421 (1931); R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

[2] J. J. Russell, F. E. Beamish, and J. Seath, *Ind. Eng. Chem., Anal. Ed.*, **9**, 475 (1937).

[3] In one experiment, 140 ml. of solution containing 12 γ of osmium were distilled according to the procedure given on p. 483 and it was found that approximately 70 per cent of the osmium was present in the first 10 ml. of distillate and 30 per cent in the second 10 ml. portion; no osmium was detectable in the third 10 ml. portion of distillate

applying the procedure described, quantities of osmium ranging from 7 to 40 γ could be recovered to the extent of 90 per cent or better from 50 ml. of solution (Table 76).

Osmium can be distilled but slowly from solutions in which it is present as chloroosmate, and the presence of chloride should therefore be avoided. If chloroosmate is present, it is preferable to distil from concentrated sulfuric acid to reduce the time required, or from concentrated sulfuric acid containing a small amount of nitric acid if ruthenium is absent. Osmium is not readily distilled from concentrated sulfuric acid alone if present as bromoosmate. Ruthenium will not distil from a nitric acid solution so long as the nitric acid concentration is less than 40 per cent by volume. The other platinum metals will not pass into the distillate, nor will they interfere with the volatilization of osmium tetroxide.

TABLE 76

COLORIMETRIC DETERMINATION OF OSMIUM AFTER DISTILLATION OF TETROXIDE

Addition			
Iron, Gram	Ru^{III} γ	Os taken, γ	Os found, γ
—	—	7.5	7
—	—	18.8	17
—	—	37.5	36
1	—	7.5	7
1	—	18.8	18
1	—	37.5	34
1	25	18.8	18
1	50	18.8	17
1	50	18.8	18
1	25	3.8	3

Osmium tetroxide can be extracted from aqueous solution by carbon tetrachloride. The partition coefficient

$$[OsO_4]_{CCl_4}/[OsO_4]_{H_2O}$$

has a value of approximately 12 for a dilute, neutral solution.[4] Since osmium tetroxide has weakly acidic properties, it is extracted less easily from basic solutions. In 0.059 *N* sodium hydroxide the partition coefficient is equal to 2.2, and in 0.028 *N* sodium hydroxide to 3.8. It should be possible to transfer osmium tetroxide from carbon tetrachloride to aqueous phase by using a strong solution of sodium hydroxide.

[4] D. M. Yost and R. J. White, *J. Am. Chem. Soc.*, **50**, 81 (1928). See also L. H. Anderson and D. M. Yost, *ibid.*, **60**, 1823 (1938); L. Chugaev and A J. Lukashuk, *Z. anorg. allgem. Chem.*, **172**, 223 (1928).

Osmium (IV) can be isolated by hydrolytic precipitation of the hydrous oxide. A 10 per cent sodium bicarbonate solution is added to the boiling solution until a precipitate appears and suddenly coagulates.[5] A few drops of bromphenol blue indicator solution are added and the addition of bicarbonate continued until the indicator becomes bluish (*p*H 4).[6] The solution is boiled for 5 minutes, the precipitate filtered off on an inorganic medium and washed with 1 per cent ammonium chloride.

It has been shown that small quantities (a few milligrams) of osmium can be collected in a lead button by fire assay.[7]

II. Methods of Determination

A. The Thiourea Method

Thiourea reacts with osmium as tetroxide or chloroosmate to give a soluble red complex. Chugaev[8] isolated a red compound $Os[(NH_2CSNH_2)_6]Cl_3 \cdot OH$ as one of the reaction products formed when sodium chloroosmate was heated with thiourea in slightly acid solution. This reaction has been used for the detection of osmium[9]; it may also be used for the determination of the element, but hardly any data are available on the quantitative application. The sample solution should be strongly acid and should be free from oxidizing agents. When osmium is present as the tetroxide in 2 or 4 *N* hydrochloric acid solution the color appears very shortly after the addition of thiourea, even at room temperature, and reaches full development in approximately five minutes.[10] On the other hand, when osmium is present as chloroosmate the red color appears only slowly on boiling. The addition of a little stannous chloride produces a rapid development of the color on heating in this case.

Ruthenium gives a blue color with thiourea (p. 529).

Directions are given below for the determination of osmium by thiourea in the absence of interfering substances (Procedure A) and in the presence of foreign substances which make necessary a separation of osmium as tetroxide (Procedure B).[10]

[5] Probably a little ferric iron can be added to give ferric hydroxide to gather very small amounts of hydrous osmium dioxide.

[6] The precipitation of osmium is complete in the *p*H range 1.5–6.3 (Gilchrist).

[7] J. J. Russell, F. E. Beamish, and J. Seath, *Ind. Eng. Chem., Anal. Ed.*, **9**, 475 (1937).

[8] L. Chugaev, *Z. anorg. allgem. Chem.*, **148**, 65 (1925).

[9] L. Chugaev, *Compt. rend.*, **167**, 235 (1918); R. Gilchrist, *Bur. Standards J. Research*, **6**, 421 (1931).

[10] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **16**, 342 (1944). For a recent study of the thiourea method, see G. H. Ayres and W. N. Wells, *Anal. Chem.*, **22**, 317 (1950).

Apparatus

There is required an all-glass distilling apparatus consisting of a round-bottomed flask (provided with an inlet tube for addition of reagents) which is connected by means of a ground-glass joint to a water-cooled condenser. The distilling apparatus used by Robinson, Dudley, Williams, and Byers,[11] for distilling selenium and arsenic from soil samples is suitable. In this apparatus the thistle tube for addition of reagent solutions

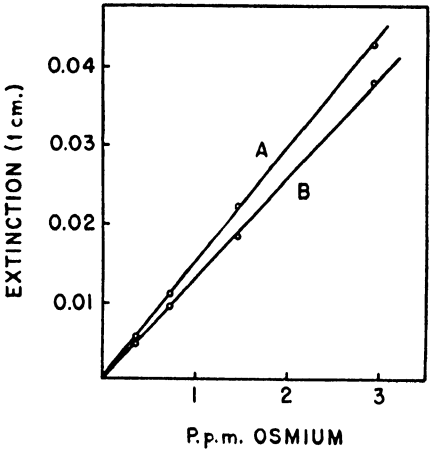


Fig. 57. Extinction-concentration curves for osmium tetroxide-thiourea solutions. *A*. 8 ml. 1:1 hydrochloric acid and 0.5 ml. of 10 per cent thiourea in total volume of 25 ml. *B*. Osmium tetroxide solution treated with 10 ml. of 1:1 hydrochloric acid saturated with sulfur dioxide, allowed to stand 15 minutes at room temperature, 0.5 ml. of 10 per cent thiourea solution added, and the whole diluted to 25 ml. with water.

is fused into a ground-glass connection, so that it is easy to remove any insoluble material from the flask at the end of the distillation and examine it for osmium. The distilling flask may have a volume of 250 to 500 ml.

Special Solutions

Osmium tetroxide, 0.005 per cent osmium in 0.1 *N* sulfuric acid. This solution is prepared by dilution of a stronger one, which may be obtained as follows: Make a number of scratches with a file on a 0.5-gram ampoule of osmium tetroxide and weigh the ampoule. Drop the ampoule into a glass-stoppered bottle (200 ml.) containing about 50 ml. of water. Break the ampoule by shaking the bottle, and when the osmium tetroxide has dissolved, decant off most of the supernatant liquid into a volumetric flask (250 ml., for example). Rinse the bottle well with successive portions of water and transfer these to the volumetric flask, taking care to leave all the glass fragments in the bottle. Then transfer the glass fragments to a weighed filter crucible and obtain the weight of the

[11] W. O. Robinson, H. C. Dudley, K. T. Williams, and H. G. Byers, *Ind. Eng. Chem., Anal. Ed.*, **6**, 274 (1934).

whole after drying. The weight of the osmium tetroxide used to prepare the stronger solution is thus obtained by difference.

Thiourea, 10 per cent aqueous solution.

Potassium permanganate, 5 per cent solution.

Hydrochloric Acid–Sulfur Dioxide Solution, 1 to 1 hydrochloric acid freshly saturated with sulfur dioxide.

§ Procedure A

Add 0.50 ml. of thiourea solution to about 10 ml. of sample solution which is 4 *N* in hydrochloric acid and which should preferably contain more than 10 γ of osmium; if osmium is present as chloro- or bromoosmate add also 0.10 ml. of 10 per cent stannous chloride solution in 1:4 hydrochloric acid. In the latter case heat the mixed solution in a water bath for 10 or 15 minutes; otherwise (with osmium present as the tetroxide) simply allow the solution to stand at room temperature for 5 minutes. Cool to room temperature and dilute with water to 25 ml. or a smaller volume if possible. Determine the transmittancy with the aid of a green or blue filter (540 mμ).

§ Procedure B

The sample solution should have a volume such that when it is ready for distillation, after addition of nitric acid and permanganate, the total volume is less than 50 or 60 ml. Chlorides must be absent, and if permanganate oxidation is necessary the solution should be about 1 *N* in sulfuric acid. Transfer the solution to the distilling flask, and if ferrous iron or other reducing substances are present, add potassium permanganate solution until an excess of a drop is present as indicated by the color change; avoid getting permanganate on the neck of the flask. Next add approximately 50 mg. of ferrous ammonium sulfate hexahydrate to destroy permanganate and higher oxides of manganese. The volume of the solution at this point should be 35 to 40 ml.

Add a few small grains of pumice, connect the flask to the condenser, and heat the solution slowly to near the boiling point to make certain that higher manganese oxides have been brought completely into solution. Dip the end of the condenser into 10 ml. of hydrochloric acid–sulfur dioxide solution contained in a 100-ml. graduate, the upper half of which has been cut off (a large vial or test tube marked to indicate 20 ml. may be substituted). Add 15 ml. of concentrated nitric acid through the inlet tube of the flask and distil at such a rate that 10 ml. of distillate are collected in 10 to 15 minutes. Transfer the distillate mixture to a 25-ml. volumetric flask, rinsing the condenser and receiver with a few milliliters of water, add 0.50 ml. of thiourea solution, and make up to the mark with water. Determine the transmittancy of the solution after 5 minutes (longer standing

does no harm), using green light. In constructing the standard curve add 0, 25, and 50 micrograms of osmium as the tetroxide to distillates obtained from osmium-free nitric acid mixtures as already described.

If the amount of osmium is likely to be less than 10 micrograms, use 5 ml. of hydrochloric acid–sulfur dioxide solution contained in a 25-ml. graduate for collecting 10 ml. of the distillate. Add 0.3 ml. of thiourea solution, read the volume of the solution in the graduate (which has been checked for accuracy), and determine the transmittancy as described above.

B. Other Methods

There are various organic compounds that give more or less sensitive color reactions with osmium and may find some quantitative application. Thus the following all react with osmium tetroxide: potassium thiocyanate (blue soluble compound in acid solution, extractable by ether or amyl alcohol),[12] ephedrine hydrochloride (orange color in sodium hydroxide solution, extractable by carbon tetrachloride),[13] thiocarbanalide (red color, extractable by ether),[14] tolidine, benzidine,[15] and tetramethyl-*p*-phenylenediamine.[16] See also p. 530.

Osmium (and also ruthenium) in the octavalent and quadrivalent states strongly catalyzes the reaction between arsenic (III) and cerium (IV) in acid solution, which normally proceeds with extreme slowness.[17] The same reaction is catalyzed by iodine and a photometric method for the determination of iodine based on the rate of reduction of cerium (IV) by excess arsenite has been described.[18] It may be expected that essentially the same method can be applied in the determination of osmium.[19] The catalytic effect of osmium is even stronger than that of iodine, being perceptible with a few thousandths of a microgram of osmium in 5 ml. of solution. Chloride reduces the catalytic power of osmium and its amount in the solution must be controlled.

[12] M. Hirsch, *Chem. Ztg.*, **46**, 390 (1922); W. Singleton, *Ind. Chemist*, **3**, 121 (1927).

[13] S. O. Thompson, F. E. Beamish, and M. Scott, *Ind. Eng. Chem., Anal. Ed.*, **9**, 421 (1937).

[14] L. Wöhler and L. Metz, *Z. anorg. allgem. Chem.*, **138**, 368 (1924).

[15] N. A. Tananaeff and A. N. Romanjuk, *Z. anal. Chem.*, **108**, 30 (1937). For a color reaction with ferrocyanide see this paper.

[16] L. M. Kul'berg, *J. Gen. Chem., U.S.S.R.*, **8**, 1139 (1938).

[17] K. Gleu, *Z. anal. Chem.*, **95**, 385 (1933).

[18] A. L. Chaney, *Ind. Eng. Chem., Anal. Ed.*, **12**, 179 (1940).

[19] J. J. Ivan has shown (unpublished investigation, University of Minnesota, 1940) that traces of osmium can be determined through the agency of its catalytic activity on the reaction mentioned by using the chronometric technique (*cf.* E. B. Sandell and I. M. Kolthoff, *Mikrochim. Acta*, **1**, 10 (1937). In this study use was made of the extractability of osmium tetroxide from aqueous solutions by carbon tetrachloride.

III. Application of the Thiourea Method: Determination of Osmium in Meteoric Iron

The osmium content of the iron-nickel phase of meteorites appears to lie in the range 1 to 10 p.p.m. When an attempt is made to determine osmium in the presence of metallic iron by dissolving the latter in dilute nitric acid in a distilling flask and then distilling the solution (p. 483), the results are markedly low. The reason for this is connected with the evolution of nitric oxide. (Presumably low results would also be obtained if an attempt were made to dissolve metallic lead, in which osmium has been collected by fire assay, in nitric acid and distilling.) This difficulty can be circumvented by dissolving the iron in sulfuric acid (with the help of hydrochloric acid), oxidizing ferrous iron with permanganate, and then distilling with nitric acid as described above. The application of this method to the determination of osmium in meteorites has not been investigated in a thorough manner, but judging from the results obtained with osmium added to ingot iron (Table 76) the procedure is feasible. A determination in the Cañon Diablo siderite was made as follows:

A 1-gram sample was heated near the boiling point with 10 ml. of 6 *N* sulfuric acid in an Erlenmeyer flask until there was practically no further action. The solution was decanted from the unattacked sample and reserved. The remainder of the metal was dissolved in 10 ml. of hot 6 *N* hydrochloric acid. The solution was then treated with 10 ml. of 6 *N* sulfuric acid and evaporated to fumes of sulfuric acid. The evaporation to fumes was repeated after dissolving the salts in water. The residue was then heated with about 10 ml. of water to bring all but a small amount of insoluble material into solution. This solution and the reserved sulfuric acid solution were transferred to the distilling flask and the ferrous iron was oxidized with permanganate. After addition of nitric acid, the solution was distilled and osmium was determined as described above (5 ml. of hydrochloric acid–sulfur dioxide solution were used to collect 10 ml. of distillate).

The small amount of insoluble material remaining in the solution after distillation was collected in a small porous porcelain filter crucible, the bottom of which had been covered with a thin layer of quartz powder to facilitate the subsequent removal of the insoluble material. The collected material was dried by washing with acetone, transferred to a nickel crucible, mixed with 1 gram of sodium peroxide, and heated at low redness for 30 minutes. The melt was extracted with 20 ml. of water and the solution heated near the boiling point to decompose peroxide. The solution was transferred to the distilling flask and treated with 10 ml. of 6 *N* sulfuric acid. Approximately 50 mg. of ferrous ammonium sulfate were added and the solution was heated to destroy nickelic oxide. Nitric acid was then added and the distillation made as already described. No osmium was detected in this distillate.

CHAPTER XXXII

PALLADIUM

I. Separations

For the isolation of palladium with the other noble metals by cupellation, reference must be made to the literature.[1]

Minute amounts of palladium can be coprecipitated with elemental tellurium obtained by reduction of a tellurite with stannous chloride or similar strong reducing agent. Palladium is probably carried down in the precipitate as the telluride. Gold, platinum, and presumably other platinum metals accompany palladium. This method is a very valuable one, because iron, copper, arsenic, etc. do not interfere. Tellurium can be volatilized from the collected precipitate by ignition. The procedure is described in detail on p. 491.

Very small quantities of palladium can be completely precipitated with hydrogen sulfide in the presence of lead.[2]

The slight solubility of palladium dimethylglyoxime and other oximes in dilute (0.25 *N*) mineral acid solution enables fairly small amounts of palladium to be separated from most other metals except gold[3] (platinum tends to contaminate palladium dimethylglyoxime). Such precipitation fails at the low palladium concentrations frequently encountered. Possibly the extractability of certain palladium oximes by organic solvents may find application in the separation of traces. Thus, palladium α-furildioxime can be extracted by chloroform.

According to Yoe and Overholser,[4] gold can be separated satisfactorily from palladium, preliminary to colorimetric determination of the latter, by extraction of chloroauric acid from hydrochloric acid solution by ether or ethyl acetate. The latter is said to be the more efficient extractant. The solution to be extracted should have as small a volume as conveniently

[1] J. Seath and F. E. Beamish, *Ind. Eng. Chem., Anal. Ed.*, **12**, 169 (1940).

[2] G. Lunde, *Mikrochemie*, **5**, 119 (1927), adds 0.1 g. lead acetate to 100 ml. of the 1 per cent acetic acid solution and precipitates hot, continuing the passage of hydrogen sulfide until the solution cools. Two micrograms of palladium could be recovered without loss.

[3] See, for example, F. E. Beamish and M. Scott, *Ind. Eng. Chem., Anal. Ed.* **9**, 460 (1937).

[4] J. H. Yoe and L. G. Overholser, *J. Am. Chem. Soc.*, **61**, 2058 (1939). See further p. 342 of this book.

possible (approximately 10 ml.) and should be about 6 *N* in hydrochloric acid. It is shaken with an equal volume of ether or ethyl acetate, the aqueous layer is drawn off and the organic solvent layer is washed with a few milliliters of 6 *N* hydrochloric acid. The washings are combined with the original solution and the extraction repeated once (for 5–10 mg. gold) or twice (for 20 mg. and more). The concentration of gold should then be reduced to the point where it will not interfere in the colorimetric method given on p. 488. The authors mentioned were able to determine 5 or 10 γ of palladium in the presence of 10 to 15 mg. of gold with an average error of about 10 per cent.

For the separation of palladium from platinum, the method of Gilchrist and Wichers[5] may be applied, in which palladium is precipitated hydrolytically as the hydrous dioxide. Rhodium and iridium accompany palladium. Yoe and Overholser use ferric hydroxide as a collector for the palladium precipitate. The procedure is as follows. Two or three tenths of a milligram of ferric iron and 100 mg. of sodium chloride are added to the solution and the latter evaporated to dryness. If the solution contains nitric acid, hydrochloric acid is added and evaporation to dryness is carried out several times. The residue is treated with 2–3 drops of hydrochloric acid and dissolved in approximately 25 ml. of water. The solution is heated to boiling and 2 ml. of 10 per cent sodium bromate solution are added, followed by 10 per cent sodium bicarbonate solution until cresol red just turns pink (the indicator is allowed to flow down the stirring rod to mix with adhering drop at the end). Two ml. more of sodium bromate solution are added and the boiling continued for 15 minutes. The precipitate is collected in a porous porcelain or sintered glass filter crucible and washed several times with small portions of hot 1 per cent sodium chloride solution of *p*H 6–7. The washed precipitate is dissolved in a few milliliters of hydrochloric acid, and if colorimetric determination of palladium according to the method described on p. 488 is to follow, the solution is evaporated to incipient dryness to remove the acid. This procedure permits the quantitative separation of as little as 2 γ of palladium from 20 mg. of platinum.

Silver cannot be separated satisfactorily from palladium by precipitation as chloride because of the strong coprecipitation of palladium, unless palladium is first converted into a tetrammine salt. This can be done[6] by treating the hot solution of the nitrates with ammonia until the precipitate first formed redissolves and the solution becomes colorless. The solution is then acidified with acetic acid and treated hot with a slight excess of dilute hydrochloric acid.

[5] R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

[6] W. R. Schoeller and A. R. Powell, *Analysis of Minerals and Ores of the Rarer Elements*. Griffin, London, 1940, p. 261.

II. Methods of Determination

A. Nitrosophenylamino Method

Compounds containing the *p*-nitrosophenylamino group, $p\text{-}NOC_6H_4N<$, form strongly colored complexes with palladous salts.[7] Thus *p*-nitrosodimethylaniline gives the bright red compound $Pd[NOC_6H_4N(CH_3)_2]_2Cl_2$ with palladium chloride in weakly acid solution. Both *p*-nitrosodimethylaniline and *p*-nitrosodiphenylamine may be used for the colorimetric determination of palladium.[7,8] The former reagent is preferable for the determination of palladium in pure solution, since it gives a color that

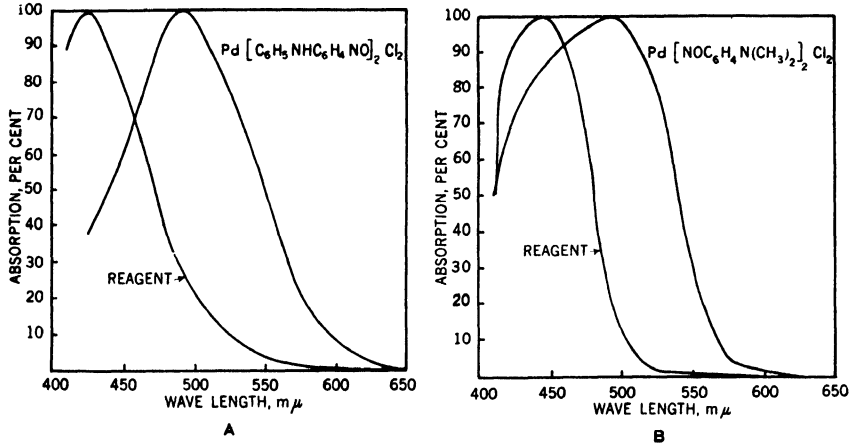


Fig. 58. Absorption curves of (A) *p*-nitrosodiphenylamine and its complex with $PdCl_2$, and (B) *p*-nitrosodimethylaniline and its complex with $PdCl_2$. (Overholser and Yoe.)

develops more rapidly and is more stable than that given by nitrosodiphenylamine, and moreover it is better suited for a spectrophotometric determination (*cf.* Figs. 58A and 58B). However in practical work the diphenyl compound may be the better reagent because of the higher limiting concentrations of iron, copper, and gold allowed by it. Neither reagent can be used in solutions having high neutral salt concentration (decrease in color intensity), the upper limits being 0.03 and 0.05 *M* in the case of sodium chloride for *p*-nitrosodiphenylamine and *p*-nitrosodimethylaniline respectively. The *p*H of the medium must be regulated fairly closely with both. The palladium complex yielded by nitrosodimethylaniline is more soluble than that given by nitrosodiphenylamine, which explains the longer period

[7] L. G. Overholser and J. H. Yoe, *J. Am. Chem. Soc.*, **63**, 3224 (1941).
[8] J. H. Yoe and L. G. Overholser, *J. Am Chem. Soc.*, **61**, 2058 (1939).

of time required for the latter reagent to give the maximum color intensity (formation of a colloidal suspension).

The procedures with the two reagents are similar, the only differences being in the *p*H of the solutions and the time of standing before color comparison. Both procedures are giver below. Oxidizing agents, cyanide, and iodide interfere. Quadrivalent platinum does not react with either reagent, but except in small amounts it interferes because of its color, and the same is true for the other platinum metals. Divalent platinum gives a sensitive color reaction very similar to that of palladium with the reagents. Gold reacts in much the same manner as palladium but much less sensitively. Silver naturally interferes, except in very low concentrations, by giving a turbidity in chloride solutions. Palladium can be determined in the presence of as much as 200 p.p.m. of silver with *p*-nitrosodiphenylamine as reagent by using a mixture of sodium acetate and nitric acid (pH 1.2) in place of sodium acetate-hydrochloric acid, and proceeding as described in (*2*) below.

1. General Procedure with p-Nitrosodimethylaniline

Solutions

p-Nitrosodimethylaniline. Dissolve 25 mg. in 50 ml. of 95 per cent ethyl alcohol and dilute to 100 ml. with water.

Sodium acetate–hydrochloric acid mixture. Dilute 80 ml. of 1 *N* hydrochloric acid and 200 ml. of 1 *M* sodium acetate solution to 1 liter with water. The *p*H of the mixture is about 4.8.

Standard palladium solution, 0.001 per cent palladium in *ca.* 1 *N* hydrochloric acid. The solution may be prepared by dissolving palladium metal in aqua regia and evaporating to dryness several times with hydrochloric acid.

§ Procedure

The sample solution should be substantially free from neutral salts (p. 488 and should be only slightly acid. Transfer an aliquot containing up to 10 γ of palladium to a 50 ml. volumetric flask, add 10 ml. of sodium acetate–hydrochloric acid mixture and 0.5 ml. of *p*-nitrosodimethylaniline solution, dilute to the mark with water, and mix. After 5 minutes determine the extinction of the solution at 525 mμ. Beer's law is obeyed up to a concentration of 1:5,000,000.

2. General Procedure with p-Nitrosodiphenylamine

Solutions

p-Nitrosodiphenylamine. Dissolve 5 mg. in 50 ml. of 95 per cent alcohol and dilute to 100 ml. with water.

Sodium acetate–hydrochloric acid mixture. Dilute 240 ml. of 1 *N* hydrochloric acid and 200 ml. of 1 *M* sodium acetate solution to 1 liter with water.

§ Procedure

Transfer a suitable amount of sample solution (substantially free from salts (p. 488) and only slightly acid), which may contain up to about 5 γ of palladium, to a 50 ml. volumetric flask. Add 10 ml. of sodium acetate–hydrochloric acid mixture and 1 ml. of reagent, and dilute to the mark with water. Mix and allow to stand at room temperature for 30 minutes but not longer than one hour. Obtain the extinction of the solution at 510–525 mμ.

If the standard series method is used, as little as 1 γ of palladium per square centimeter cross-section of solution will produce enough color for maximum accuracy in comparison.

B. Other Methods

Diethylaminobenzylidenerhodanine reacts with palladium in dilute hydrochloric acid solution to give a slightly soluble red complex which may be made the basis of a colorimetric method. Although very sensitive (in the neighborhood of 0.01 γ Pd per square centimeter in 0.08 *N* hydrochloric acid), this reaction is not very important from the practical standpoint because gold interferes even in the smallest amounts (p. 346) by giving a very similar color. Silver in small quantities is practically without effect if the reaction is carried out in dilute hydrochloric acid. The acidity has a strong effect and must be carefully regulated.

Phenoxthin, thioglycolic acid, and thiomalic acid produce yellow colorations with palladium (II).[9] Beer's law is followed in the range 1 to 10 p.p.m. of palladium. The thioglycolic acid compound shows maximum absorption at 325 mμ.

p-Fuchsin (*p*-rosaniline hydrochloride) has been used as a sensitive qualitative reagent for palladium; in weakly acidic medium the color of the reagent is bleached by palladium (II).[10]

Iodide develops a brown color with very dilute palladium solutions, but this reaction is of little importance in practical trace analysis.

III. Applications

Minute quantities of palladium can be determined in sulfide minerals, meteorites, etc. by first isolating the element by coprecipitation with tellurium and then applying the *p*-nitrosodiphenylamine method. Results obtained by the method given below are shown in Table 77. There is a slight loss of palladium in the procedure, but on the whole the results are satisfactory, especially when it is considered that large amounts of iron,

[9] O. König and W. R. Crowell, *Mikrochem. ver. Mikrochim. Acta*, **33**, 298, 300 (1948).
[10] P. W. West and E. S. Amis, *Ind. Eng. Chem., Anal. Ed.*, **18**, 400 (1946).

copper, nickel, arsenic, etc. may be present. Silver does not interfere to any serious extent if present in amounts of a few tenths of a milligram, but causes low results if present in larger quantities. If the gold content of the sample is less than 50 p.p.m. there is no interference from this element under the conditions of the determination. Small amounts of the other platinum metals are without effect.

TABLE 77

DETERMINATION OF PALLADIUM

Addition	Volume ml.	Amount of Te mg.	Pd taken γ	Pd found γ
	50	0.5	5.0	4.4
0.5 g. Fe	20	1.0	0.20	0.15
0.5 g. Fe	15	1.0	0.5	0.35
0.5 g. Fe	15	1.0	1.0	0.95
0.5 g. Fe	15	1.0	2.0	1.7
1.0 g. Fe	25	0.5	0.1	0.085
1.0 g. Fe	25	1.0	0.25	0.18
1.0 g. Fe	25	0.5	0.5	0.4
1.0 g. Fe	25	1.0	1.0	0.85
1.0 g. Fe	25	0.5	1.0	1.0
1.0 g. Fe	25	0.5	5.0	4.8
0.5 g. Ni	55	1.0	1.0	0.85
0.5 g. Ni	55	1.0	0.5	0.45
0.5 g. Ni	55	1.0	0.10	0.075
0.5 g. Cu	25	1.0	1.0	0.9
1.0 g. Fe, 0.05 mg. Ag	25	0.5	1.0	0.9
1.0 g. Fe, 0.2 mg. Ag	25	0.5	0.5	0.4
1.0 g. Fe, 2.0 mg. Ag	25	0.5	1.0	0.75
1.0 g. Fe, 1.0 mg. Ag	25	0.5	0.5	0.35

§ Procedure

Bring a 0.5 to 1 g. sample (0.1–5 p.p.m. of Pd) into solution by appropriate treatment, as for example with nitric and hydrochloric acids, and remove nitric acid and any other oxidizing agents by repeated evaporation with hydrochloric acid. The final solution may have a volume of 25 to 75 ml. and should be 2 to 3 *N* in hydrochloric acid.

Add tellurous oxide (hydrochloric acid solution, p. 349) equivalent to 0.5 mg. Te to the solution, and then while stirring or swirling the liquid add in the cold a 20 per cent solution of stannous chloride dihydrate in 2 *N* hydrochloric acid until a precipitate of tellurium appears, and finally an excess of 3 to 5 ml. for a volume of 50 ml. Heat the solution to boiling, and keep at the boiling point until the precipitate is well coagulated,

Filter through a small porous porcelain filter crucible (capacity about 7 ml.), and wash the precipitation vessel and crucible thoroughly with small portions of cold 1 *N* hydrochloric acid. Dissolve the precipitate in approximately 0.5 ml. of warm concentrated nitric acid which has first been poured into the precipitation vessel to dissolve any tellurium in it, followed by 1 ml. of concentrated hydrochloric acid. Allow the mixture to remain in the crucible for a few minutes and then draw it through, collecting the solution directly in a small silica or porcelain crucible. Wash the filter crucible with small portions of hot water.

Add 3 or 4 mg. of potassium sulfate to the combined filtrate and washings and evaporate the solution to dryness. Heat the crucible strongly over a Meker burner for 10 minutes to volatilize all of the tellurium, cool, add a drop of concentrated nitric acid and 2 or 3 drops of concentrated hydrochloric acid, and evaporate to dryness. Add approximately 1.5 ml. of 1:500 hydrochloric acid to the warm crucible, and allow to stand for a few minutes. If the solution is turbid, which is rarely the case, filter it through a small porcelain or sintered-glass filter crucible; otherwise transfer it directly to a 20 ml. flat-bottomed tube of about 1.5 cm. internal diameter. Add 50 mg. of potassium pyrosulfate to the crucible, heat at low redness for a few minutes and then strongly for 5 minutes or until practically all of the pyrosulfate has been decomposed into sulfate. To the cold melt add a drop of nitric acid and two or three drops of hydrochloric acid, evaporate to dryness, and finally heat the residue for about 5 minutes on a low temperature hot plate. Take up the residue in 1 ml. of 1:500 hydrochloric acid, filter through a small porcelain or glass filter crucible, wash with small portions of 1:500 hydrochloric acid, and add the washings to the tube containing the reserved solution. The total volume should be approximately 5 ml. The solution should show no color.

Prepare standards containing suitable amounts of palladium. Each tube should contain the same volume of 1:500 hydrochloric acid as the unknown, and potassium sulfate equivalent to 50 mg. of potassium pyrosulfate. The added potassium sulfate is preferably obtained by strongly igniting potassium pyrosulfate until practically all of the excess sulfur trioxide has been expelled. To the unknown and standard solutions add 3 ml. of hydrochloric acid–sodium acetate mixture (p. 489) and 0.10 ml. of *p*-nitrosodiphenylamine solution, mix, and compare the colors after one half to one hour.

CHAPTER XXXIII

PLATINUM

I. Separations

The metals of the platinum group, together with gold and silver, may be isolated from other elements by the general method of fire assay. This procedure has been used to isolate the most minute amounts of platinum and its congeners not only in sulfide minerals but also in silicates and silicate rocks.[1]

Platinum can be coprecipitated with elemental tellurium obtained by adding a suitable reducing agent to an acid solution containing tellurous acid.[2] The isolation of traces of platinum in this manner has not been studied from the quantitative standpoint, but since it has been shown that minute amounts of palladium (p. 486) and gold (p. 341) can be quantitatively coprecipitated with tellurium thrown down by stannous chloride, it may be expected that platinum will behave in the same manner. The tellurium in the precipitate can be volatilized by strong ignition and the residual platinum brought into solution with aqua regia.

Extraction of chloroplatinous acid with ether or ethyl acetate (p. 496) may be of value at times for separation of platinum from iron, copper, and many other metals.

Little attention has been paid to the separation of small amounts of platinum from large quantities of the other platinum metals. The general procedure for the separation of the platinum metals given by Gilchrist and Wichers[3] should be of service. In this procedure, osmium and ruthenium are first separated by volatilization of the tetroxides, and the residual solution is boiled in the presence of bromate at *p*H 8 to precipitate the hydrous oxides of palladium, iridium, and rhodium; platinum (IV) is left in solution. The precipitate must be redissolved and the precipitation repeated one or more times.

The separation of gold from platinum can be accomplished by precipitating gold with a reagent such as oxalic acid, sulfur dioxide, nitrous acid,

[1] G. Lunde, *Z. anorg. allgem. Chem.*, **161**, 1 (1927); *Mikrochemie*, **5**, 102 (1927). G. Lunde and M. Johnson, *Z. anorg. allgem. Chem.*, **172**, 167 (1928).

[2] For a study of the detection of platinum based on this separation see S. K. Hagen, *Mikrochemie*, **15**, 180 (1936). See also footnote 8.

[3] R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

or hydroquinone (p. 342) which does not reduce platinum to the metal (a reprecipitation is required however), or by extracting chloroauric acid with ether from a hydrochloric acid solution of Pt(IV) (p. 34). Silver may be separated by precipitation as chloride with a slight excess of hydrochloric acid, if the precipitate is dissolved in ammonia and again thrown down by acidification to release coprecipitated platinum.[4] Platinum will occur as the ammine compound in the filtrate from the reprecipitated silver chloride and in order to convert it into chloroplatinic acid, it is necessary to evaporate the solution, destroy ammonium nitrate with hydrochloric and nitric acids, evaporate to fumes with sulfuric acid and, after elimination of most of the latter, to treat with dilute aqua regia.

For the separation of platinum and the other platinum metals in the silver assay bead, see Beamish and Scott.[5]

Platinum and the other platinum metals except iridium can be adsorbed from very dilute acid solution with activated charcoal. Thus Wölbling,[6] using "carboraffin," was able to reduce the concentration of platinum, palladium, osmium, and ruthenium to 10^{-8} g. per liter of 0.01 *N* hydrochloric acid solution; the concentration of rhodium solution could be reduced to 10^{-7} g. per liter. Unlike the adsorption of gold and silver by charcoal, the adsorption of the platinum metals does not involve reduction to the respective metals, since the platinum metal salts can be washed out of the charcoal with hot concentrated sodium chloride solution or strong hydrochloric acid. The platinum metals are strongly adsorbed by silica gel from ammoniacal solution, but only slightly from acid solution.

According to Wölbling, platinum (and also iridium, rhodium, and ruthenium) can be quantitatively precipitated by ammonium hydroxide if a sufficient amount of ferric iron or aluminum is present.

II. Methods of Determination

The stannous chloride and the iodide methods for platinum described below have approximately the same sensitivity but the former method has the advantages of being generally freer of interference from other substances and of giving very rapid color development.

A. The Stannous Chloride Method

The yellow color which is obtained when stannous chloride is added to an acid solution of quadrivalent platinum is usually ascribed to chloroplatinous ion. The color intensity depends upon the hydrochloric acid concentration. A suitable final acidity is about 0.25 *N*. For a solution con-

[4] R. Gilchrist, *J. Research. Natl. Bur. Standards*, **20**, 749 (1938).
[5] F. E. Beamish and M. Scott, *Ind. Eng. Chem., Anal. Ed.*, **9**, 460 (1937).
[6] H. Wölbling, *Ber.*, **67**, 773 (1934); *Angew. Chem.*, **45**, 720 (1932).

taining 1 p.p.m. of platinum, it was found that the color intensity at a hydrochloric acid concentration of 1.25 *N* was three-fourths of that at 0.3 *N*, and at 0.05 *N* the intensity was less than half that at 0.3 *N*. The color development is so rapid at an acidity of 0.3 *N* that constant transmittancy is obtained by the time the solution has been mixed and the first readings can be made. The color is quite stable. Thus a solution containing approximately 1 p.p.m. of platinum gave the following extinctions at various times after the stannous chloride was added (procedure below): 5 minutes, 0.041; 20 minutes, 0.040; 1 hour, 0.040; 2 hours, 0.039; 4½ hours, 0.039; 24 hours, 0.040.

TABLE 78

DETERMINATION OF PLATINUM WITH STANNOUS CHLORIDE

(Final volume 50 ml. Transmittancy determined 5 minutes after mixing. Jena filter BG 12)

Pt present γ	Pt found γ
5	6
10	10.5
50	48
50 + 50 γ Pd	83
50 + 50 γ Rh	50
50 + 50 γ Ir	48.5
50 + 50 γ Ru	55.5
50 + 55 γ Au	54
50 + 50 mg. Fe (III)[a]	54
50 + 10 mg. Cu (II)	50

[a] 8 ml. 10% $SnCl_2\ 2H_2O$ solution for reduction.

The metal interfering most strongly is palladium, which gives a color nearly as intense as that of platinum.[7] Ruthenium gives a weak color under the conditions, and produces an error of about +10 per cent if present in an amount equal to platinum. Rhodium and iridium in low concentrations do not interfere seriously. Gold is precipitated as the metal but small amounts can be tolerated as Table 78 shows. Iron and copper in small quantities do no harm. In the presence of copper the platinum solution shows a greenish yellow instead of the normal orange-yellow color, but when a blue filter is used there is no appreciable error if the copper concentration is less than 200 p.p.m.

Chloroplatinous acid can readily be extracted with ethyl ether and ethyl

[7] H. Wölbling, *Ber.*, **67**, 773 (1934), avoids the interference of palladium by first making the sample solution ammoniacal, adding hydrochloric acid to make the acidity about 1 *N*, and then adding stannous chloride.

acetate[8] if the aqueous solution contains a sufficiently high concentration of hydrochloric acid, namely 1 *N* or greater. If 2 ml. of ethyl acetate are shaken with 10 ml. of a 1:9 hydrochloric acid solution containing 0.5 γ of platinum together with stannous chloride in a 1.8 × 15 cm. tube, the organic solvent layer shows a faint but distinct yellow color when examined transversely. Comparison of the color of the ethyl acetate layers of a series of

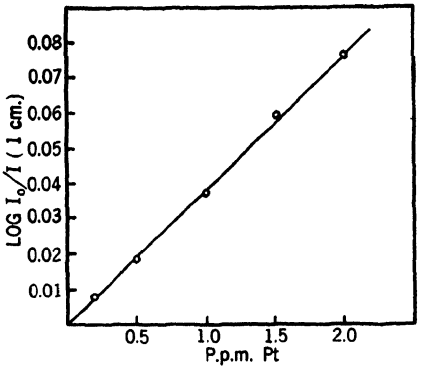


Fig. 59. Determination of platinum by the stannous chloride method (blue filter, Jena BG-12).

standards with the layer of a sample solution in this manner is a useful method for determining very small quantities of platinum.

Special Solutions

Stannous chloride, 10 per cent solution of the dihydrate in 2 *N* hydrochloric acid.

Standard platinum solution, 0.01 per cent. This is conveniently obtained by dilution of a 0.1 per cent solution prepared as follows. Heat 0.100 g. of pure platinum with a few milliliters of aqua regia until all has dissolved and evaporate the solution practically to dryness. Add 5 ml. of concentrated hydrochloric acid and 0.1 g. of sodium chloride and evaporate to dryness. Dissolve the residue in 20 ml. of 1:1 hydrochloric acid and dilute the solution to exactly 100 ml. Dilute this solution with 1:10 hydrochloric acid to give a 0.01 per cent solution.

§ Procedure

Transfer the sample solution, containing 25–100 γ of platinum, to a 50 ml. volumetric flask, add 10 ml. of 1:10 hydrochloric acid together with

[8] For the use of these extractants in the determination of platinum see N. A. Figurovskii, *Ann. secteur platine, Inst. chim. gén. U.S.S.R.*, No. 15, 129 (1938). N. S. Poluektov and F. G. Spivak, *Zavodskaya Lab.*, 11, 398 (1945), employ ethyl acetate to extract chloroplatinous acid after coprecipitation of platinum with metallic mercury produced by stannous chloride. Any tellurium in the precipitate is removed by heating with ammonium iodide. The lower limit of the method is reported as 0.03 p.p.m. of platinum with a 10 g. sample.

enough water to make the volume 30–40 ml. Then add 2.0 ml. of stannous chloride solution, dilute to volume with water, mix, and determine the transmittancy of the solution, using a blue filter. The standards should have the same hydrochloric acid concentration as the sample.

B. The Iodide Method

Iodide reacts slowly with chloroplatinate in slightly acidic medium to give a rose-colored solution of the iodoplatinate. A high acidity is undesirable because of the increased tendency toward liberation of iodine in such a medium. The color develops more rapidly if the solution is heated. The following elements, among others, must be absent: palladium, gold, iron, copper, and bismuth. Oxidizing agents liberating iodine, as well as reducing agents which reduce quadrivalent platinum, must not be present. Rhodium gives a color similar to that given by platinum, but only on long standing (more rapidly on heating).

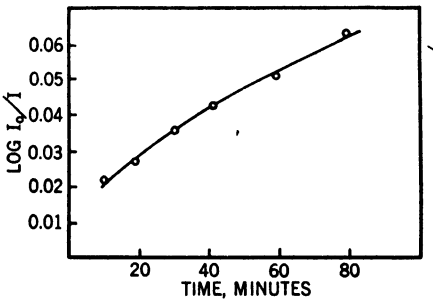


Fig. 60. Effect of time on color intensity in the iodide method for platinum (*ca.* 2 p.p.m. of Pt).

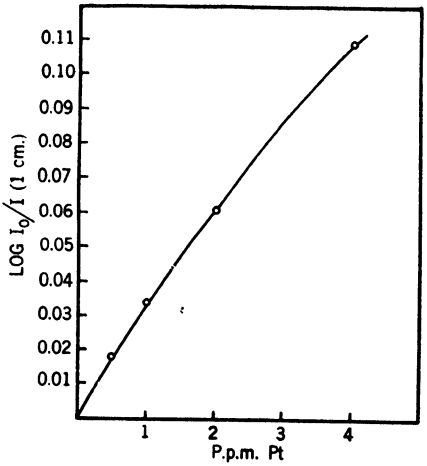


Fig. 61. Determination of platinum by the iodide method. Transmittancy determined after one hour with a blue-green filter.

§ Procedure

Transfer the neutral sample solution containing 25–300 γ of platinum (IV) to a 50 ml. volumetric flask and add 1.0 ml. of 1:10 hydrochloric acid and 1.00 ml. of 5 per cent potassium iodide solution. Dilute to volume with water and allow to stand for 1 hour or longer in the dark. Obtain the transmittancy of the solution with a blue-green filter.[9] The standard solutions must be allowed to stand for the same length of time as the sample.

[9] Iodoplatinate shows a minimum in its transmission curve at about 490 mμ.

CHAPTER XXXIV

POTASSIUM

The methods for the colorimetric determination of potassium are all indirect and require the isolation of the element as some slightly soluble compound containing a constituent capable of giving a strongly colored product with a suitable reagent. Two of these methods are described below. A third method involving precipitation of potassium as $K_2NaCo(NO_2)_6$ with sodium cobaltinitrite is usually of inferior accuracy because of the variable potassium/sodium ratio in the precipitate. Depending upon various factors such as the manner of precipitation, the sodium content of the solution, and the composition of the reagent, the ratio K/Na may be greater or less than 2. Under standardized conditions, and with sample solutions not showing too great a variation in sodium and potassium content, useful results can be obtained. Either the nitrite or cobalt content of the precipitate can be determined.[1]

When traces of potassium must be determined in the presence of large amounts of sodium, a preliminary separation from most of the latter will be required and can be obtained by precipitation with sodium cobaltinitrite in cold solution.[2] Separation of potassium as the perchlorate, based on the insolubility of the latter in various organic solvents,[3] should find application in the isolation or concentration of moderately small amounts of potassium in the presence of much sodium as well as of most other metals whose perchlorates are soluble under the conditions. In the determination of traces of potassium in certain heavy metal salts, electrolysis with a mercury cathode is a useful method of removing the heavy metal.

[1] For cobaltinitrite procedures see F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis* Van Nostrand, New York, 1936, p. 432. Also W. S. Hoffman, *Photelometric Clinical Chemistry.* Morrow, New York, 1941, p. 182. An exhaustive survey of the many methods proposed may be found in Fresenius and Jander, *Handbuch der Analytischen Chemie*, Part III, vol. Ia, p. 198 (1940).

[2] An even more insoluble precipitate can be obtained by using silver cobaltinitrite as precipitant to give $K_2AgCo(NO_2)_6$, when chloride is absent.

[3] The solubility of potassium perchlorate in ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol, and ethyl acetate is respectively 12, 10, 4.5, and 1.5 mg. per 100 g. of the solvent at 25° according to H. H. Willard and G. F. Smith, *J. Am. Chem. Soc.*, **45**, 286 (1923).

A. Chloroplatinate Method[4]

The gravimetric determination of potassium as chloroplatinate, based on the very slight solubility of the salt in alcoholic solution, has long been regarded as the standard method for macro and micro quantities of the element. Instead of weighing the precipitate one can readily determine its amount by dissolving it in water, adding stannous chloride, and measuring the intensity of the yellow color due to $PtCl_4^=$. Potassium iodide may be used in place of stannous chloride to give a wine-red solution ($PtI_6^=$), but then the solution must be allowed to stand for some time, since the color with iodide develops slowly.

The solubility of potassium chloroplatinate in alcohol-water solutions at 20° is as follows:[5]

Weight per cent C_2H_5OH	Gram K_2PtCl_6 in 100 g. solution
100	0.0009
90	0.0025
80	0.0085
70	0.0128

The precipitate of potassium chloroplatinate may be washed with 95 per cent alcohol saturated with the salt, after freeing the precipitate as much as possible from chloroplatinic acid. The temperature coefficient of solubility of potassium chloroplatinate in alcohol is small.

Apparatus

The precipitation and filtration of less than 1 mg. of potassium chloroplatinate is best made by microtechnique. The precipitate can be collected by centrifugation or by filtration with the use of a filter stick. A Pyrex filter stick with an asbestos plug, such as illustrated in Fig. 62, will be found very suitable. As precipitation vessel, a 5 or 10 ml. Pyrex beaker of ordinary form will serve.

The apparatus illustrated in Fig. 63 is recommended for filtration. It consists of a wide-mouth belljar (which may be obtained by cutting an ordinary 250 ml. wide-mouth bottle about 9 cm. from the top and grinding the cut edge smooth) resting on a plate of ground glass. If the surfaces are well ground it will not be necessary to use a lubricant on the plate to render the jar sensibly air-tight. The left-hand tube is connected to a suction line. The other tube should have a narrow bore and its ends should be drawn down as shown. The filter stick is connected by means of a short section of narrow rubber tubing.

Reagents

Chloroplatinic acid, 5 per cent platinum.

[4] For the application of the chloroplatinate method to the determination of potassium in biological samples see R. M. Tenery and C. E. Anderson, *J. Biol. Chem.*, **135**, 659 (1940); P. W. Salit, *ibid.*, **136**, 191 (1940).

[5] E. H. Archibald, W. G. Wilcox, and B. G. Buckley, *J. Am. Chem. Soc.*, **30**, 747 (1908).

Ethyl alcohol, saturated with potassium chloroplatinate. Shake 95 per cent alcohol with a small amount of pure potassium chloroplatinate at room temperature (preferably at the same temperature that the precipitation is made). Prepare only enough solution for daily use.

Stannous chloride, 10 per cent solution of the dihydrate in 2 *N* hydrochloric acid.

Standard potassium solution, 0.100 mg. K (0.191 mg. KCl) per ml.

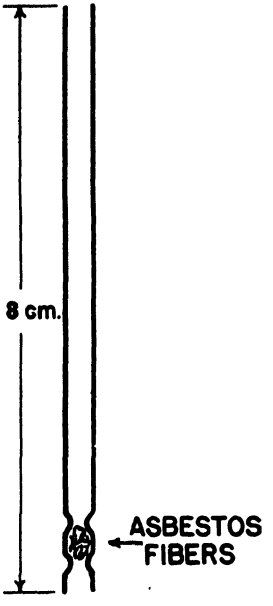


Fig. 62. Filter stick for use in the determination of potassium as chloroplatinate or dipicrylaminate.

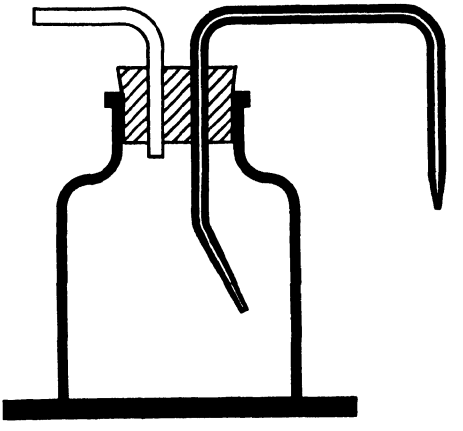


Fig. 63. Apparatus for filtration with a filter stick.

§ Procedure

The solution may conveniently contain from 0.02 to 0.3 mg. of potassium. Evaporate to a volume of a few drops, add 0.2 ml. of chloroplatinic acid, and evaporate to the point where a moist residue remains. Cool to room temperature and add 2 or 3 ml. of 95 per cent alcohol. Allow to stand covered at room temperature for 30 minutes, stirring at intervals. Draw off the liquid as completely as possible with a filter stick, and add *ca.* 0.5 ml. of alcohol saturated with potassium chloroplatinate in such a manner as to rinse the walls of the precipitation vessel. Draw off the alcohol and repeat the washing 2 or 3 times more. Allow the alcohol to evaporate completely, hastening the process if desired by warming at about 50°.

Add 5 ml. of hot water to the precipitation vessel to dissolve the precipitate and draw the solution through the filter stick over into a small beaker.

Wash with hot water until it is certain that all of the salt has been removed. Cool the solution to room temperature and transfer to a 25 ml. volumetric flask. Add 5 ml. of 1:10 hydrochloric acid, dilute to about 20 ml. if necessary, and add 1.0 ml. of stannous chloride.[6] Dilute to volume and obtain the extinction of the solution, using a blue filter. Obtain the standard curve by carrying known amounts of potassium through the procedure.

The above procedure can be used to determine potassium in the presence of comparable amounts of sodium. The upper limit of the quantity of sodium that may be present has not been ascertained.

Determination of potassium in soil extracts.[7] Evaporate the neutral ammonium acetate extract to dryness, add 10 ml. of aqua regia, evaporate to dryness, and repeat the aqua regia treatment to assure the destruction of ammonium salts and other nitrogen compounds. Add 5 ml. of 60 per cent perchloric acid and fume off the excess. Next add 0.5 ml. of concentrated sulfuric acid and heat to fuming to convert the salts to sulfates. Dissolve the residue in dilute hydrochloric acid, make up to volume, and transfer to a 50 ml. round bottom centrifuge tube an aliquot of the solution containing about 0.1 mg. of potassium (range 0.01 to 0.5 mg.). Evaporate to dryness. Then add 1 to 5 drops of concentrated hydrochloric acid (depending upon the amount of calcium sulfate present), 0.5 ml. of 1 per cent chloroplatinic acid, and 1 ml. of water. Evaporate to dryness on the steam bath; avoid prolonged heating after the residue is dry. Cool to room temperature, add 1 ml. of a 2 per cent suspension of talc (previously extracted with hydrochloric acid and washed with water) in 80 per cent alcohol. Wash the precipitate by centrifugation with 10 ml. of 80 per cent alcohol saturated with potassium chloroplatinate. Repeat three times. Finally drain the tubes by inversion and remove all alcohol by passing a stream of air through the tube. Dissolve the precipitate in water and complete the determination as described above.

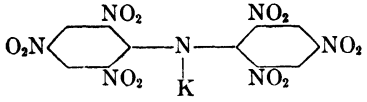
B. Dipicrylamine Method[8]

Potassium may be precipitated as the relatively insoluble red dipicrylaminate (hexanitrodiphenylaminate) by the addition of lithium, sodium,

[6] If it is desired to use iodide instead of stannous chloride to develop a color with platinum, acidify the aqueous solution of potassium chloroplatinate with 1 ml. of 1:10 hydrochloric acid, dilute to about 20 ml., add 1.0 ml. of 5 per cent potassium iodide solution, make up to 25 ml. and allow to stand for 2 hours in the dark before determining the transmittancy with a blue-green filter (490 mμ).

[7] C. Hurwitz and H. W. Batchelor, *Soil Sci.*, **63**, 351 (1947). These authors use iodide for the final colorimetric determination.

[8] I. M. Kolthoff and G. H. Bendix, *Ind. Eng. Chem., Anal. Ed.*, **11**, 94 (1939); J. Kielland, *Ber.*, **71B**, 220 (1938). For applications of the method in the determination of potassium in bio material see C. R. Harrington, *Biochem. J.*, **35**, 545 (1941); R. H. Cotton, *Ind. Eng. Chem., Anal. Ed.*, **17**, 734 (1945).



or magnesium dipicrylaminate to a neutral or slightly alkaline solution. The precipitate may be washed with ice cold water and a saturated aqueous solution of potassium dipicrylaminate, dissolved in acetone, and the solution made up to volume with dilute sodium hydroxide (to repress hydrolysis of the salt). This solution shows maximum absorption below 400 mμ. Beer's law is obeyed. The aqueous solution is quite stable, no perceptible change in color intensity occurring in a week.

TABLE 79

TYPICAL RESULTS OBTAINED IN THE COLORIMETRIC DETERMINATION OF POTASSIUM WITH DIPICRYLAMINE

Foreign ion	Potassium taken γ	Potassium found γ	Error γ
	10	9	−1
	30	31	+1
	50	50	0
	100	94	−6
	100	100	0
3 mg. Na	50	48	−2
3 mg. Na	25	36	+11
1 mg. Li	50	50	0
1 mg. Ca	50	54	+4

Rubidium, cesium, and thallium (I), as well as ammonium ion yield slightly soluble dipicrylaminates. Certain other metals (lead and mercury) are stated to give crystalline precipitates with sodium dipicrylaminate, and many other metals will, of course, be precipitated as hydroxides or basic salts by the alkaline reagent. Small amounts of metals yielding precipitates in basic medium may be removed by boiling the solution with a slight excess of magnesium oxide. Potassium can be determined directly in the presence of moderately large amounts of sodium, lithium, magnesium, and calcium (Table 79). Barium is markedly coprecipitated. The magnesium reagent is not suitable when phosphate is present and sodium dipicrylaminate (3 per cent) should then be substituted.

Special Solutions

Magnesium dipicrylaminate, 3 per cent. Add 100 ml. of water to 3 g. of dipicrylamine and 1.3 g. of magnesium oxide, mix well, allow to stand at room temperature for 15–20 hours and then filter. CAUTION: Dipicrylamine and its salts produce blisters when brought in contact with the skin.

Wash liquid (1). Water cooled to 0° C.

Wash liquid (2). Add excess potassium dipicrylaminate to water at room temperature, immerse the solution in ice water, stir at intervals, and draw off the supernatant liquid by means of a filter stick after a few hours.

§ Procedure

The following directions may be applied in the determination of 0.01 to 0.1 mg. of potassium.

Evaporate the solution to dryness in a suitable vessel, such as a 20 ml. Pyrex beaker. Add 3 drops of magnesium dipicrylaminate solution, place the beaker in ice water, and after not less than 15 minutes draw off the supernatant liquid (keep the beaker in the ice bath) with a filter stick which in this case may advantageously have the form shown in Fig. 62. The filter stick should be cooled to 0° C. before use. Wash the precipitate with 2 drops of wash liquid (1), then with 7–10 drops of wash liquid (2) (cooled to 0°), and finally with one drop of wash liquid (1).

Dissolve the precipitate in the filter stick by filling the portion above the asbestos with acetone (use a medicine dropper) and forcing the latter into the beaker in which the precipitation was made; repeat until the acetone runs through colorless. Dilute the acetone to 50–100 ml. (or any other convenient volume) with approximately 0.001 *N* sodium hydroxide solution in water. Compare or determine the color intensity in any convenient way. In transmission measurements use light of wave length 400 mμ or a suitable filter transmitting a narrow band in the blue or violet.[9] The standard solutions for comparison or the construction of the standard curve are prepared in the same manner as the sample solution.

Notes. 1. According to Amdur[9] it is not necessary to carry out the precipitation at 0°. One can work at room temperature if the reagent and wash solution have been saturated with potassium dipicrylaminate at the temperature at which the precipitation is made. By precipitating at room temperature, and omitting the washing with water, Amdur determined 100 γ of potassium with the respective errors 0, 0, and +1 per cent, and 50 γ with errors of +1 and +2 per cent.

2. If the amount of potassium is not too small, it may be determined indirectly by finding the amount of dipicrylaminate remaining in solution after precipitation. A procedure has been given by Amdur.[9]

[9] E. Amdur, *Ind. Eng. Chem., Anal. Ed.*, 12, 721 (1940), recommends a filter composed of 5.5 mm. of Corning glass No. 556 and 3.8 mm. of Corning No. 429. This filter gives practically a linear relation between extinction and concentration over a wide range of dipicrylaminate concentration.

CHAPTER XXXV

THE RARE EARTH ELEMENTS

I. Separations

The isolation of the rare earth elements has been investigated by Noddack[1] in connection with their determination in meteorites by X-ray spectrography. Since the procedure is of more or less general application and since it is stated that amounts of the rare earth elements in the range 1–10 p.p.m. can be quantitatively isolated in this way, an outline of the Noddack procedure will be given. The silicate sample (100 g.) is treated with hydrofluoric acid and evaporated to dryness to eliminate silica. The residue is evaporated to fumes several times with sulfuric acid to remove fluorine, and water is added to extract all soluble matter. The mixture is filtered and the filtrate (solution 1) reserved. The residue consists chiefly of calcium sulfate containing a sizable fraction of the total amount of the rare earths present. The calcium sulfate residue is boiled with sodium carbonate to transform it into calcium carbonate which is filtered off and dissolved in hydrochloric acid. To this solution is added the hydrochloric acid solution of the ammonia precipitate obtained from the filtrate from the calcium carbonate precipitation by acidifying and adding an excess of ammonia. The combined solutions are precipitated with ammonia to throw down iron, chromium, etc. together with the rare earths. The precipitate is dissolved in acid and the ammonia precipitation is repeated to eliminate calcium. The precipitate is dissolved in acid and the solution (2) reserved.

The main solution (1), containing magnesium, most of the iron, aluminum, nickel, chromium, the rare earths, etc. is treated with ammonia to separate iron and the other precipitable elements from calcium, magnesium, and nickel. The precipitate is dissolved and again thrown down. The hydroxides of iron, the rare earths, etc. are dissolved in hydrochloric acid and iron is removed by extraction of ferric chloride with ether from the acid solution. The metals remaining in solution are precipitated with ammonia, and aluminum is dissolved out of the precipitate with dilute sodium hydroxide. The residue is dissolved in acid, chromium is oxidized to the sexivalent state, and an ammonia precipitation is made to separate the rare

[1] Ida Noddack, *Z. anorg. allgem. Chem.*, **225**, 337 (1935).

earths and other precipitable elements from chromium. The slightly acidic solution of the precipitate is treated with hydrogen sulfide to precipitate lead and other sulfide-forming elements. Then another ammonia precipitation is made to separate any manganese that may still be present. The solution of the precipitate of the hydrous oxides is combined with solution (2) above.

This solution contains all of the rare earth elements together with more or less iron and manganese, and most of the titanium originally present. Titanium is volatilized by repeated evaporation with hydrofluoric acid, and most of the residual iron is removed by ether extraction of ferric chloride. The rare earths are thus left with a few milligrams of the major constituents of the sample. By repetition of the precipitations in a very small volume, practically all of the remaining amounts of most of the foreign elements can be eliminated; or, the rare earths can be precipitated as the fluorides or oxalates (see below).

The method of concentration described above depends upon the precipitation of the rare earth hydroxides by ammonia, with a slightly soluble hydrous oxide such as that of iron.[2] Other important separation reactions are those with oxalic and hydrofluoric acids. The oxalates and fluorides of the rare earth elements and thorium are but slightly soluble in dilute solutions of the respective acids. Fluoride precipitation gives more complete separation than oxalate precipitation according to Hillebrand. Ferric iron, titanium, zirconium, aluminum, uranium (VI), columbium, and tantalum remain in solution when an excess of hydrofluoric acid is used. When it is a matter of precipitating the rare earth elements as fluorides or oxalates from very dilute solutions, a collector must obviously be used. The corresponding slightly soluble calcium or strontium salts should be suitable collectors. The trivalent ionic radii (Goldschmidt) in the series La—Eu range from 1.22 to 1.13 Å., and in the series Gd—Lu from 1.11 to 0.99 Å. (the radius of yttrium ion is 1.06 Å). The ionic radii of calcium and strontium are respectively 1.06 and 1.27 Å. It is known that calcium and yttrium fluorides form mixed crystals. Strontium fluoride may be expected to be better than calcium fluoride for gathering lanthanum fluoride. These fluoride precipitates are not very easy to filter and wash. The

[2] The rare earth hydroxides (especially of the more basic earths) require an excess of ammonia for complete precipitation, and much ammonium salt is harmful (R. C. Wells, quoted in W. R. Schoeller, *Analytical Chemistry of Tantalum and Niobium*, Nordeman, New York, 1937, p. 166). Low concentrations of the elements cannot be precipitated unless a collector is used. Solutions should be cooled before filtration. Tannin facilitates the hydroxide precipitation (Schoeller). In sodium hydroxide solution some of the rate earth hydroxides (lutecium, also scandium) are appreciably soluble.

oxalate precipitates are easier to handle, and should also be useful for collecting the rare earth metals, but few data on this point are available.[3]

Europium, samarium, and ytterbium can be extracted from aqueous medium by shaking with sodium amalgam.[4]

For the separation of the rare earths from each other by ion-exchange on synthetic resins see a series of papers in the November, 1947, number of the *Journal of the American Chemical Society*.

Among other separation methods possibly useful for isolating small amounts of the rare earth elements, may be mentioned the extraction of the thiocyanates from aqueous solution with butyl alcohol.[5]

Electrolysis with a mercury cathode is useful for removing large quantities of many heavy metals (p. 31).

II. Methods of Determination

For the determination of cerium (IV) see p. 251.

A. By the Colors of the Rare Earth Ions in Aqueous Solution

Solutions of lanthanum, cerium (III), gadolinium, terbium, and yttrium salts are colorless, showing no appreciable absorption in the range 350–1000 mμ. The other elements show more or less strong absorption bands in this range (*cf.* Fig. 6), and can thus be determined spectrophotometrically. A very narrow band of wave lengths must be used, because the absorption maxima of the solutions of the rare earth salts are very sharp. Unfortunately the sensitivity is not great, so that the method is of limited value in trace analysis. The original sample must be large if this method is to be applied to material low in the rare earths. The spectrophotometric

[3] I. D. Borneman-Starynkevich, S. A. Borovik, and I. B. Borovskiĭ, *Doklady Akad. Nauk, S.S.S.R*, **30**, 227 (1941), have isolated the rare earths as a group by coprecipitation with calcium oxalate preparatory to determination spectrographically (in soils and plant ash). H. Lux *Z anorg. allgem. Chem.*, **240**, 21 (1938), also made use of calcium oxalate as a collector for the rare earth elements in determining them in bones. A lengthy procedure was then followed in removing phosphate, calcium, iron, etc. Only about one-third of the original quantity of the earths was recovered. W. O. Robinson, *Soil Sci.*, **56**, 1 (1943), applied oxalate precipitation of the rare earths in isolating them from plant ash and soil. According to Robinson (private communication) difficulties are encountered in applying the fluoride separation because of the formation of slightly soluble aluminum fluoride hydrate, and he therefore prefers the oxalate separation. For the isolation of rare earths in phosphate rock see Robinson, *Soil Sci.*, **66**, 317 (1948).

[4] J. K. Marsh, *J. Chem. Soc.*, **1942**, 398.

[5] D. B. Appleton and P. W. Selwood, *J. Am. Chem. Soc.*, **63**, 2029 (1941). Fractional extraction with immiscible solvents was first applied by W. Fischer, W. Dietz, and O. Jübermann, *Naturwiss.*, **25**, 348 (1937).

method has been studied by Rodden,[6] who used solutions of the rare earth nitrates. See the summary in Table 80 which also contains some data of Spedding. Beer's law is generally followed. Deviations that are observed with praseodymium and samarium may be due to insufficiently monochromatic light. Slight absorption by another rare earth at the wave length at which the element being determined absorbs strongly may be corrected for by finding the amount of the interfering element from its absorption at the wave length of minimum transmittancy.

TABLE 80

SPECTROPHOTOMETRIC DETERMINATION OF THE RARE EARTH METALS AS NITRATES

Element	Suitable wave lengths, mμ	Sensitivity, $\gamma/cm.^2 \equiv 0.001E$	Remarks
Pr	446	23	Sm absorbs at this wave length, but Nd only slightly.
Nd	521		Less sensitive than 798 mμ; Er interferes.
	740		
	798	9	Pr and Sm do not interfere; Dy interferes
Sm	402	45	Nd and Pr interfere slightly.
Eu	396	150	Sm must be absent.
Gd	273		
Dy	910	50	Ho, Yb and Er (slightly) absorb at this wave length.
Ho	643	50–60	Tm and especially Er absorb.
Er	521	90	Ho and Tm (slightly) absorb.
	653	90	Tm and especially Ho absorb.
Tm	684	40–50	Ho and Er absorb slightly.
Yb	950	—	Dy and Er (slightly) absorb; less sensitive than 973 mμ.
	973	50	Dy absorbs (less than at 950 mμ); Er also interferes.

B. By Fluorescence

Various members of the rare earth group can be detected and determined by the fluorescence exhibited in liquid and solid solution. Both trivalent and divalent rare earth ions fluoresce under suitable conditions of excitation. The fluorescence of the trivalent ions will be considered first. Haitinger[7] made use of the fluorescence of certain of the rare earths in borax or phosphate beads for their detection. An iron arc was used for excitation. Cerium is the only element of the cerium earths that fluoresces; it

[6] C. J. Rodden, *J. Research Natl. Bur. Standards*, **26**, 557; **28**, 265 (1942). *Cf.* F. H. Spedding et al., *J. Am. Chem. Soc.*, **69**, 2817 (1947).

[7] M. Haitinger, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt.* **IIA**, **142**, 339 (1933).

gives a blue color in a borax bead. Europium, samarium, and gadolinium give strong red, reddish yellow, and orange-yellow colors, respectively. Dysprosium fluoresces an intensive yellow, thulium a violet-blue, and holmium a weak yellow. *Cf.* also Table 81. No fluorescence was noted with lanthanum, praseodymium, erbium, ytterbium, and lutecium. Metals other than the rare earths show a fluorescence in the borax bead according to Haitinger—copper and gold yellow, manganese rose and tin light yellow; the fluorescence spectra of these are continuous. In addition, a yellowish green fluorescence is shown by uranium under the same conditions (*cf.* p. 597).

TABLE 81

FLUORESCENCE OF THE RARE EARTH ELEMENTS IN BORAX BEADS EXCITED WITH AN IRON ARC

Element	Character of spectrum	Limiting concentration in bead
Ce	Continuous, maximum intensity at 450 mμ	1:10,000
Eu	Three bands in red, orange and yellow	1:500
Sm	Bands in red (2), orange, yellow, green and blue-green	1:1000
Tb	Bands in red, orange, green, and blue-green	1:5000
Dy	Narrow band in orange, broad band close by in yellow	1:1000
Tm	Broad band in the blue	
Ho	As for Dy, but weaker	

For the detection of the rare earths by fluorescence after incorporation in calcium tungstate see the work of Servigne.[8]

Terbium, cerium (III), and europium may be determined in *aqueous solution* by their fluorescence spectra; the respective limits are 10^{-6}, 10^{-5}, and 10^{-2} per cent.[9] Gadolinium gives only a weak fluorescence.

Przibram and others[10] have studied the fluorescence of divalent rare earth ions in the lattice of calcium fluoride and other substances. Europium (II) in calcium fluoride shows a blue fluorescence (center of band at 429 mμ), and ytterbium (II) in the same host gives a yellow-green fluorescence (570 mμ) at liquid-air temperature. The divalent ions may be

[8] M. Servigne, *Ann. chim. anal. chim. appl.*, **22**, 273 (1940).

[9] A. Zaĭdel, Y. Larionov, and A. N. Filipov, *J. Gen. Chem., U.S.S.R.*, **8**, 943 (1938). According to L. Mazza, *Ann. chim. applicata*, **30**, 47 (1940), the fluorescence of cerous ion is excited by radiation in the range 350–410 mμ; nitrate and ferric ion inhibit the fluorescence.

[10] K. Przibram, *Mikrochim. Acta*, **3**, 69 (1938); further references will be found in this paper.

obtained by exposing the preparation to radium radiation and also to X-rays and short-wave ultraviolet. Divalent europium in sodium chloride also gives a blue fluorescence. In this case it suffices to heat the sodium chloride crystals (obtained by evaporation from a solution containing trivalent europium) to 300° to reduce the europium and produce fluorescence on exposure to ultraviolet radiation from a quartz lamp. The concentration limit of detection of europium by this procedure is of the order 10^{-6}. Since the fluorescence can readily be observed with 1 mg. of sodium chloride, as little as 0.001 γ of europium is detectable. Samarium (II) in anhydrous calcium sulfate, exposed to radium radiation, shows a red fluorescence band (619 mμ). The limit of detectability is 5×10^{-8}. The limit is even lower with calcium fluoride, for it was found that calcium fluoride prepared from the purest calcium salt still gave a red fluorescence. Thulium in calcium sulfate gives a red fluorescence (same band position as for samarium) at liquid-air temperature. One part of thulium in 10^8 parts of calcium sulfate gives a distinct fluorescence. It remains to be seen what practical analytical use can be made of these interesting phenomena.

C. Other Methods

Various lake-forming reagents may be used for the detection and presumably for the determination, of the rare earth elements. For example, addition of quinalizarin, followed by sodium hydroxide, to a rare earth solution produces a blue color, or blue precipitate. The following approximate limiting concentrations have been found[11]: Ce, 1:1,000,000; La, 1:500,000; Nd, 1:2,000,000; Pr, 1:1,000,000; Th, 1:150,000; Zr, 1:150,000 (all on the test tube scale).

Sodium alizarinsulfonate gives a violet color with lanthanum in acetate-buffered solution.[12] After 10 hours or more flocculation takes place. The determination is carried out by adding 1 ml. of buffer (2 *N* in ammonium acetate and in acetic acid) and 0.4 ml. of 0.1 per cent sodium alizarinsulfonate to 10 ml. of the virtually neutral lanthanum solution, and comparing against freshly prepared standards. From 0.1 to 2 p.p.m. of lanthanum can be determined. Many other metals react or interfere under these conditions.

Cochineal has been recommended as a color reagent for the rare earths.[13] When cochineal tincture is added to a neutral earth solution, a red-violet color is obtained. Thorium gives a blue color, and various other metals also react with the production of different colors or colored precipitates. The limiting concentration for the rare earth metals is stated to be 10 γ

[11] A. S. Komarovsky and I. M. Korenman, *Z. anal. Chem.*, **94**, 247 (1933).
[12] I. M. Kolthoff and R. Elmquist, *J. Am. Chem. Soc.*, **53**, 1217 (1931)
[13] G. Beck, *Mikrochemie ver. Mikrochim. Acta*, **27**, 49 (1939).

per ml. On addition of dilute acetic acid, the violet color becomes reddish orange with the cerite earths (lanthanum-samarium). Terbium and the erbium earths require stronger acetic acid to change the violet color to red, and a change to the original reddish orange of the cochineal takes place only when quite concentrated acetic acid is used.

The rare earth metals can be precipitated as phosphate, the washed precipitate dissolved in hydrochloric acid, and phosphorus in the solution determined by the molybdenum blue method to give an indirect determination of the rare earth.[14]

[14] E. Bamann and E. Heumüller, *Ber.*, **75**, 1514 (1942).

CHAPTER XXXVI

RHENIUM

Considerable work has been done on the colorimetric determination of rhenium, and satisfactory methods now exist for its determination, particularly in the presence of molybdenum.

I. Separations

A. Volatilization and Precipitation Methods

A good method for the separation and isolation of small amounts of rhenium is based on volatilization of the element as the heptoxide from a hot acid solution of high boiling point. The volatilization or distillation can be carried out in a number of ways. In one procedure (described on p. 519) a sulfuric acid solution is steam distilled at 270° C.,[1] and in another, a sulfuric acid or perchloric acid solution containing hydrochloric or hydrobromic acid is distilled.[2]

Small amounts of molybdenum may accompany the rhenium into the distillate, apparently mainly as a result of mechanical carrying over. The colorimetric method used in the subsequent determination must therefore be one in which small amounts of molybdenum may be tolerated, unless a further separation is made. Such a separation can be effected with α-benzoinoxime, which precipitates molybdenum in rather strong (4 to 7 N) sulfuric acid medium.[3]

For the isolation of small amounts of rhenium in the distillate obtained by the procedure mentioned above, hydrogen sulfide precipitation with arsenic sulfide[4] as collector may be used. Hoffman and Lundell[2] give the following directions. Neutralize the distillate (100 ml.) with ammonia,

[1] C. F. Hiskey and V. W. Meloche, *Ind. Eng. Chem., Anal. Ed.*, **12**, 503 (1940); L. C. Hurd and C. F. Hiskey, *ibid.*, **10**, 623 (1938). The distillation method of Geilmann and Weibke, *Z. anorg. allgem. Chem.*, **199**, 120 (1931), involves passage of a mixture of hydrogen chloride and carbon dioxide through a strong sulfuric acid solution.

[2] J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **23**, 497 (1939). Very little molybdenum accompanies rhenium if the distillation is made from hydrobromic-perchloric-phosphoric acid medium. *Cf.* Table 8.

[3] A. D. Melaven and K. B. Whetsel, *Anal. Chem.*, **20**, 1209 (1948).

[4] N. S. Poluektov, *J. Applied Chem., U. S. S. R.*, **11**, 534 (1938), uses osmium sulfide (from added osmium tetroxide) to collect traces of rhenium by hydrogen sulfide precipitation.

add 3 ml. of concentrated sulfuric acid and 5 mg. of trivalent arsenic, and saturate with hydrogen sulfide. Allow the solution to stand overnight, then filter, and, without washing, dissolve the precipitate in ammonium hydroxide containing hydrogen peroxide. Evaporate to dryness and determine rhenium according to IIA.[5]

B. Extraction Methods

An extraction method that has been found useful in effecting a fairly sharp separation of much molybdenum from minute quantities of rhenium makes use of the reduction of molybdenum to the quinquevalent condition by mercury in a solution of regulated acidity and the extraction of molybdenum (V) thiocyanate by ether. Rhenium is not reduced and remains in the aqueous phase. This procedure is the basis of the colorimetric determination given below (p. 516) and details will be found there. Joint isolation of small quantities of molybdenum and rhenium can be carried out by ether extraction after addition of thiocyanate and stannous chloride (see p. 521).

A sharp separation of rhenium from molybdenum can be obtained by extracting the former as tetraphenylarsonium perrhenate by chloroform.[6] The following equilibria are involved:

$$R_4As^+ + Cl^- \rightleftharpoons (R_4AsCl)_{CHCl_3} \qquad \frac{[R_4As^+][Cl^-]}{[R_4AsCl]_{CHCl_3}} = 5 \times 10^{-3}.$$

$$R_4As^+ + ReO_4^- \rightleftharpoons (R_4AsReO_4)_{CHCl_3} \qquad \frac{[R_4As^+]\,[ReO_4^-]}{[ReAsReO_4]_{CHCl_3}} = 5 \times 10^{-7}$$

Combination of the two equilibrium expressions gives:

$$\frac{[R_4AsReO_4]_{CHCl_3}}{[ReO_4^-]} = 10^4 \times \frac{[R_4AsCl]_{CHCl_3}}{[Cl^-]}.$$

Since the reagent is extracted into the chloroform as the chloride, increase of the chloride ion concentration in the aqueous phase diminishes the concentration of tetraphenylarsonium ion therein and consequently less rhenium partitions into the chloroform. If the concentration of tetraphenylarsonium chloride in the aqueous phase is made 0.01 *M* (the solubility of the reagent in water is 0.072 *M*) and the chloride concentration is 0.1 *M* the ratio of the concentration of rhenium in the chloroform to that in the aqueous phase will be 1000, a very favorable extraction coefficient. Since both tetraphenylarsonium chloride and tetraphenylarsonium perrhenate

[5] The reliability of this procedure is attested by the following results obtained by Hoffman and Lundell. In one analysis, 10 γ of rhenium were added to the distillation flask and 20 γ molybdenum to the resulting distillate; 9 γ of rhenium were found. In another trial, 5 γ of rhenium (with 200 γ added molybdenum) were taken and 4.5 γ found.

[6] S. Tribalat, *Anal. Chim. Acta*, 3, 113 (1949).

are salts of a strong acid and a strong base the extractability of rhenium should be substantially independent of the acidity of the solution. This has been verified by Tribalat, who found the extraction coefficient to agree with the calculated value within 10–15 per cent in the range 6 *N* hydrochloric acid to pH 13. Rhenium is not easily extracted from concentrated hydrochloric acid.

In the *p*H range 7 to 13, molybdenum (VI) is neither precipitated by the reagent nor extracted by chloroform. See p. 520 for determination of rhenium in molybdenite on the basis of this separation.

The behavior of other metals is not mentioned by Tribalat, but it is known that chloro complexes of various metals (bismuth, cadmium, ferric iron, stannic tin, zinc, etc.) are precipitated by tetraphenylarsonium chloride. The effect of such elements on the rhenium-molybdenum separation requires investigation.

II. Methods of Determination

In preparing samples for analysis the possibility of loss of rhenium by volatilization of the heptoxide must be borne in mind. Such loss may occur from hot sulfuric and perchloric acid solutions above *ca.* 200°, and from acid melts. It appears that there is no loss from boiling hydrochloric or nitric acid solutions.

A. Thiocyanate Method

When an acid solution of perrhenate is treated with thiocyanate and stannous chloride a yellowish color appears,[7] which has been ascribed to the formation of $ReO(CNS)_4$.[8] This reaction is very similar to the one given by molybdenum under the same conditions, and there is no satisfactory procedure available for the direct determination of minute amounts of rhenium in the presence of much molybdenum by this reaction.[9] A neat

[7] W. Geilmann, F. W. Wrigge, and F. Weibke, *Z. anorg. allgem. Chem.*, **208**, 217 (1932); W. Geilmann and G. Lange, *Z. anal. Chem.*, **126**, 321 (1944); W. Geilmann and H. Bode, *Z. anal. Chem.*, **128**, 489, 495 (1948).

[8] According to S. Tribalat, *Compt. rend.*, **223**, 34 (1946), the complex contains rhenium in the quadrivalent and quinquevalent states, the average valence being close to 4.5.

[9] If the ratio of molybdenum to rhenium is not too unfavorable, the effect of the molybdenum can be decreased to a large extent by making use of the greater stability of the rhenium complex in strongly acid solution. In a solution having an optimum concentration of 5 *N* in hydrochloric acid and approximately 9 *N* in sulfuric acid, the color of the molybdenum complex fades fairly rapidly whereas that of the rhenium complex remains relatively unchanged (see L. C. Hurd and C. F. Hiskey, *Ind. Eng. Chem., Anal. Ed.*, **10**, 623 (1938)). C. F. Hiskey and V. W. Meloche, *ibid.*, **12**, 503 (1940), were able to determine 100 γ Re in the presence of 5 to 10 mg. Mo by this method with an error of *ca.* +10 per cent by comparing after60–75 minutes, and with an error of *ca.* +5 per cent after 90 minutes. On the other hand, Melaven and Whetsel[3] report unfavorable results by this procedure.

method for separating molybdenum and rhenium and determining the latter has been described by Hoffman and Lundell.[10] In this method, which has already been referred to above, an approximately 2 *N* hydrochloric acid solution of molybdenum (VI) and rhenium (VII) is treated with thiocyanate and shaken with mercury and ether. The molydenum

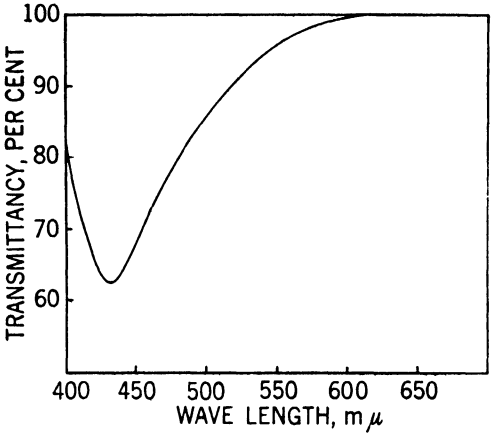


Fig. 64. Transmission curve of rhenium thiocyanate in ether (1.07 p.p.m. Re, 1 cm. cell, 2 day-old solution). (Hoffman and Lundell.)

is reduced and forms molybdenum (V) thiocyanate which is extracted by the ether (the presence of a little iron aids in the extraction of the molybdenum). Rhenium remains largely unchanged[11] in the aqueous layer, and can be determined by the addition of stannous chloride and extraction of the Re (VI) thiocyanate complex with ether. The color of the rhenium complex is fairly stable; a solution in ether having a concentration of 1 mg. Re per liter faded 2.5 per cent in 2 days, and another containing 5 mg. per liter increased in color intensity by 0.5 per cent. Slight deviation from Beer's law is shown by rhenium thiocyanate solutions in ether, but this may be due to the slight instability of the solutions rather than to true deviations. Butyl acetate may be used instead of ethyl ether in the extraction but has no particular advantages.

Among the non-interfering elements in the procedure the following are included: cerium, cobalt, chromium, gallium, germanium, indium, iridium,

[10] J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **23**, 497 (1939).

[11] Under the conditions prescribed in the procedure following, a small proportion of the rhenium, varying from 1 to 5 per cent, passes into the ether with the molybdenum.

lead, nickel, osmium, ruthenium, thallium, uranium, and vanadium (all in 2 mg. quantities). Chromium in large amounts (40 mg.) imparts a slight green tint to the ether. Platinum, rhodium and tungsten interfere by coloring the ether layer. Copper, gold, palladium, selenium, and tellurium do not color the ether, but they separate and contaminate the mercury.

TABLE 82

DETERMINATION OF RHENIUM IN THE PRESENCE OF MOLYBDENUM BY THE THIOCYANATE METHOD OF HOFFMAN AND LUNDELL

Molybdenum present mg.	Rhenium present γ	Rhenium found γ
10	1.0	0.9
10	5.0	4.8
10	10.0	10.9
5	80	78
10	100	97

The determination of rhenium in pure solution has been studied by Hurd and Babler,[12] who recommend that the concentration of hydrochloric acid be 2 per cent, of potassium thiocyanate 0.4 per cent, and of stannous chloride 0.2 per cent, that the mixture be allowed to stand 7 minutes before extraction with ether, and that shaking not be unnecessarily prolonged.

The procedure of Hoffman and Lundell follows.

Special Solutions

Potassium thiocyanate, 20 per cent.

Stannous chloride. Dissolve 35 g. of $SnCl_2 \cdot 2H_2O$ in 20 ml. of 1:1 hydrochloric acid and dilute to 100 ml. with water.

Ether for dilution. To 100 or 200 ml. of ethyl ether in a separatory funnel add 25 ml. of 1:4 hydrochloric acid, 2 ml. of 20 per cent potassium thiocyanate solution, and about 10 g. of mercury. Shake vigorously for one minute. Draw off the mercury and acid and reserve the ether.

Standard rhenium solution, 0.01 or 0.001 per cent Re. Dissolve 0.0155 g. of pure potassium perrhenate in water, add 5 ml. of 6 *N* sulfuric acid and dilute to 100 ml. with water (1 ml. = 100 γ Re). From this solution prepare one containing 10.0 γ Re per ml. by dilution with *ca.* 0.3 *N* sulfuric acid.

§ Procedure

The sample may contain as much as 10 mg. of molybdenum and as little as 1 γ of rhenium.

[12] L. C. Hurd and B. J. Babler, *Ind. Eng. Chem., Anal. Ed.*, **8**, 112 (1936). See Melaven and Whetsel[3] for a procedure for the determination of rhenium in sulfuric acid medium, without extraction, following precipitation of small amounts of molybdenum with α-benzoinoxime.

Separation of Molybdenum and Rhenium. Evaporate the sample solution to practical dryness and add about 10 mg. of iron as ferric chloride (if iron is not already present) and 1–2 drops of saturated potassium permanganate solution. Add a slight excess of ammonia and heat on the steam bath for a few minutes to make certain that molybdenum and rhenium are present in their highest valences (VI and VII respectively). Dissolve the residue in 25 ml. of cool 1:4 hydrochloric acid and 2 ml. of potassium thiocyanate solution. Transfer the solution to a separatory funnel containing 25 g. of mercury. At once add 20 ml. of analytical grade ethyl ether and shake until the aqueous solution becomes colorless (or until the color of ferric thiocyanate has disappeared if chromium, nickel, etc. are present); usually 1 minute of shaking suffices. Allow the phases to separate, and draw off the mercury and aqueous layer into another separatory funnel. Add to the latter 1 ml. of potassium thiocyanate and 15 ml. of ether, shake vigorously for a minute, and draw off the mercury and acid solution as before. Again add 1 ml. of potassium thiocyanate and 15 ml. of ether to the funnel containing the mercury and the aqueous solution, and shake vigorously. Deliver the mercury and aqueous layer into a separatory funnel. If the ether layer is colorless or very nearly so, the extraction of molybdenum is complete; if the ether shows an appreciable color, the aqueous solution must be extracted once more. When all the molybdenum has been removed, separate the mercury from the aqueous solution containing the rhenium.

Determination of Rhenium. To the acid solution from which the mercury has been withdrawn, add 1 ml. of potassium thiocyanate solution and 1 ml. of stannous chloride solution, mix, and allow to stand for 5 minutes. Add 20 ml. of ether, shake vigorously, allow the phases to separate, and run the aqueous layer into another separatory funnel. Repeat the extraction with ether twice, using 15 ml. portions. Discard the acid solution. Combine the ether extracts, shake well with 10 ml. of 1:4 hydrochloric acid (to remove iron which might otherwise oxidize and give a pink color) and run the ether into a 50 ml. volumetric flask. Dilute to the mark with the specially prepared ether.

Prepare the standards for comparison or for the construction of the standard curve as follows. Transfer the standard rhenium solution to a separatory funnel containing 10 mg. of iron as ferric chloride and 25 ml. of 1:4 hydrochloric acid. Add 2 ml. of potassium thiocyanate and 1 ml. of stannous chloride solution. Mix, allow to stand for 5 minutes, and then proceed with the extraction of the rhenium thiocyanate complex as described in the preceding paragraph.

Determine the extinction of the ether solutions at 432 mμ (an extinction of 0.001 corresponds to about 0.005 γ Re per cm.^{2} at this wave length). If

only a few micrograms of rhenium are present, one extraction with 20 or 10 ml. of ether should be made to keep the volume small, and the standards treated similarly. If the standard series method is used, tubes having a cross-section of 1–2 cm.^{2} may be used with the smaller volumes of ether; less than 0.5 γ of rhenium can then be determined.

B. Indirect Determination by Catalysis of Reduction of Sodium Tellurate by Stannous Chloride

Perrhenic acid and its salts catalyze the reduction of sodium tellurate to elemental tellurium by stannous chloride.[13] Other things being the same, the amount of tellurium precipitated is proportional to the concentration of rhenium. If a protective colloid is added to the solution the tellurium remains in colloidal suspension and the concentration of rhenium can be obtained by determining the transmittancy of the suspension and comparing against a similar standard. By the procedure given below, 0.001 to 0.1 γ of rhenium can be determined with an error of 10 to 20 per cent. Molybdenum interferes and must be separated if present in appreciable amounts. Nitric acid suppresses the reaction and other acids affect the degree of coloration, but the procedure following provides for the latter effect, the standards being prepared by addition of rhenium to the sample solution.

Reagents

Sodium tellurate, 5 per cent aqueous solution.
Tartaric acid, 45 g. in 100 ml. of solution.
Gelatin, 0.5 per cent solution.
Stannous chloride, 100 g. tin dissolved in 250 ml. of hydrochloric acid.
Perrhenic acid standard solutions, containing for example 0.01 and 1 γ Re per ml.

§ Procedure

Transfer aliquots of the sample solution containing from 0.001 to 0.1 γ Re to three graduated test tubes. To two of the tubes add standard perrhenic acid solution corresponding to 0.002–0.01 and 0.02–1 γ of Re respectively. Dilute the solutions to 1.5 ml. and treat each (including a blank of 1.5 ml. of water) with 1 ml. of reaction mixture prepared by mixing 5 ml. of sodium tellurate, 2 ml. of tartaric acid, 1.5 ml. of gelatin, and 1.5 ml. of stannous chloride solutions. Mix and allow to stand for 1–2 hours, or until next day if no color is developed in the sample in this time. Obtain the extinction of the solutions at 430–470 mμ, comparing against the stronger standard if allowed to stand 1–2 hours or against the weaker if allowed to stand one day. Calculate the amount, x, of rhenium in the sample from the formula:

[13] N. S. Poluektov, *J. Applied Chem. U.S.S.R.*, **14**, 702 (1941).

$$x = aE_x/(E_{a+x} - E_x),$$

where a = amount of Re added to one or the other of the two comparison solutions
E_x = extinction of the sample solution
E_{a+x} = extinction of the sample solution containing added Re.

If a photometer is not available, the suspensions may be compared by diluting the stronger to equal color intensity with the other with a mixture of 10 ml. reagent solution and 15 ml. of water.

III. Applications of the Thiocyanate Method

A. Determination of Rhenium in Molybdenite

Two methods are described below, the first based on isolation of rhenium by volatilization of the heptoxide from a sulfuric acid solution, the other by an extraction procedure. The accuracy of the two methods appears to be comparable, but the second method is simpler and more rapid.

Method I

The procedure given below is that described by Hiskey and Meloche. These authors avoid in large measure the difficulty caused by the presence of small amounts of molybdenum in the distillate by allowing the solution which has been treated with stannous chloride and thiocyanate to stand for a relatively long time before comparison until the color of the molybdenum thiocyanate complex has faded practically to zero. Ether is not used for extraction.

Apparatus

The distilling flask (300 ml.) must be provided with an inlet tube passing through a ground glass stopper nearly to the bottom of the flask; the exit tube is coiled for a distance of about 10 cm. to serve as an air-condenser, and is attached by means of a ground glass connection to a water condenser. A thermometer is suspended inside the flask.[14]

§ Procedure

Transfer 4 g. of pulverized molybdenite to a 250 ml. Erlenmeyer flask and add 20 ml. of concentrated nitric acid. After any initial frothing has ceased, add 5 ml. of fuming nitric acid and shake at intervals until vigorous reaction has subsided. Then heat the mixture just below the boiling point on a hot plate until red fumes have disappeared and carefully add 50 ml. of concentrated hydrochloric acid. Evaporate, with occasional replacement of the hydrochloric acid, until no more chlorine is evolved

[14] For an illustration of the distillation apparatus see L. C. Hurd and C. F. Hiskey, *Ind. Eng. Chem., Anal. Ed.*, **10**, 624 (1938).

(usually 125–150 ml. of hydrochloric acid must be added). Reduce the volume to 25 ml. (do not allow to go to dryness), and cautiously add 75 ml. of concentrated sulfuric acid. Transfer the solution, together with any separated molybdic oxide, to the distilling flask. Distil at 260–270° while passing a mixture of two parts dry steam and one part air or carbon dioxide through the solution. Collect the distillate in a receiver immersed in an ice bath. Distil for $2^1/_2$ hours at such a rate that 250 ml. of distillate are collected in that time.

Destroy any sulfur dioxide in the distillate by adding a few drops of strong aqueous bromine solution in an alkali bromide (add only enough to give a faint yellow color). To the distillate and three similar standard solutions containing 10, 50 and 100 γ of rhenium, add 100 ml. of concentrated hydrochloric acid and (after cooling) 10 ml. of 20 per cent sodium thiocyanate solution, followed by 10 ml. of 20 per cent stannous chloride solution.[15] Allow the solutions to stand until the color of the molybdenum complex has faded out (30 or 45 minutes) and compare against the proper standard in 100 ml. Nessler tubes (vary the volume of one or the other of the solutions and measure the heights of the columns at the point of balance). Check the color intensities after 20–30 minutes to see whether the molybdenum color has faded completely from the sample solution.

TABLE 83

DETERMINATION OF RHENIUM IN THE PRESENCE OF MOLYBDENUM BY THE METHOD OF HISKEY AND MELOCHE

(4 g. sample of MoO_3 in each case)

Re added p.p.m.	Re found p.p.m.	Error p.p.m.
0.0	0.0	0.0
0.25	0.75	+0.5
1.0	1.5	+0.5
1.0	0.75	−0.25
2.5	3.25	+0.75
6.25	5.25	−1.0
13.75	13.25	−0.5
25.0	24.25	−0.75
10.0[a]	11.75	+1.75

[a] 4 g. ammonium molybdate, 7.9 mg. Se.

Notes. 1. If the sample contains selenium, more or less of the latter will accompany rhenium into the distillate and be reduced to red colloidal selenium when stannous chloride is added. The selenium can be removed by the following method after the

[15] Alternatively, take a 50 or 60 ml. aliquot of the 250 ml. distillate, transfer to a 100 ml. Nessler tube and add 20 ml. of hydrochloric acid, 2 ml. of thiocyanate and 2 ml. of stannous chloride solution.

sample has been brought into solution. The solution is made at least 8 or 10 *N* with hydrochloric acid, 1 g. of sodium sulfite is added and the solution allowed to stand for 10–15 minutes. The solution is filtered, the precipitate washed, and the filtrate reduced to a volume of 25 ml. by slow evaporation. The determination is then continued in the regular way.

2. It seems possible that rhenium may be determined in the distillate by the method of Hoffman and Lundell after precipitation with hydrogen sulfide in the presence of arsenic (p. 511).

Method II[6]

In the following procedure, rhenium is separated from molybdenum by chloroform extraction of tetraphenylarsonium perrhenate (p. 512). The colorimetric determination is made by evaporating the chloroform extract to a small volume, adding stannous chloride and thiocyanate, and shaking with amyl alcohol to extract the thiocyanate complex of rhenium. The accuracy of the method is reported to be ±10 per cent for 100 p.p.m. of rhenium and about 50 per cent for 1 p.p.m. Doubtless some refinements in the procedure would improve the accuracy.

§ Procedure

Decompose 1 g. of molybdenite with 10 ml. or more of fuming nitric acid by heating on a steam bath. Remove the excess nitric acid by evaporating with concentrated hydrochloric acid to a small volume. When the volume of the solution has been reduced to 2 ml., add 10 *N* sodium hydroxide solution to approximate neutrality. Then bring the *p*H of the solution to 8–9 by adding sodium bicarbonate. Dilute the solution accurately to 20 ml.

To a 5 ml. aliquot of this solution add 10 mg. of tetraphenylarsonium chloride (or 0.5 ml. of 0.05 *M* solution) and 10–15 ml.of chloroform. Shake for a few minutes. Separate the chloroform and shake it with a little powdered anhydrous calcium chloride; filter through a small paper which has been moistened with chloroform. Repeat this operation to remove every trace of aqueous solution containing molybdenum.

Evaporate the chloroform on the water bath to a volume of about 1 ml. and transfer to a color comparison tube. Add 1–2 ml. of concentrated hydrochloric acid, 0.2 ml. of 20 per cent ammonium thiocyanate, and 0.2 ml. of 10 per cent stannous chloride in concentrated hydrochloric acid, shaking after each addition. Extract the mixture with 1 ml. of isoamyl alcohol. Compare the color of the organic solvent layer with standards prepared in the same manner. If no yellow color is visible, less than 1 γ of rhenium is present ($<$ 4 p.p.m. of sample). In that case take the 15 ml. of sample

solution remaining, extract with 10–15 ml. of chloroform after adding 3 mg. of reagent, and proceed as before. The limit of detectability is 1–2 p.p.m. of rhenium.

When it is necessary to determine less than 2 p.p.m. of rhenium in molybdenite, decompose 3 g. of sample, dilute the solution of adjusted *p*H to 60 ml. and add enough tetraphenylarsonium chloride to make its concentration 10^{-4} *M* (1.2 ml. of 0.005 *M* solution). Extract with 10 ml. of chloroform, treat the latter with calcium chloride as already described, evaporate to a volume of 2 ml., and shake for a few minutes with an equal volume of concentrated hydrochloric acid. Separate the phases and determine rhenium in the hydrochloric acid, using 0.5–1 ml. of isoamyl alcohol for the extraction of the rhenium thiocyanate complex. In this way 2 γ of rhenium can be detected.

When the rhenium content of the sample is of the order 1 p.p.m. it is advisable to run a blank on a molybdate solution to make sure that the procedure followed does not permit the survival of entrained molybdenum to the final step.

B. Determination of Rhenium in Pyrolusite[16]

The concentration of rhenium in pyrolusite may attain a maximum of a few parts in ten million. The procedure for the determination of rhenium in this material will be briefly outlined. One hundred grams of pulverized pyrolusite are dissolved in warm hydrochloric acid, and insoluble material is filtered off after dilution of the solution to about 300 ml. The filtrate is treated with 20 per cent stannous chloride solution to reduce ferric iron and give a clear pink solution. Sufficient potassium thiocyanate is added to give a concentration of 0.6 g. per 100 ml., followed by enough stannous chloride to give 0.5 g. per 100 ml. After 5 minutes approximately 60 ml. of ethyl ether are added to the cold solution, and molybdenum and rhenium thiocyanates are extracted. The extraction is repeated until the absence of any appreciable color in the ether layer shows that all the molybdenum and rhenium has been removed. The combined ether extracts are heated on a water bath at 70° C. until the volume has been reduced to 5 or 10 ml., and 15 ml. of 1:1 hydrochloric acid are then added. The remaining ether is evaporated by blowing air over the surface of the residue. Thirty per cent hydrogen peroxide is added dropwise until all brown, red or orange color disappears. The solution is allowed to stand for 15 minutes, with occasional addition of hydrogen peroxide to prevent the return of any color. The solution is diluted to 200 ml. with sulfuric

[16] L. C. Hurd and C. F. Hiskey, *Ind. Eng. Chem., Anal. Ed.*, **10**, 623 (1938).

acid (sp. gr. 1.8) and distilled as described on p. 519. The distillate should smell only faintly of sulfur dioxide. The separation of sulfur leads to low results. Bromine vapor is bubbled into the distillate to destroy the sulfur dioxide (faint yellow color). The colorimetric determination is made as already described (p. 519).

A similar procedure should be applicable to other minerals low in molybdenum. It is possible that the distillation of the mixture of the isolated rhenium and molybdenum can be omitted and the procedure of Hoffman and Lundell (p. 516) applied.

CHAPTER XXXVII

RHODIUM

I. Separations

In the systematic analysis of the platinum group metals, osmium and ruthenium are first separated by volatilization of the tetroxides, and palladium, rhodium, and iridium are then precipitated as the hydrous oxides in the presence of bromate at a regulated acidity.[1] The hydrolytic precipitation of rhodium is complete at *p*H 6. A reprecipitation of the hydrous rhodium oxide is required to free it from platinum. Palladium is separated as the dimethylglyoxime compound, and rhodium is then precipitated as metal, and thus separated from iridium, by reduction with titanous chloride in hot sulfuric acid solution. The rhodium must be dissolved and reprecipitated to eliminate the small amount of iridium which has been carried down. No data are available to show how well these separations succeed when very small amounts of rhodium are associated with large amounts of the other metals of the group.

Hydrogen sulfide produces little precipitation of rhodium from a very dilute solution in sulfuric acid. Precipitation takes place more readily from hydrochloric acid solution but is not complete.

II. Methods of Determination

A. Stannous Chloride Method

By far the best color reaction for rhodium is that with stannous chloride, which when heated with a hydrochloric acid solution of rhodium (III) slowly produces a red color.[2] The color is brownish at first in solutions not too dilute, and passes into a reddish on continued heating.[3] The resulting solution turns yellow if diluted with relatively much water but remains red if diluted with 2 *N* hydrochloric acid. It seems likely that rhodium is reduced to a lower valence state (not to the colloidal metal) and that the formation of one or more chloro complexes is involved. The color change is reversible. The yellow product is readily transformed into

[1] R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

[2] V. N. Ivanov, *J. Russ. Phys. Chem. Soc.*, **49**, 601 (1917); **50**, 460 (1918). W. Singleton, *Ind. Chemist*, **3**, 121 (1927).

[3] J. J. Neumayer, University of Minnesota, 1949.

the red by addition of an alkali chloride or hydrochloric acid. The red form of reduced rhodium is stable. A solution containing 1 p.p.m. of reduced rhodium in 2 *N* hydrochloric acid showed no appreciable change in transmittancy for 90 minutes.[3] On the other hand, the transmittancy of a solution of the yellow form (1 p.p.m. of rhodium) decreased for approximately 60 minutes after dilution to volume, remained constant for 15 minutes, and then slowly increased. Either the red or yellow form may be

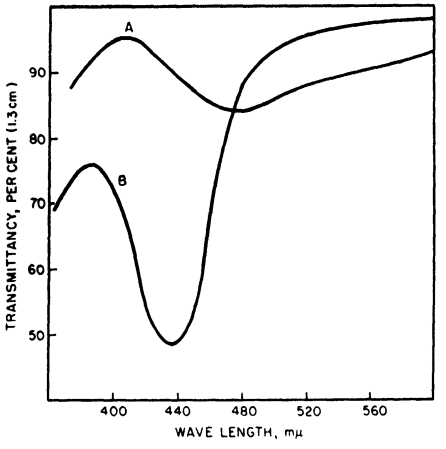


Fig. 65. Transmission curves of product obtained by reduction of rhodium (III) chloride with stannous chloride in hydrochloric acid medium. Curve A: red form (dilution with hydrochloric acid). Curve B: yellow form (dilution with water). Rhodium concentration 2 p.p.m. in each case. (From data of J. Neumayer.)

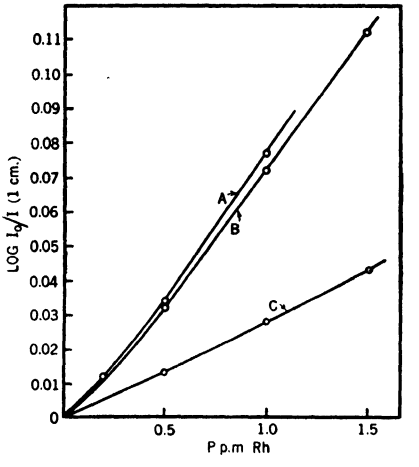


Fig. 66. Determination of rhodium with stannous chloride. Five ml. of rhodium solution heated at 100° for 1 hour with 10 ml. of 10 per cent stannous chloride in 2 *N* hydrochloric acid; then diluted to 50 ml. with water and transmittancy determined with blue filter (Jena BG-12) after 30 minutes (curve B) and after 1 hour (curve A). Curve C represents dilution with 2 *N* hydrochloric acid and measurement at 480 mμ.

made the basis of a photometric method, the former being preferable when the amount of rhodium is not too small. When the rhodium concentration is very low it may be necessary to sacrifice the advantages of the red form to obtain the greater sensitivity provided by the yellow form (Figs. 65 and 66). The successful use of the yellow product requires moderately careful control of the chloride concentration and the time of standing.

The reduced rhodium complex can be extracted by ethyl acetate and similar organic solvents from aqueous solutions having a sufficiently

high (> 2 *N*) concentration of hydrochloric acid. The organic solvent is colored yellow.

The other platinum metals (particularly platinum and palladium) interfere by giving more or less strongly colored solutions under the conditions of the determination. The quantitative effect of iridium is of interest, since in the method of separation referred to in I the rhodium is finally left with this element, from which it is separated by precipitation with titanous chloride; some iridium is coprecipitated with the metallic rhodium. A solution containing 50 γ of rhodium and approximately 200 γ of iridium (IV) showed 78 γ of rhodium when analyzed by the procedure given below, the yellow color obtained on dilution with water being measured. The error can possibly be reduced by measuring at a suitable wave length the transmittancy of the red solution of rhodium obtained by dilution with hydrochloric acid; iridium gives a brown solution after heating with stannous chloride.

According to Neumayer, very small amounts of silver (as the argentochloride ion) shift the equilibrium from the red to the yellow form of reduced rhodium, but the red form can still be obtained if the chloride ion concentration is increased above that specified in the procedure below.

Special Solutions

Stannous chloride, 10 per cent solution of the dihydrate in 2 *N* hydrochloric acid.

Standard rhodium solution, 0.01 per cent. This may be prepared by fusing 10 mg, of finely divided rhodium metal with a gram or two of potassium pyrosulfate in a silica crucible until all the metal has been brought into solution, dissolving the melt in 1 *N* sulfuric acid, and diluting to 100 ml. with the same acid.

§ Procedure

Transfer the neutral or only slightly acid sample solution (10 to 100 γ of rhodium) to a test tube or a 1.8 × 15 cm. flat-bottomed color comparison tube, dilute to 5.0 ml. with water, and add 10.0 ml. of stannous chloride solution. Mix and heat for 0.5 to 1 hour in a bath of boiling water. At the same time, treat in the same manner standard solutions for comparison or for construction of the reference curve. Cool to room temperature and dilute to 50 ml. in a volumetric flask with (*a*) 2 *N* hydrochloric acid, or (*b*) with water. If (*a*) is followed, the transmittancy of the red solution may be determined at once with the aid of a green or blue filter (480 mμ); if (*b*) is followed, allow the mixed solution to stand at room temperature for 1 hour before determining the extinction with a blue filter (435 mμ).

When very small amounts of rhodium are present, the solutions may advantageously be compared in the usual tubes (p. 52). As little as 1 γ of rhodium will impart a faint pink tinge to a solution having a cross-section of 2 cm.^{2}

B. Other Methods

When a rhodium (III) solution is heated with potassium iodide (about 1 per cent) in the presence of hydrochloric acid (0.5 *N*) a brown color develops slowly. The reaction product is slightly soluble, as shown by the formation of a turbidity in solutions containing as little as 10 p.p.m. of rhodium. This reaction can probably be applied in colorimetric trace analysis. The iodine liberated by air oxidation must be destroyed.

Rhodium (III) can be oxidized to the quinquevalent state (violet color) in acid medium by strong oxidizing agents such as sodium bismuthate and persulfate.[4] J. J. Neumayer has studied the oxidation with ammonium persulfate in the presence of silver ion as catalyst as a basis for a colorimetric determination. The sulfuric acid concentration of the solution should be below 0.2 *M* to prevent formation of brown silver peroxide. The reaction is carried out at room temperature and 15 minutes is allowed for completion of the oxidation. The color intensity remains constant in the next 30 minutes (0.2 g. ammonium persulfate and 10 mg. of silver nitrate in 10 ml.). The transmission curve of the violet solution shows a primary minimum at 360 mμ or below and a secondary minimum at 505 mμ. A serious drawback of the method is its low sensitivity (0.15 γ rhodium per sq. cm. per 0.001 extinction at 360 mμ, 0.23 γ at 525 mμ). It may be possible to develop a more sensitive indirect method based on oxidation of the ferrous complex of *o*-phenanthroline by quinquevalent rhodium after its oxidation by bismuthate or persulfate.

[4] V. S Syrokomsky and N. N. Proshenkova, *J. Anal. Chem. Russ.*, **2**, 247 (1947); *Analyst*, **73**, 361 (1948).

CHAPTER XXXVIII

RUTHENIUM

I. Separations

It is likely that the macro method for the separation of ruthenium by volatilization of the tetroxide can be extended to traces, but no data are available. Briefly, the method is carried out as follows.[1] The solution from which osmium tetroxide has been distilled is evaporated to dryness on the steam bath, the residue is taken up in a little hydrochloric acid, and the liquid evaporated. The evaporation with hydrochloric acid is repeated until oxides of nitrogen are no longer evolved. The residue is dissolved in 1:3 sulfuric acid and the solution evaporated until sulfuric acid fumes appear.[2] The solution is transferred to a special distilling flask (p. 479) and diluted with water to give a solution containing approximately 10 per cent by volume of sulfuric acid. Ten per cent sodium bromate solution equal to the volume of the sample is added to the distilling flask, the solution is heated to boiling, and the distillation continued for one and one-half hours while a slow current of air is passed through the apparatus. The ruthenium tetroxide is absorbed in 1:1 hydrochloric acid saturated with sulfur dioxide. To assure the complete expulsion of ruthenium, more bromate (about one-fourth of the original amount) is added and the distillation is continued for one hour.

Isolation of ruthenium from the distillate can be effected by hydrolytic precipitation of hydrous ruthenium (III) oxide. The absorbing solution is first evaporated to a moist residue on the steam bath, a few milliliters of concentrated hydrochloric acid are added, and the covered beaker is heated on the steam bath for one-half hour. Water is added (about five times the volume of the acid) and boiled to bring all the ruthenium into

[1] R. Gilchrist, *Bur. Standards J. Research*, **3**, 993 (1929); **12**, 283 (1934). R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935). See further Thiers, Graydon, and Beamish.[5]

[2] The purpose of this treatment is to remove chloride which hinders the volatilization of ruthenium tetroxide. Ruthenium can be distilled directly from the solution from which osmium has been eliminated if sodium bromate and more nitric acid are added, but the minimum time for complete distillation of ruthenium (macro amounts) is then three and one-half hours. Elimination of hydrochloric acid before distillation has the added advantage of preventing the possible deposition of ruthenium dioxide on the walls of the distilling apparatus. Distillation of ruthenium tetroxide from alkaline solution in the presence of chlorine is not advisable because of possible loss of ruthenium by carrying down with the precipitated iridium hydroxide.

solution.[3] Any silica in the solution may be filtered off at this point. The solution is heated to boiling and treated with 10 per cent sodium bicarbonate until a precipitate forms (possibly a little aluminum may be added to give aluminum hydroxide to collect amounts of ruthenium too small to precipitate alone). Bromcresol purple indicator solution is added and the addition of bicarbonate continued until the indicator changes from yellow to blue (ruthenium is completely precipitated at *p*H 6). The solution is boiled for 5 minutes to coagulate the precipitate and filtered through an inorganic filter. The precipitate may be washed with 1 per cent ammonium sulfate and dissolved in dilute hydrochloric acid for the colorimetric determination of ruthenium (p. 531).

Solutions other than hydrochloric-sulfurous acid may be used to absorb ruthenium tetroxide. A 3 per cent solution of hydrogen peroxide (free from acetanilide) has been recommended for the purpose.[4] Ten milligrams of ruthenium distilled as described above from a volume of about 225 ml. could be quantitatively caught in two solutions of hydrogen peroxide having the respective volumes of 35 and 15 ml. The absorbing solutions must be cooled in ice. The hydrogen peroxide remaining after the absorption can be destroyed by adding a little hydrochloric acid (0.5 ml. per 100 ml. of solution) and boiling. This method would seem to have advantages for collecting ruthenium for colorimetric determination and should be studied further from this standpoint.

Losses of ruthenium in fire assay procedures have been investigated and found to be appreciable.[5] A new procedure has been described for the isolation of ruthenium from the lead button. The latter is dissolved in perchloric acid[6] and ruthenium is distilled from the hot solution. Undissolved metallic ruthenium in the distillation flask is brought into solution by fusion with sodium peroxide or by treatment with sodium hypochlorite, and ruthenium tetroxide is then distilled in the presence of chlorine.

II. Methods of Determination

A. Methods Based on the Use of Thiourea and Derivatives

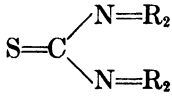
Strongly colored products are obtained when an acid solution of a ruthenium salt is heated with thiourea and its derivatives of the type

[3] This solution may perhaps be used for colorimetric determination without further treatment.

[4] W. J. Rogers, F. E. Beamish, and D. S. Russell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 561 (1940). These authors precipitate ruthenium from the absorbing solution with thionalide.

[5] R. Thiers, W. Graydon, and F. E. Beamish, *Anal. Chem.*, **20**, 831 (1948).

[6] Ruthenium tetroxide cannot be completely volatilized from solutions obtained by dissolving lead in nitric acid.



(R = H, alkyl, aryl, or NHR_1). Osmium also reacts with some of these compounds. Various reagents of this type have been studied qualitatively by Steiger,[7] and his findings are partially summarized in Table 84.

Rubeanic acid also reacts with ruthenium (blue color, limit of detection 0.2 γ Ru per ml.).[8]

The hue and the strength of the color given by thiourea with ruthenium depend markedly upon the acid concentration. In the acidity range 0.1 to 4 *N* (hydrochloric acid) the color varies from greenish to blue, the intensity being greater at the higher acidities. In 6 *N* hydrochloric acid a

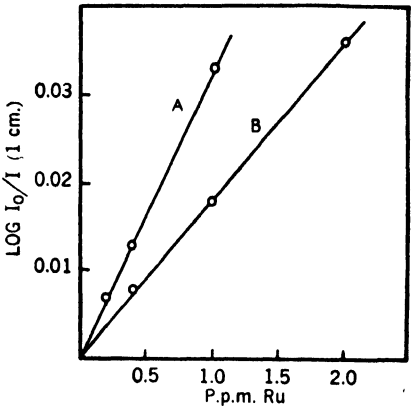


Fig. 67. Determination of ruthenium with phenylthiosemicarbazide (A) and with thiourea (B).

violet color is obtained whose intensity is about the same as that of the blue color at 4 *N*. The reaction may conveniently be carried out at 2–4 *N* acidity, preferably the latter. The color develops rapidly on heating, and is moderately stable. Water may be used for diluting the acid solution to volume. The reaction product is apparently only slightly soluble. A solution containing 50 γ of ruthenium in 10 ml. gives a slight turbidity on heating, but one containing 25 γ in the same volume does not. Ferric iron produces a turbidity due to separation of sulfur.

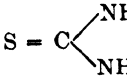
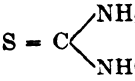
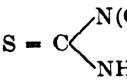
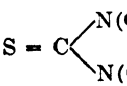
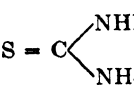
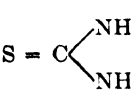
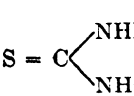
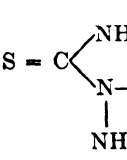
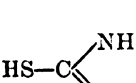
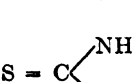
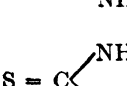
Among the derivatives of thiourea, the writer has tried only phenylthiosemicarbazide for the determination of ruthenium. It gives a beautiful red or red-violet color in hot acid solution. The color intensity is much

[7] B. Steiger, *Mikrochemie*, 16, 193 (1934–35).

[8] H. Wölbling and B. Steiger, *Mikrochemie*, 15, 295 (1934).

TABLE 84

COLORIMETRIC REAGENTS FOR RUTHENIUM

No.	Reagent	Color of product	Limit of detection Ru γ/ml.
1		Blue	0.08
2		Blue	0.08
3		Red	0.13
4		Violet	0.13
5		Red → green	0.14
6		Violet	—
7		Violet	0.025
8		Violet	0.017
9		Violet	0.025
10		Red	0.6
11		Violet	—

The ruthenium compounds of 5, 7, and 8 (and perhaps others) can be extracted with ether. Osmium reacts with 6, 7, 9, 11 (green colors) but not with 2, 3, 5.

greater in 4 *N* hydrochloric acid than in 1 *N*. The sensitivity is greater than that of the thiourea reaction. The visual sensitivity amounts to about 0.5 γ ruthenium per cm.[2] The colored compound can be extracted with butyl alcohol from the diluted acid solution, and 0.5 γ of ruthenium will impart a color to 0.5 ml. of the alcohol. Ferric iron interferes by giving a turbidity and, if present in more than very small amounts, a red color. Practically, the effect of iron is not important since ruthenium will as a rule be isolated by distillation of the tetroxide before it is determined. Determinations of 5 and 10 γ of ruthenium in the presence of 0.1 mg. of ferric iron yielded the values 7 and 11 γ respectively. Reduction of ferric iron by stannous chloride is of limited value only, since the color given by ruthenium under these conditions is diminished in intensity.

§ Procedure

To 10 ml. of sample solution 4 *N* in hydrochloric acid and containing up to 25 γ of ruthenium, or more if thiourea is to be used as reagent, add either 0.5 ml. of freshly prepared 1 per cent alcoholic solution of phenylthiosemicarbazide or 0.5 ml. of 5 per cent aqueous thiourea solution. Heat in a bath of boiling water for 10 minutes, cool to room temperature, and dilute to 25 ml. or a smaller volume with water. Determine the transmittancy of the solution without undue delay, using a blue or green filter (phenylthiosemicarbazide as reagent) or a red one (thiourea as reagent).

B. The 5-Hydroxyquinoline-8-carboxylic Acid Method[9]

This reagent produces a strong bluish black coloration when heated with a hydrobromic acid solution of bromo- or chlororuthenate. The color does not develop in the presence of nitric acid or nitrites, and hydrochloric acid weakens it. The color intensity is proportional to the concentration of ruthenium. Osmium gives very little color under the conditions of the determination: iridium and platinum give much weaker colors. Iron also produces a color.

§ Procedure

Isolate ruthenium by distilling as the tetroxide and absorbing in hydrogen peroxide (p. 528). To 50 ml. of the solution add 2.5 ml. of 1:20 hydrobromic acid and boil for 10 minutes. Cool and add 5.0 ml. of 6 *N* sulfuric acid and 10 ml. of 0.05 per cent solution of the sodium salt of the reagent (suspend 0.5 g. of 5-hydroxyquinoline-8-carboxylic acid in 1 liter of water,

[9] J. G. Breckenridge and S. A. G. Singer, *Canadian J. Research*, **B25**, 49 (1947). Quinoline-8-carboxylic acid, 5-amino-quinoline-8-carboxylic acid, and 5-hydroxyquinoline do not give colorations with ruthenium.

add 0.5 g. of sodium carbonate, and heat to 40° C.). Boil for 5 minutes, cool, and dilute to 50 ml. with water. Obtain the transmittancy of the solution at once, using a combination of Wratten 66 and 15 filters (the maximum absorption by the solution appears to lie in the range 500–560 mμ).

C. Other Methods

Among the many other sensitive color reactions for ruthenium the following may be mentioned as possibly having value for quantitative application.

Ruthenium (III) in hydrochloric acid shows a strong brownish color.[10] The color intensity is greatly dependent on the acid concentration, increasing with the latter. In 6 *N* hydrochloric acid the sensitivity is approximately 0.5 γ ruthenium per cm.^{2} The chloro complex is not appreciably extracted from 1:1 hydrochloric acid by ethyl acetate.

Thiocyanate gives a pink color with low concentrations of ruthenium (III) in dilute acid solution. The color is stronger in dilute (0.2–1 *N*) hydrochloric acid than in stronger (4 *N*) acid. The sensitivity corresponds to 0.5 γ or less of ruthenium per cm.^{2} in 0.2 *N* hydrochloric acid. Phosphoric acid and fluoride diminish the color intensity or destroy the color, as does also stannous chloride. The colored compound can be extracted with butyl alcohol.

8-Hydroxyquinoline yields a green coloration with ruthenium (III) in acetate medium. The hydroxyquinolate can be extracted with chloroform.

An ammoniacal solution of ruthenium heated with sodium thiosulfate becomes pink.

[10] The bromo complex of ruthenium (III) is also strongly colored (red-brown); it has been made the basis of a colorimetric method for ruthenium by McBryde and Yoe (p. 343), who find that Beer's law holds at 400 mμ in 20 per cent hydrobromic acid solution.

CHAPTER XXXIX

SCANDIUM

I. Separations

A. Precipitation Methods

Ammonia precipitation separates scandium from the alkaline earth metals and magnesium.[1] In the presence of aluminum it is probable that no significant amount of scandium will remain in solution. Anions forming complexes with scandium (carbonate, oxalate, fluoride) must be absent. Thiocyanate does not interfere with the precipitation.

Separations based on the use of sodium hydroxide are of problematical value. Scandium hydroxide is somewhat soluble in sodium hydroxide solutions. However, in the presence of metals whose hydroxides are not amphoteric it seems that scandium can be completely precipitated, especially when the metals have a similar ionic radius (*e.g.*, cobalt). In this way it may be possible to enrich scandium in the hydroxide precipitate when it is associated with much aluminum.

Ammonium scandium tartrate is but slightly soluble in hot ammoniacal medium. Fischer and Bock[2] treated 100 ml. of scandium solution with 100 ml. of 10 per cent ammonium tartrate and 2 ml. of 25 per cent ammonia solution and found not more than 0.03 mg. scandium oxide in the filtrate. In this way, scandium can be partially separated from zirconium, thorium, iron, and manganese; it is difficult to effect a quantitative separation of these metals, even if a reprecipitation is made. The yttrium earths accompany scandium.

It seems likely that aluminum can largely be removed by precipitation of its hydrated chloride with hydrogen chloride and scandium left in solution.

Phytic acid, $C_6H_6O_3[OP(OH)_3]_6$, yields a very slightly soluble salt with scandium, which has served for the isolation of scandium from bio material.[3]

[1] Possibly a separation can also be made from iron if mercaptoacetic acid is added as in the case of aluminum or beryllium (p. 196).

[2] W. Fischer and R. Bock, *Z. anorg. allgem. Chem.*, **249**, 146 (1942).

[3] G. Beck, *Mikrochem. ver. Mikrochim. Acta*, **34**, 62 (1948).

B. Extraction Methods

Ferric iron can be separated almost completely by ether extraction of its chloride from 1:1 hydrochloric acid solution. Some other metals are more or less completely removed at the same time (p. 34).

Ferric iron, as well as titanium, zirconium, and vanadium (V), can be precipitated in mineral acid medium with cupferron. Presumably these cupferrates can be extracted by chloroform and a separation thus made from scandium.[4]

A fresh approach to the problem of separation of scandium from otherwise troublesome elements was made by Fischer and Bock[2] in the extraction of scandium by ethyl ether from a solution containing a high concentration of ammonium thiocyanate. Their experiments were made with relatively large amounts of scandium, but their findings may be applicable to trace analysis. Scandium probably goes into the ether as $HSc(CNS)_4$ or a similar compound. The percentage of scandium partitioning into the ether phase increases with the ammonium thiocyanate concentration up to about 30 g. per 100 ml. (Table 85). The distribution coefficient is constant between

Table 85

Influence of Thiocyanate Concentration on Extraction of Scandium Thiocyanate by Ethyl Ether

(0.19 g. Sc_2O_3 in 100 ml. aqueous phase; *p*H 3–5)

Grams NH_4CNS in 100 ml. aqueous phase	2.1	16.0	28.0	40.0	49.0	55.0	58.5
Percentage of total Sc in ether[a]	3.2	39	69	75	73	70	78

[a] On basis of equal volumes of aqueous and ether phases.

a hydrochloric acid concentration of 0.1 and 1 *N* (Table 86). Below an acidity of 0.1 *N* the hydrolysis of scandium ion decreases the amount of scandium extracted. The distribution coefficient is the same whether the original scandium concentration is about 20 or 1710 mg. of Sc_2O_3 per 100 ml., from which it may perhaps be concluded that the extraction will also be successful at low scandium concentrations. Sulfate and phosphate diminish the amount of scandium extracted by ether.

The behavior of other metals in the thiocyanate-ether extraction is shown in Table 87. It will be seen that a good separation should be obtained from the rare earths, thorium, zirconium (at low acidity), as well as manganese, magnesium, and calcium. Confirmatory experiments showed that a good separation of scandium from the yttrium earths and

[4] C. C. Miller, *J. Chem. Soc.*, 1947, 1347, has applied chloroform extraction for the removal of these metals in the detection of scandium.

thorium could actually be obtained in this way (in 0.5 *N* hydrochloric acid or at *p*H 4 to 5). The separation from zirconium (and hafnium) was not as good as expected. Less zirconium is extracted at *p*H 4–5 than in 0.5 *N* hydrochloric acid, but more scandium remains in the aqueous phase in the almost neutral medium. A good separation of scandium from titanium

TABLE 86

EFFECT OF HYDROCHLORIC ACID CONCENTRATION ON EXTRACTION OF SCANDIUM AS THIOCYANATE BY ETHYL ETHER

(0.18 g. Sc_2O_3 and 53 g. NH_4CNS in 100 ml. original aqueous phase)

$[H^+]$	*p*H	Percentage of Sc in ether
	3.5	74.2
	2 0	90 8
0.1		93.6
0.5		94 1
1 0		94.6
2 0		88 5

TABLE 87

EXTRACTION OF VARIOUS METALS FROM AQUEOUS THIOCYANATE SOLUTION BY ETHYL ETHER

(53 g. NH_4CNS in 100 ml. original aqueous solution; hydrochloric acid concentration 0.5 *N*[a])

Metal	Amount of oxide in 100 ml., g.	Percentage of total metal in ether[b]
Be	—	>50[c]
Mg	3.6	0 02
Ca	4.4	0 04
Al	0 2	49
In	0.3	59
ΣY[d]	1.4	0 07
La	9.7	0 002
Ti[e]	0.7	2 4
Zr	6.2	0.034[f]
Th	1.6	0.13
U (VI)	0.3	4.6
Mn (II)	3.15	0 17
Fe (III)	0.19	52

[a] Fischer and Bock also give figures for the extraction of metals from a solution of *p*H 3.5; these values are a little smaller because of hydrolysis of the metal salts.

[b] On basis of equal volumes of the two phases; some values rounded off.

[c] Qualitative only.

[d] 70 per cent Y_2O_3.

[e] 0.3–1 *N* HCl.

[f] At *p*H 0.9, percentage extracted = 0.001.

can be obtained by working at *p*H 3–4. Elements that are extracted to a large extent with scandium are beryllium, aluminum, probably gallium, indium, ferric iron, cobalt, and possibly a few others such as molybdenum and rhenium.

Fischer and Bock give the following directions for separating scandium by this method in the absence of zirconium and thorium. The hydrochloric acid solution of the sample is evaporated to a moist mass, 60 ml. of 0.5 *N* hydrochloric acid are added, and then 53 g. of ammonium thiocyanate. The solution (volume now about 100 ml.) is shaken with 100 ml. of ethyl ether and the phases are separated. Approximately 94 per cent of the scandium passes into the ether. Most of the remainder is removed by adding 5 ml. of 2 *N* hydrochloric acid (the ether removes almost all the hydrogen ions in the form of thiocyanic acid) to the water phase and repeating the extraction with 50 or 100 ml. of ether. The combined ether extracts are evaporated after the addition of a few milliliters of hydrochloric acid. Nitric acid is then added cautiously dropwise at water bath temperature to destroy thiocyanate. Finally the residue is boiled with a little concentrated nitric acid until the orange-red decomposition products of thiocyanic acid are destroyed.

II. Determination with Morin

The color[5] and fluorescence reactions of scandium known at the present time are not specific and have only limited applicability.

A promising method for the determination of scandium in the absence of aluminum, beryllium, gallium, and some other metals reacting similarly involves the formation of a fluorescent complex with morin in neutral or faintly acid solution (p. 127). This reaction has been investigated only slightly from the quantitative standpoint. It appears that variation of the *p*H of the medium is of limited value in differentiating scandium from the other metals reacting with morin.[6] It is true that in strongly basic

[5] Murexide has been used by G. Beck, *Anal. Chim. Acta*, 1, 69 (1947), for the detection of scandium. A color change from purple to yellow-orange is produced by scandium, rare earths, calcium, zirconium (as chloride or nitrate), thorium (as chloride or nitrate), zinc, cadmium, iron (II), nickel, cobalt, manganese, and uranium (VI). Bismuth gives a red color, copper a yellow-brown. Scandium can be distinguished from the rare earths, calcium, thorium, zirconium by the action of nitrilotriacetate, $N(CH_2COOH)_3$, which restores the violet color of the reagent if the color change was due to scandium, but does not affect the color given by the other metals. Aluminum gives no color with murexide. For a color test for scandium with *o*-aminophenylarsonic acid and salicylaldehyde see V. I. Kuznetsov, *J. Gen. Chem.* (*U. S. S. R.*), **14**, 897 (1944); *Chem. Abst.*, **39**, 4810.

[6] G. Beck, *Mikrochim. Acta*, **2**, 9 (1937), states that scandium fluoresces best in dilute mineral acid solution, but we have been unable to observe any great difference in the effect of *p*H on the fluorescence of scandium and aluminum in the acid range.

solution (sodium hydroxide) aluminum and gallium no longer fluoresce, but then beryllium gives an intense fluorescence. Scandium hydroxide precipitated in the presence of morin with sodium hydroxide shows fluorescence presumably because of the adsorbed morin. Magnesium hydroxide behaves in the same manner.

In connection with the use of morin it is of interest that certain salts or compounds of scandium with organic acids can be extracted from aqueous medium by such organic solvents as butyl alcohol, amyl alcohol, and ethyl acetate. The addition of an alcoholic solution of morin to the organic solvent phase produces a greenish fluorescence. In this way the concentration sensitivity of the morin reaction for scandium can be increased. This extraction method for the determination of scandium has been investigated in a preliminary way by S. E. J. Johnsen.[7] In his work, scandium was extracted as the thiocyanate or the benzoate. Unfortunately a number of elements, including ferric iron, aluminum, beryllium, gallium, and indium, are extracted under the same conditions as scandium, so that the extraction is valuable only as a means of concentration of scandium with consequent increase in sensitivity and not as a means of separation. Benzoate is preferable to thiocyanate in the extraction, since the interference of traces of iron is less with the former. Ferric iron in the organic solvent does not give a fluorescence when morin is added, but interferes by absorbing ultraviolet radiation. Aluminum, beryllium, gallium, and indium all fluoresce in the organic phase. The extraction of scandium is best made from a neutral or very slightly acid medium. Ammonium acetate may conveniently be used to buffer the solution to a *p*H of approximately 7. It is important that the sample and the comparison solutions have very nearly the same *p*H (a difference of 0.2 in *p*H will give rise to a large error). Under these conditions magnesium, zinc, and thorium give no fluorescence. Phosphate and fluoride hinder or prevent the extraction of scandium as well as of aluminum.

Johnsen gives the following directions for the determination of scandium by the extraction method in the absence of the interfering metals mentioned.

Reagents

Ammonium acetate, 50 g. in 100 ml. of water.
Sodium benzoate, 25 g. in 100 ml. of water.
Morin, 0.01 per cent in alcohol or acetone solution.
Standard scandium solution, 0.001 per cent Sc in 0.1 *N* sulfuric acid.

[7] Unpublished work, University of Minnesota, 1942.

§ Procedure

The sample solution may have a volume of 5 to 15 ml. and may contain from 0.2 to 5 γ of scandium. If the solution is appreciably acid it should be brought to approximate neutrality with sodium hydroxide (free from aluminum). Treat the sample and standard solutions in 25 ml. glass-stoppered tubes as follows. Add 2.0 ml. of ammonium acetate and 1.0 ml. of sodium benzoate, mix, and add 2.0 ml. (or 3–4 ml. for quantities of scandium in the neighborhood of 5 γ) of ethyl acetate. Shake well and allow the phases to separate. Add 0.05 ml. of morin solution to the upper layer and mix by gentle agitation. Compare the fluorescence of the upper layers of the tubes in ultraviolet light.

CHAPTER XL

SILVER

I. Separations

In the absence of large amounts of metals giving sulfides insoluble in mineral acid medium, silver may be advantageously isolated by precipitation with hydrogen sulfide from a dilute sulfuric or nitric acid solution. The acidity of the solution may be in the neighborhood of 0.1 *N*. Chlorides and other halides should preferably be absent. Copper and mercury sulfides may be used as collectors. Copper need not be subsequently removed in either the rhodanine or cupric dithizonate methods if present to the extent of 0.5–1 mg. Mercury interferes in both methods and would have to be removed by gentle ignition of the precipitate. Since silver sulfide is one of the least soluble sulfides, it may be expected that the most minute amounts of silver can be isolated in this way under proper working conditions. The method should be applicable to such varied materials as silicates, meteorites, and biological substances. However, there are no data available to show the reliability of the method when very minute quantities of silver are involved.

Extraction by dithizone from acid solution offers another possibility for the isolation of minute amounts of silver in the absence of gold, palladium, mercury, or much copper. Anions such as the halides and thiocyanate which form slightly soluble or complex silver salts must be absent. The value of the equilibrium constant of silver dithizonate is of such magnitude (p. 545) that small volumes of dithizone solution suffice to remove silver practically completely from fairly acid solutions. Silver may be separated in this way from moderate amounts of copper (*cf.* p. 546) but when the ratio Cu/Ag is very large the separation fails.

Another method of isolation which may be of use in colorimetric analysis, although primarily intended for the final determination of silver by cupellation, involves coprecipitation of silver with a precipitate of mercury-mercurous chloride produced by adding magnesium metal to a hydrochloric acid solution containing mercuric chloride, or coprecipitation with mercury-mercuric amino salt obtained by adding ammonia to a solution containing mercuric nitrate.[1]

[1] W. E. Caldwell and K. N. McLeod, *Ind. Eng. Chem., Anal. Ed.*, 9, 530 (1937).

It may be possible to precipitate silver with stannous chloride from acidic medium in the presence of tellurite (*cf.* p. 341).

Precipitation of silver as chloride,[2] or better as bromide, with a slight excess of precipitant should be a useful method of separation in certain cases.[3] Mercurous bromide may be used as the gathering agent.[4] The mercury would have to be completely volatilized before the silver could be determined colorimetrically. An unpleasant feature of halide precipitation of silver is the necessity for the conversion of the precipitate into a soluble salt, which of course must precede the determination of silver by any colorimetric method. Removal of chloride can be effected by fusion with potassium pyrosulfate.

II. Methods of Determination

The most suitable reagents for the colorimetric determination of small amounts of silver are *p*-diethylaminobenzylidenerhodanine and dithizone. Neither reagent is specific for silver. Gold, palladium, and mercury will react with both under the conditions of the silver determination. Much higher acidities and neutral salt concentrations are permissible in the dithizone method than in the rhodanine method and moreover colored ions do not interfere in the former. Anions forming complex or slightly soluble salts with silver interfere seriously in both methods.

The possibility of the adsorption of silver by glassware must be borne in mind in the determination of small amounts of the metal. From a neutral solution silver is appreciably adsorbed by soft glass, only slightly by Pyrex, and not at all by fused silica. The adsorption is either much decreased or prevented if the silver solution is slightly acidified. If a silver solution must be concentrated by evaporation, a silica dish should be used. Very dilute standard silver solutions should be freshly prepared by dilution of a stronger stock solution.

A. The *p*-Dimethyl- or *p*-Diethylaminobenzylidenerhodanine Method

These reagents give a very slightly soluble red-violet precipitate with silver in acidic medium (p. 128). Both direct and indirect methods for the determination of silver by the use of the methyl or ethyl compound

[2] *Cf.* D. G. Higgs, *Analyst*, **69**, 270 (1944), for chloride isolation of silver for its determination in brass.

[3] E. E. Jelley, *J. Soc. Chem. Ind.*, **51**, 191T (1932), isolates silver as the bromide, dissolves the precipitate in ammonia, and determines silver in the solution with sodium dithionite (p. 549).

[4] Other possibilities are thallium (I) bromide and lead bromide, which in small amounts would not furnish enough metal to require removal before the determination of silver.

have been worked out. The direct method is to be preferred when less than 1–2 γ of silver is to be determined.

Direct Method. One drawback of this method is the necessity for close control of the acidity of the sample solution so that it is exactly the same as that of the comparison solution. A suitable acidity is 0.05 *N*. At higher acidities the sensitivity is strongly decreased. The color intensity depends upon the excess of reagent as well as upon the acidity.

The silver-rhodanine precipitate is very slightly soluble and forms a stable, very finely divided, dispersion. When the silver concentration is

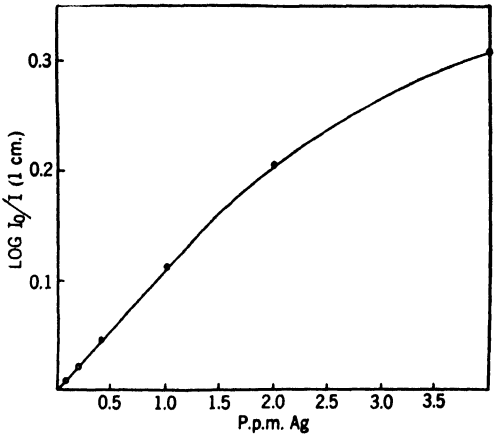


Fig. 68. Determination of silver with diethylaminobenzylidenerhodanine (green filter). Acidity 0.05 *N* (nitric acid); 0.50 ml. 0.05% rhodanine reagent in a final volume of 25 ml. Extinctions represent constant values.

in the neighborhood of 1 p.p.m. the maximum color is obtained practically at once after the addition of the reagent and shows no significant change in the next half hour, but at lower concentrations (0.1–0.5 p.p.m.) the maximum intensity is not reached until after 15–20 minutes under the conditions recommended in the procedure below. Beer's law holds in the range 0.1 to 1 p.p.m. of silver (Fig. 68). Neutral salts may affect the color intensity.[5] Potassium nitrate in 1–2 per cent concentration changes the color strength only slightly, but 2 per cent of potassium sulfate was found to increase the extinction of a 0.4 p.p.m. solution of silver from the normal value of 0.047 to 0.070.

[5] According to I. C. Schoonover, *J. Research Natl. Bur. Standards*, **15**, 377 (1935), the general tendency of dissolved salts (calcium carbonate, sodium nitrate, potassium sulfate, etc.) is to increase the color intensity. Sulfuric acid in small amounts is also stated to increase the color strength.

Lead and copper in small amounts are without great effect. Thus a solution containing 10.0 γ of silver in 25 ml. yielded the value 9.2 γ in the presence of 20 mg. of lead, and 9.8 γ in the presence of 19 mg. of copper (as cupric sulfate) when the blue color of the copper was compensated by the use of a similar reference solution.

Special Solutions

p-Diethylaminobenzylidenerhodanine, 0.05 per cent solution in ethyl alcohol. The methyl compound may also be used.

Standard silver solution, 0.01 or 0.001 per cent in 0.1 *N* nitric acid. Prepare by diluting a 0.100 per cent solution (0.158 g. of silver nitrate, dried at 110°, in 100 ml. of 0.1 *N* nitric acid solution).

§ Procedure

To 20 ml. of sample, 0.05 *N* in nitric acid, with a silver content of 0.1–2 p.p.m., add 0.50 ml. of rhodanine reagent, dilute to 25 ml. and mix. Determine the transmittancy of the dispersion (green filter or light of 495 mμ) after 5 minutes for amounts of silver in the neighborhood of 1 p.p.m. or after 20 minutes with 0.1–0.5 p.p.m. The standards for the construction of the reference curve must have precisely the same acidity as the sample solution, and moreover should contain the same concentration of foreign salts as the sample.

Indirect method. Ringbom[6] has determined small amounts of silver by precipitating the rhodanine complex in dilute sulfuric acid medium, dissolving the washed precipitate in alkaline potassium cyanide solution, measuring the color intensity of the yellow solution, and finding the silver concentration from the stoichiometric relation between the rhodanine and silver. The precipitate tends to carry down some of the reagent, but the latter can be washed out with alcohol. Nitric acid must not be present because it oxidizes the reagent. Chloride must be absent; it can be removed by fuming with sulfuric acid or by fusing the sample with potassium pyrosulfate.

The method has been applied with success to the determination of traces of silver in metallic copper. Gold is said not to interfere, since it is not appreciably attacked by molten pyrosulfate which is used to bring the copper into solution. The concentration of iron in copper is so small that it does not interfere.

Reagents

p-Dimethylaminobenzylidenerhodanine, 20 mg. in 100 ml. of ethyl alcohol. This is the precipitating solution. Doubtless the ethyl compound can be used as well.

[6] A. Ringbom, *Acta Acad. Aboensis, Math. Phys.*, **14**, 1 (1943).

p-Dimethylaminobenzylidenerhodanine, 20 mg. of reagent, recrystallized from alcohol, in 100 ml. of 0.01 *N* sodium hydroxide (for standards).

Potassium cyanide, 5 g. in 1 liter of 0.001 *N* sodium hydroxide.

§ Procedure

General directions. To 50 ml. of solution containing 10–70 γ of silver, add enough sulfuric acid to make its concentration *ca.* 0.4 *N*, followed by 3 ml. of alcoholic rhodanine solution. (For less than 10 γ of silver, make the precipitation in 0.1 *N* acid and use smaller volumes so that the final solution can be diluted to 25 ml.) Allow the solution to stand in the dark for at least 2 hours (preferably overnight). Filter through a glass filter crucible (Jena G4 or equivalent fineness) and wash with a little water. Place the crucible in the beaker in which the precipitation was made and pour 40 ml. of ethyl alcohol into the crucible and the beaker. Cover with a watch glass and boil very gently for 15 minutes. Suck off the alcohol in the crucible and wash the latter and the beaker with cold alcohol; the last portion must be entirely colorless. Empty and clean the suction flask.

Pour 5 ml. of potassium cyanide solution into the precipitation beaker and thence into the crucible, using a stirring rod to distribute the solution over the walls of the vessels. Draw off the solution and wash with a little water. Repeat the treatment with 5 ml. of cyanide solution. Transfer the solution from the suction flask to a 50 ml. volumetric flask and dilute

TABLE 88

INDIRECT DETERMINATION OF SILVER WITH *p*-DIMETHYLAMINOBENZYLIDENERHODANINE[a]

Addition	Ag taken, γ	Ag found, γ
In 0.3 *N* sulfuric acid	50.0	49.0
In 0.4 *N* sulfuric acid	50.0	50.5, 50.5
In 0.5 *N* sulfuric acid	50.0	50.0, 50.5
In 1.0 *N* sulfuric acid	50.0	48.8, 49.3
In 1.2 *N* sulfuric acid	50.0	47.5, 47.8
In 0.4 *N* sulfuric acid	10.0	10.0, 10.1
In 0.1 *N* sulfuric acid	5.0	5.1
In 0.5 *N* sulfuric acid	5.0	4.0
In 0.1 *N* sulfuric acid	1.0	1.1
In 0.5 *N* sulfuric acid	1.0	0.5
2 g. potassium sulfate, 0.5 *N* sulfuric acid	50.0	50.4
4 g. potassium sulfate, 0.5 *N* sulfuric acid	50.0	50.2
1 g. copper sulfate, 0.5 *N* sulfuric acid	50.0	51.8
0.1 g. copper metal	100 p.p.m.	105 p.p.m.
0.1 g. copper metal	213 p.p.m.	215 p.p.m.
0.1 g. copper metal	265 p.p.m.	264 p.p.m.
0.1 g. copper metal	339 p.p.m.	342 p.p.m.

[a] Selected figures from Ringbom, *loc. cit.*

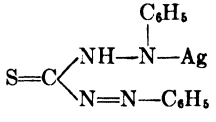
to volume. Without undue delay obtain the transmittancy of the solution with the aid of a blue filter (460 mμ).

Prepare the standard curve by measuring out 0.1 . . . 1 ml. of the aqueous rhodanine solution, diluting to 50 ml. with 0.001 *N* sodium hydroxide, and finding the transmittancy. One part of the rhodanine corresponds to 0.408 part of silver. Beer's law is obeyed when a sufficiently selective filter is used.

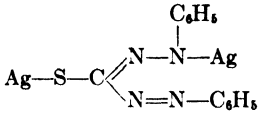
Silver in copper. Transfer 0.6–0.7 g. of electrolytic copper (10–20 p.p.m. of silver) or 0.1 g. of anode copper (100–500 p.p.m. of silver) to a silica crucible. Add 6–7 g. of potassium pyrosulfate for the larger amount of copper or 3 g. for the smaller amount, heat the covered crucible carefully until all the copper has been dissolved and then for a few minutes more. Place the crucible in a 150 ml. beaker and add 50–100 ml. of water and 3 ml. of 5 *N* sulfuric acid. When solution of the melt is complete, add 3 ml. of alcoholic rhodanine solution and proceed according to the above directions.

B. The Dithizone Method[7]

Silver reacts quantitatively with dithizone even in 0.5 *N* mineral acid solution to yield the keto dithizonate



which dissolves in chloroform or carbon tetrachloride to give a yellow solution. In neutral or basic medium the enol compound



is formed, which is red-violet and virtually insoluble in carbon tetrachloride or chloroform. It is not important analytically, although it might find use as a separation form for silver.

Silver keto dithizonate is stable in the presence of alkalies, so that once formed it is not appreciably converted into the enol form, even when the carbon tetrachloride solution is shaken with 5 per cent sodium hydroxide solution. Therefore, after reaction of the silver with dithizone the excess of the latter can be removed from the carbon tetrachloride by shaking with

[7] H. Fischer, G. Leopoldi, and H. von Uslar, *Z. anal. Chem.*, 101, 1 (1935). For the determination of silver in mineral waters by the use of dithizone, see K. Kuroda, *Bull. Chem. Soc. Japan*, 17, 419 (1942); *Chem. Abst.*, 41, 4595.

dilute ammonia, and silver then determined colorimetrically by comparison against a standard solution of silver dithizonate. Beer's law holds.

Silver may be determined more expeditiously by the mixed color method (p. 546), especially if a photometer is available. If copper is absent, a dilute solution of dithizone may be used as reagent, and the mixed color varies from some shade of green to a yellow. The transmittancy of the solution may be determined with a yellow filter; a plot of log 10 I/I_0 gives almost or entirely a straight line, the values increasing with the silver content in accordance with the amount of dithizone converted into silver

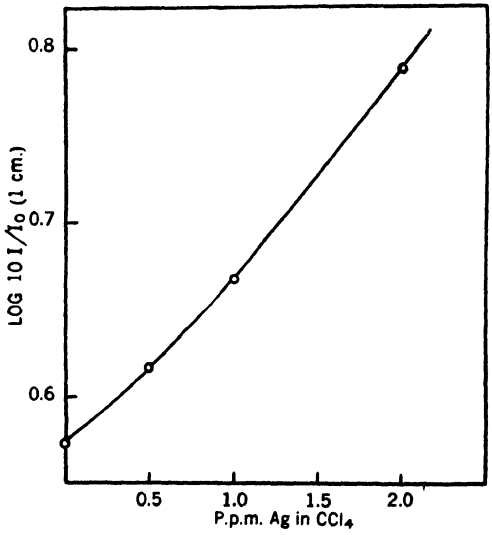


Fig. 69. Determination of silver with dithizone by the mixed color method (yellow filter).

dithizonate (Fig. 69). Metals such as lead and zinc, which react quantitatively with dithizone only in neutral or slightly basic medium do not interfere except when they are present in extremely high concentrations. The equilibrium constant for silver dithizonate has not been determined exactly but it appears to have a value of the order 10^7 (carbon tetrachloride), so that silver can be extracted quantitatively in 0.5–1 *N* acid solutions from which only minute traces of the metals mentioned are extracted unless excessive amounts are present.

The extraction of silver is incomplete from the analytical standpoint when the solution is 6 *N* in sulfuric acid and only a slight excess of dithizone is present. Thus two 6 *N* sulfuric acid solutions containing respectively 10 and 15 γ of silver yielded the values 9.5 and 13.9 γ when analyzed

according to the procedure given on p. 547 (10 ml. aqueous phase, 5 ml. dithizone).

In the presence of copper, silver can be determined by the mixed color method if cupric dithizonate is employed as reagent, the mixed color then ranging from violet to yellow. With a suitable yellow filter, a linear relation is found between log 10 I/I_0 and the silver concentration in the carbon tetrachloride. Moderate amounts of copper are nearly without effect, but as the quantity increases the values for silver show a negative error. The magnitude of the error is illustrated by the following figures obtained in determining silver according to the procedure given below, the

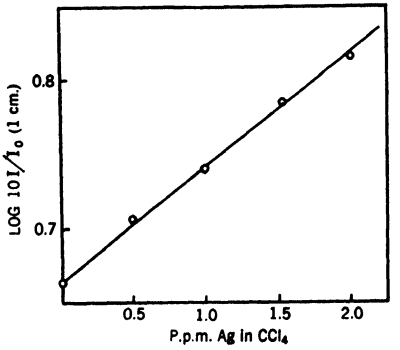


Fig. 70. Determination of silver with cupric dithizonate (yellow filter).

aqueous phase having a volume of 10 ml. (0.5 *N* in sulfuric acid) and the carbon tetrachloride a volume of 5 ml.:

Cu present, mg.	Ag present, mg.	Ag found, mg.
10.0	0.010	0.0082
5.0	0 010	0.0091
2.5	0.010	0.0095

The mixed color method with copper dithizonate as reagent is recommended for general use. No special purification of acids, distilled water, etc. is required to remove traces of copper or other metals, as would be required in the dithizone mixed color method, and especially in the mono color method.

As already mentioned, silver cannot be determined with dithizone when palladium, gold, and mercury are present because these metals have an even greater affinity than does silver for dithizone.

1. The Mixed-Color Method

In the absence of copper a dilute solution of dithizone may be used as reagent, but otherwise a solution of cupric dithizonate must be used.

Special Solutions

Dithizone, 0.001 per cent (weight/volume) in analytical reagent carbon tetrachloride. Purification of the dithizone is not required, but the carbon tetrachloride should preferably be redistilled.

Copper dithizonate. Shake 0.001 per cent dithizone solution with a slight excess of dilute copper sulfate solution in about 0.05 *N* sulfuric acid for a minute or two, and then wash the carbon tetrachloride with 0.01 *N* sulfuric acid to remove suspended droplets of aqueous copper solution.

Standard silver solution, 0.001 per cent Ag in 0.1 *N* sulfuric or nitric acid (see p. 542).

§ Procedure

With Dithizone as Reagent. Transfer 5–20 ml. of sample, approximately 0.5 *N* in sulfuric acid,[8] to a glass stoppered tube (1.8 × 15 cm. with flat bottom). Add 2.0 ml. of dithizone solution for 1 to 5 γ of silver and correspondingly smaller or larger volumes for other quantities. Shake well for 15 seconds, allow the carbon tetrachloride to settle, and compare the hue of the latter with that of a series of standards obtained in the same way. Make the color comparison against a white background in good light. Alternatively, make the comparison by colorimetric titration, *i.e.*, add standard silver nitrate solution to a comparison tube containing the same volume of dithizone and 0.5 *N* sulfuric acid solution as the unknown, with thorough shaking after each addition until the colors of the carbon tetrachloride layers match. The precision of the comparison is greatest when the solutions show the yellow-green color approximately midway between the colors of silver dithizonate and dithizone.

For amounts of silver greater than a few micrograms a photometer may be used to advantage. In this case shake the acidified silver solution in a separatory funnel with 10.0 ml. of dithizone solution (for as much as 25 γ of silver) for about one-half minute, allow the carbon tetrachloride layer to settle and clarify, and deliver the liquid into the absorption cell through the dry stem of the funnel.[9] Obtain the transmittancy of the solution with the aid of an orange or yellow filter (Fig. 69). Construct the calibration curve by shaking 10.0 ml. of dithizone with acidified silver solutions of various concentrations having approximately the same volume as the sample solution.

With Cupric Dithizonate as Reagent. Transfer 5–20 ml. of sample, approximately 0.5 *N* in sulfuric acid, to a glass stoppered tube and add 2.0 ml. of copper dithizonate solution (for 0.5 to 5 γ of silver). Shake for 2

[8] The solution may also be acidified with nitric acid (to not over 0.5 *N*) but the latter must be free from oxides of nitrogen which would oxidize dithizone and produce a yellow carbon tetrachloride solution resembling that of silver dithizonate.

[9] Greater accuracy can of course be obtained by using 5 ml. of dithizone instead of 10, but then the amount of silver must not exceed 15 γ.

minutes and compare the hue of the carbon tetrachloride with standards prepared similarly. Comparison may also be made by colorimetric titration.

If it is desired to use a photometer, transfer a sufficient volume of acidified sample solution to contain 2–10 γ of silver to a separatory funnel and shake for 2 minutes with 5.0 ml. of copper dithizonate solution. Use a yellow filter in obtaining the transmittancy of the solution (Fig. 70). The standard silver solutions for the construction of the reference curve should have about the same volume and acidity as the sample solution.

2. The Mono-Color Method

The following procedure[10] may be applied in the presence of the alkalies, alkaline earths, magnesium, aluminum, antimony, arsenic, and other metals which do not react with dithizone, as well as in the presence of such metals as lead, zinc, and cadmium which react only slightly or not at all in acid medium.

Special Solutions

Dithizone, 5 mg. of purified reagent in 100 ml. of pure carbon tetrachloride.

Ammonia wash solution, 1:1000. The solution should impart no appreciable color to the carbon tetrachloride layer when shaken with dithizone solution.

§ Procedure

The sample solution may conveniently contain 1 to 10 γ of silver per milliliter. Acidify 10 ml. (or a similar volume) with 1 ml. of 4 *N* nitric or sulfuric acid, and shake thoroughly for 1–2 minutes with 5 ml. of dithizone in a small separatory funnel. Allow the two liquids to separate and draw off the carbon tetrachloride layer into another separatory funnel. Repeat the extraction with small portions of dithizone until the silver has been completely extracted, *i.e.*, until the last portion of dithizone remains an unchanged green after shaking for a minute or two. Finally wash the aqueous solution with a milliliter or two of carbon tetrachloride.

Wash the combined extracts once or twice with 5–10 ml. of 0.1 *N* sulfuric acid. (If metals reacting with dithizone in basic solution are present they must be completely washed out, otherwise they will of course react when the carbon tetrachloride solution is washed with ammonia in the next step.) Then shake the carbon tetrachloride solution with two 5 ml. portions of ammonia wash solution to remove excess dithizone. The last portion of wash solution must be colorless; if it is yellowish, wash further.

Dilute the silver dithizonate solution to a definite volume with carbon tetrachloride and compare against a standard silver dithizonate solution

[10] Taken from H. Fischer, G. Leopoldi, and H. von Uslar, *Z. anal. Chem.*, **101**, 1 (1935).

similarly prepared from an appropriate volume of 0.001 per cent silver solution. It is permissible to separate droplets of the aqueous phase from the carbon tetrachloride prior to the color comparison by filtration of the latter through a small dry paper filter.

When a photometer is used, determine the transmittancy of the solution at 460 mμ.

C. The Chloride Method

The nephelometric determination of silver as chloride[11] lies beyond the scope of this book, but a few words may be said about the turbidimetric determination with the aid of a photometer. The relation between the concentration of silver and the extinction of the silver chloride suspension is shown in Fig. 71. The suspensions were obtained by adding all at once 2.0 ml. of 0.05 *N* hydrochloric acid to 20 ml. of silver solution in 0.10 *N* nitric acid, which was swirled during the addition. The suspension was then made up to 25 ml. with water. The reproducibility of the suspensions prepared in this way was fairly good as shown by the following replicate figures for extinction: 0.004, 0.0045; 0.0105, 0.012; 0.030, 0.029, 0.030; 0.078, 0.077; 0.120, 0.122. The transmittancy of the suspensions was determined after 20 minutes (room temperature). In the case of the dilute suspensions, the amount of light transmitted decreases considerably after this time whereas it increases with more concentrated suspensions, so that this is an arbitrary period of standing (Fig. 72).

As well known, the opacity of silver chloride dispersions depends to a greater or less extent upon the amount and kind of foreign electrolytes present and this method cannot therefore be applied indiscriminately to solutions of unknown composition. The turbidimetric method is not very sensitive, the useful lower limit of the method being 1 p.p.m. of silver when a 1 cm. cell is used. The rhodanine method is twenty-five times as sensitive (p. 541, Fig. 68).

D. Other Methods

In an ammoniacal solution containing gelatin, silver is reduced to the metal by sodium dithionite ($Na_2S_2O_4$) and a yellow sol is formed which is suitable for the determination of 1 to 20 p.p.m. of silver. A preliminary

[11] See A. B. Lamb, P. W. Carleton, and W. B. Meldrum, *J. Am. Chem. Soc.*, **42**, 253 (1920); I. M. Kolthoff and H. Yutzy, *J. Am. Chem. Soc.*, **55**, 1915 (1933); C. R. Johnson, *J. Phys. Chem.*, **35**, 540, 830, 2237, 2581 (1931); A. F. Scott and F. H. Hurley, *J. Am. Chem. Soc.*, **56**, 333 (1934); C. H. Greene, *J. Am. Chem. Soc.*, **56**, 1269 (1934); L. Bertiaux, *Chim. anal.*, **31**, 32 (1949). The last-named author dissolves isolated silver chloride in ammonia and evaporates to fumes with perchloric acid to transform silver chloride into perchlorate, after which the nephelometric chloride determination is carried out.

separation of silver from most metals is required.[12] Sucrose may also be used as a reducing agent in sodium hydroxide solution to produce a stable silver sol.[13]

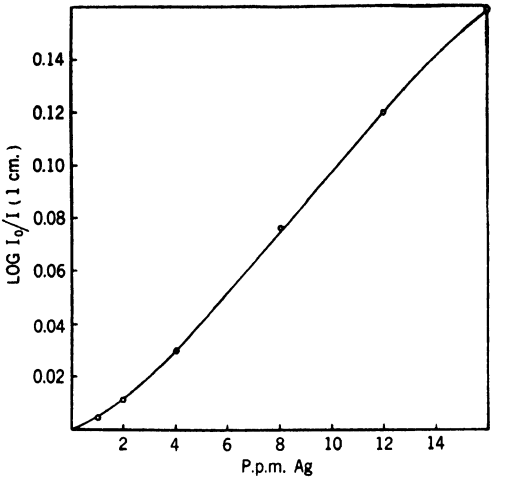


Fig. 71. Turbidimetric determination of silver with chloride.

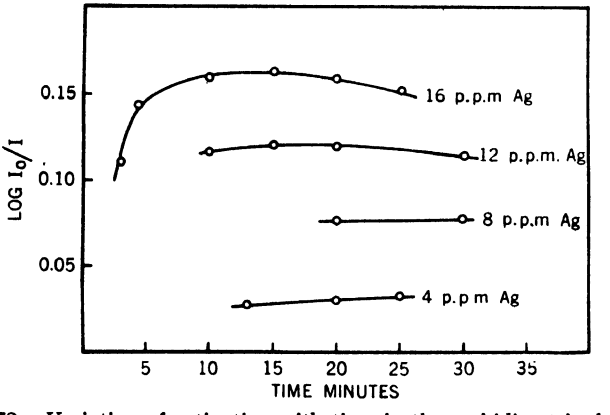


Fig. 72. Variation of extinction with time in the turbidimetric determination of silver with chloride.

Silver may be determined photometrically as the sulfide by adding hydrogen sulfide water to an ammoniacal solution (as of separated silver chloride)

[12] E. E. Jelley, *J. Soc. Chem. Ind.*, **51**, 191T (1932). For the use of tannin as a reducing agent in the determination of silver see C. G. Makris and R. Menaché, *Ann. chim. anal. chim. appl.*, **22**, 117 (1940).

[13] H. Hepenstrick, *Helv. Chim. Acta*, **32**, 364 (1949); *cf.* G. S. Whitby, *Z. anorg. Chem.*, **67**, 62 (1910).

and then acidifying to prevent the interference of such metals as iron and lead.[14]

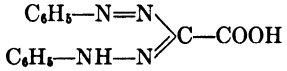
2-Thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine gives a red to purple color (due to a slightly soluble compound) with silver in neutral or slightly acidic solution.[15] This reaction has been applied to the determination of silver in very dilute solution.[16] This method is very similar to the rhodanine procedure, IIA above. The sensitivity of the two methods is of the same order and both are subject to the same interferences in general.

An indirect method for silver may be based on the reaction of a silver compound (including the halides) with potassium nickel cyanide to liberate nickel cyanide:

$$AgX + K_2[Ni(CN)_4] \longrightarrow K[Ag(CN)_2] + Ni(CN)_2 + KX,$$

which is then allowed to react with dimethylglyoxime in an ammonia–pyridine medium; the nickel dimethylglyoxime remains dissolved in the solution and imparts a yellow coloration to it, which is measured photometrically.[17]

Formazylcarboxylic acid



is said to be a specific silver reagent.[18] It produces a claret-colored precipitate with silver in acetic acid solution.

Trace quantities (1–10 γ) of silver have been determined by their catalytic effect on the reduction of cerium by hydrochloric acid.[19] The transmittancy of the ceric solution at 436 mμ is measured as a function of the time.

[14] P. W. Danckwortt, *Arch. Pharm.*, **252**, 29 (1914); T. V. Heidlberg, *Biochem. Z.*, **192**, 238 (1928); L. de Brouckère and R. Petit, *Bull. soc. chim. Belg.*, **45**, 717 (1937).

[15] S. E. Sheppard and H. R. Brigham, *J. Am. Chem. Soc.*, **58**, 1046 (1936).

[16] J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.*, **14**, 148 (1942).

[17] S. Siggia, *Anal. Chem.*, **19**, 923 (1947).

[18] L. M. Kulberg and A. M. Ledneva, *J. Anal. Chem. Russ.*, **2**, 131 (1934); abstract in *Analyst*, **73**, 352 (1948).

[19] H. Goto and T. Shiokawa, *J. Chem. Soc. Japan*, **64**, 840 (1943); *Chem. Abstr.*, **41**, 3395.

CHAPTER XLI

SODIUM

Traces of sodium are best determined by emission spectrography (arc or flame). The colorimetric determination is necessarily indirect and has the disadvantages associated with such methods, which are all the more pronounced in this case because of the relatively great solubility of any precipitation form of sodium.

I. Separations

Since there are no salts of sodium markedly insoluble in aqueous medium, the separation of small amounts of the element must generally be accomplished by the precipitation of the major constituents of the sample with appropriate reagents. Potassium is perhaps best separated as the perchlorate, which is but slightly soluble in various organic solvents. When possible, the alkali salts are converted into perchlorates by evaporation to dryness with perchloric acid and the residue is extracted with ethyl acetate or other suitable solvent to dissolve sodium perchlorate and leave most of the potassium perchlorate. Less satisfactorily, potassium can be precipitated in alcoholic solution by evaporating the aqueous solution to a small volume and adding a saturated solution of ammonium perchlorate followed by sufficient ethyl alcohol to make its volume about 75 per cent in the mixture. These methods reduce the amount of potassium in solution to the point where sodium can be successfully determined by the method described below. Lithium can be separated from sodium by making use of the solubility of lithium chloride in organic solvents (*e.g.*, alcohol + ether, p. 415) in which sodium chloride is but slightly soluble. This method will fail if the amount of sodium chloride is very small.

Electrolysis with a mercury cathode is a useful method for removing large amounts of many heavy metals (*cf.* p. 31) preparatory to the determination of small amounts of sodium.

II. Determination by the Triple Acetate Method

The only procedure which comes into practical consideration for the determination of sodium is based on the insolubility of certain triple acetates of the composition $NaMe^{II}(UO_2)_3(C_2H_3O_2)_9 \cdot aq.$ in an excess of the precipitating solution. Me^{II} may be magnesium, zinc, manganese, cobalt, and

other metals. The use of zinc[1] and magnesium[2] uranyl acetates as precipitants in aqueous solution is most common. It is only by taking special measures that sodium can be quantitatively precipitated in this way. The reagent solution must be concentrated, and further must be saturated with the triple acetate at the same temperature that exists in the precipitation; the sample solution must have a very small volume. Alcohol saturated with the triple acetate is used for washing. The precipitation is sometimes carried out in alcoholic solution, but this permits the presence of less potassium than when the precipitation is made in aqueous medium unless a double precipitation is made.[3] Potassium does not form a triple acetate but it may precipitate as potassium uranyl acetate when present in relatively high concentrations. Lithium must be absent because it may form a sparingly soluble triple acetate or will be coprecipitated with the sodium.

After the triple acetate has been quantitatively precipitated, collected, and washed, it may be dissolved in water and either uranyl ion or Me^{++} determined in the solution. Uranyl ion is fairly strongly colored and if the quantity of precipitate is not too small the absorption of the solution may be measured at a wave length of 450 mμ.[4] The sensitivity with a suitable blue filter is approximately 1 γ of sodium per cm.[2] (p. 49) and Beer's law is followed if the light is sufficiently monochromatic. However, it is usually more advantageous to add a reagent which will give a strong color with uranium. Hydrogen peroxide is very suitable for the purpose. In ammonium carbonate solution, it gives a yellow to orange color with uranyl ion.[5] The wave length of minimum transmission lies at 450 mμ or less (it appears to depend upon the uranyl concentration). A wave length of 520 mμ has been recommended by Arnold and Pray for the measurement of the

[1] H. H. Barber and I. M. Kolthoff, *J. Am. Chem. Soc.*, **50**, 1625 (1928); **51**, 3233 (1929).

[2] E. R. Caley and C. W. Foulk, *J. Am. Chem. Soc.*, **51**, 1664 (1929). E. Kahane, *Bull. soc. chim.*, **47**, 382 (1930); **53**, 555 (1933). For a good discussion of the various triple acetate methods for sodium, see L. Fresenius and E. Brennecke in R. Fresenius and G. Jander, *Handbuch der analytischen Chemie*, Springer, Berlin, 1940, p. 25, vol. Ia of Part III.

[3] For a thorough study of the determination of sodium with an alcoholic solution of magnesium uranyl acetate see F. Nydahl, *Ann. Agr. Coll. Sweden*, **6**, 37 (1937).

[4] L. Jendrassik and M. Holász, *Biochem. Z.*, **298**, 74 (1938); D. R. McCormick and W. E. Carlson, *Chemist-Analyst*, **31**, 15 (1942). The former authors dissolve the precipitate in a 20 per cent solution of sodium citrate. W. S. Hoffman, *Photelometric Clinical Chemistry*, Morrow, New York, 1941, p. 174, states that the transmittancy of the solution of the triple salt in water varies markedly with temperature (3% per 5° C.) and therefore he dissolves it in 0.1 *N* ammonium thiocyanate in which the color is virtually independent of ordinary temperature variations.

[5] This reaction has been applied to the determination of sodium by E. A. Arnold and A. R. Pray, *Ind. Eng. Chem., Anal. Ed.*, **15**, 294 (1943).

transmittancy of the solution. Beer's law is followed over a considerable range of uranium concentration. The color intensity shows no appreciable change over a period of some hours.

It may be pointed out that determination of zinc (or magnesium) in the triple acetate precipitate should be advantageous in the determination of sodium in the presence of much potassium. The latter is partially precipitated as the double acetate when present in high concentrations, and therefore gives high results when uranyl is determined but presumably would not if Me^{II} were determined. It has been proposed to use manganese uranyl acetate as a precipitant for sodium in order that the amount of precipitate may be found by oxidizing the manganese in it to permanganate.[6]

The following procedure for the precipitation of sodium is that of Barber and Kolthoff (*loc. cit.*). Potassium may be present in fairly large amounts —as much as 10 mg. of potassium chloride with 0.5 mg. Na. Amounts of ammonium, calcium, barium, and strontium equal to some milligrams and perhaps even more may be present. Sulfate does no harm, but oxalate, tartrate, etc. should be absent. Phosphate in small quantity need not be removed before the precipitation. Any uranyl phosphate precipitated will remain undissolved when the triple acetate is finally dissolved in water and may be filtered off at that point. If much phosphate is present it can be precipitated with a slight excess of calcium hydroxide (use phenolphthalein as indicator).

See a paper by Broadfoot and Browning for the determination of sodium in plant material.[7] In the procedure (gravimetric) used by these authors the interference of large amounts of potassium is minimized by the addition of a regulated amount of nitric acid to the precipitant. A modification of the triple acetate method for the determination of sodium in potassium hydroxide and in other potassium compounds that can be converted into the perchlorate is based on the separation of most of the potassium by extraction of the perchlorates with isopropanol; sodium is then precipitated as the magnesium uranyl acetate in the filtrate.[8] The method as described is a gravimetric one, but presumably sodium can be determined colorimetrically in the precipitate according to the procedure below or a similar one.

Reagents

Zinc uranyl acetate. Mix equal volumes of solutions (*a*) and (*b*), allow to stand 24 hours at the temperature at which the precipitation is to be made and filter off the precipitate of sodium zinc uranyl acetate usually formed from traces of sodium in the

[6] W. Woelfel, *J. Biol. Chem.*, 125, 219 (1938); E. Leva, *ibid.*, 132, 487 (1940).
[7] W. M. Broadfoot and G. M. Browning, *J. Assoc. Official Agr. Chem.*, 24, 916 (1941).
[8] D. Williams and G. S. Haines, *Ind. Eng. Chem., Anal. Ed.*, 16, 157 (1944).

reagents. If no precipitate appears add a little sodium chloride to saturate the solution with the triple acetate and filter. Keep the solution in a Pyrex bottle.

Solution (a). Mix 10 g. of $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, 6 ml. of 30 per cent acetic acid, and 50 ml. of water, and warm to dissolve.

Solution (b). Mix 30 g. of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$, 3 ml. of 30 per cent acetic acid, and 50 ml. of water and warm to dissolve.

Ethyl alcohol saturated with sodium zinc uranyl acetate. Shake 95 per cent alcohol at room temperature with excess triple acetate until saturated (*ca.* one-half hour) and filter. Prepare fresh every one or two days.

Ether or acetone, reagent quality.

Ammonium carbonate, saturated solution in 2 *N* ammonium hydroxide.

Hydrogen peroxide, 3 per cent. The solution should give no color with ammonium carbonate. It is best obtained by diluting the 30 per cent solution.

Standard sodium solution, 0.05 per cent Na. Prepare from sodium chloride (NaCl/Na = 2.54).

§ Procedure

The solution may conveniently contain 0.1 to 0.5 mg. of sodium in a volume not greater than 0.5 ml. If the precipitate is to be separated by filtration, a small Pyrex beaker (10–20 ml.) may be used as the precipitation vessel, but if the sample has previously been ashed in a small dish or crucible, this may be used for the precipitation after the residue has been brought into solution. The precipitate may also be formed in a centrifuge tube and separated by centrifugation. If necessary the precipitation vessel should be immersed in a bath of water to keep the temperature of its contents within a degree or so of that at which the reagent solution was saturated with the triple salt.

Add 5 ml. of zinc uranyl acetate solution and allow to stand for 30 to 60 minutes while stirring at frequent intervals to insure complete precipitation of the sodium. Then, by the use of a filter stick (see p. 500) draw off the liquid and suck the precipitate dry. Wash once with 0.5 ml. portion of zinc uranyl acetate, suck as dry as possible, and then wash with similar small portions of alcohol saturated with the triple acetate until all of the reagent solution has been removed. Finally, wash once or twice with ether or acetone and allow to stand until the latter has evaporated.

Dissolve the precipitate in water, transfer the solution to a 50 ml. volumetric flask, add 5 ml. of ammonium carbonate solution followed by 5 ml. of hydrogen peroxide, and dilute to the mark with water. Obtain the transmittancy of the solution with the aid of a blue or green filter, or light of wave length 500–525 mμ. Construct the standard curve by carrying known amounts of sodium through the procedure in the same manner as the sample.

CHAPTER XLII

THALLIUM

I. Separations

There are many possible reactions for the isolation of thallium and its separation from other elements, but only a few have been studied with reference to micro amounts of thallium. Extraction methods appear the most promising.

A. Precipitation Methods

Thionalide is a specific precipitant for thallium in a tartrate-cyanide solution containing sodium hydroxide (see p. 562).

In the case of materials not containing large amounts of heavy metals, precipitation of thallium as sulfide may be of value. Thallous sulfide (S.P. = 10^{-24}) is quantitatively precipitated in neutral or ammoniacal medium. Mercury, lead, and silver sulfides may be suggested as collectors.

The low solubilities of thallous chloroplatinate, iodide, chromate,[1] cobaltinitrite, and phosphotungstate may permit their use in the separation of small quantities of the element. Perhaps potassium or rubidium can be added to gather small amounts of thallium when chloroplatinate, cobaltinitrite, or phosphotungstate are used as precipitants; barium chromate may be expected to be useful for collecting thallous chromate. Thallic hydroxide is very slightly soluble and may be precipitated with ammonium or sodium hydroxide in a suitable oxidizing environment. Ferric hydroxide or hydrated manganese dioxide may be used as coprecipitators.

Precipitation of metallic thallium by zinc in hydrochloric or sulfuric acid solution has been used for the separation of the element from large samples (50–100 g.) of sulfides such as pyrite or sphalerite which have been brought into solution by appropriate means and oxidizing agents removed. The precipitate must be filtered off rapidly and washing omitted. The

[1] F. Ensslin, *Metall u. Erz*, **37**, 171 (1940), makes use of the precipitation of thallium as chromate in its determination in refined zinc. After the separation of lead as sulfate, sulfosalicylic acid is added to the solution, followed by excess ammonia and chromate. For other uses of sulfosalicylic acid in the separation of thallium, see L. Moser and A. Brukl, *Monatsh.*, **47**, 709 (1926).

thallium and other metals such as copper, cadmium, and lead can then be dissolved and further separations made by the methods already mentioned.

B. Extraction Methods

1. Dithizone Extraction

Thallium (I) can be extracted quantitatively from cyanide medium by dithizone in the *p*H range 9–12, the optimum *p*H being 11 for a carbon tetrachloride solution of the reagent according to H. Fischer.[2] Lead, bismuth, and stannous tin accompany thallium in this separation. From most of the other elements thallium can be separated easily in this way. Relatively much zinc, mercury, and nickel (more than 0.1 g. in 50 ml.) are said to make the extraction of thallium incomplete.[3] Manganese tends to be carried through with the thallium, and a second extraction should be made after destruction of the dithizone in the first extract if much manganese is present.

Reith and Gerritsma consider dithizone to be unsuitable for the isolation of thallium because it reacts very slowly in alkaline citrate medium.[4]

2. Ether Extraction of Chloride

Thallic chloride can be extracted from hydrochloric acid medium by ether. This method of isolation has not been studied thoroughly from the trace standpoint, but it seems that small amounts of thallium can be separated satisfactorily in this way. The investigation of Wada and Ishii[5] showed that macro quantities of thallium can be extracted best from 2 to 4 *N* hydrochloric acid solution. When 20 ml. of aqueous thallic chloride solution containing 100 mg. of thallium was shaken with 30 ml. of ethyl ether (previously shaken with hydrochloric acid), the following amounts of thallium remained in the aqueous phase at various acidities: 2 mg., 1 *N*; 1.5 mg., 2 *N*; 1 mg., 4 *N*; 2 mg., 6 *N*. Reith and Gerritsma[4] found that smaller quantities of thallium appear to be extracted less easily than these figures indicate, although the conditions were not the same since the solutions used by the latter authors contained salts. In their experiments, one-half liter of urine was evaporated to 75 ml., treated with hydrochloric acid, and organic matter destroyed with potassium chlorate. This solution (apparently about 2 *N* in hydrochloric acid) was extracted with three

[2] With a chloroform solution of dithizone the extraction takes place best at a *p*H of about 9 according to P. A. E. Kamerman, *J. South African Chem. Inst.*, **27**, 22 (1944).

[3] L. A. Haddock, *Analyst*, **60**, 394 (1935).

[4] J. F. Reith and K. W. Gerritsma, *Rec. trav. chim.*, **65**, 770 (1946). C. W. Sill and H. E. Peterson, *Anal. Chem.*, **21**, 1268 (1949), successfully isolated thallium from a citrate–cyanide medium by chloroform-dithizone extraction at *p*H 9.5–10.2 or higher.

[5] I. Wada and R. Ishii, *Bull. Inst. Phys. Chem. Research Tokyo*, **13**, 264 (1934).

portions of ethyl ether, each of the same volume as the aqueous phase. The ether extracts contained respectively 6.7, 2.6, and 0.8 mg. of thallium when 10 mg. were added at the beginning. In a similar experiment with 5 mg. of added thallium, the fourth ether extract was found to contain 7 and 8 γ of thallium in two trials. There is indication here that the partition coefficient of thallic chloride does not become unfavorable at very low concentrations, and that thallium in microgram quantities can be isolated in this way.

Among other elements extracted by ether (see Table 7) may be mentioned gold, ferric iron, antimony, tin, and gallium. Reith and Gerritsma separate thallium from most of the iron by shaking the ether extracts with a few milliliters of aqueous sulfur dioxide. Thallium then goes into the water phase, whereas most of the iron remains in the ether. It is said that about 1 per cent of the iron present is finally left with the thallium. Less than 0.05 mg. of mercury, from an original amount of 10 mg. as mercuric chloride, accompanies thallium.

3. Ether Extraction of Bromide

Thallic bromide is ether-extractable from aqueous solutions of relatively low hydrobromic acid concentration. No data are available for the behavior of microgram quantities of thallium in the extraction, but the accompanying figures for large amounts are pertinent (Table 89).[5] The best hydrobromic acid concentration is 1 *N* when iron is present. At this concentration hardly any ferric iron and gallium, and very little indium, are extracted; other elements extracted to a small extent are tellurium, zinc,

TABLE 89

EXTRACTION OF THALLIUM AND OTHER ELEMENTS FROM HYDROBROMIC ACID SOLUTION BY ETHYL ETHER[5]

(20 ml. of aqueous solution shaken with 30 ml. of ether previously shaken with hydrobromic acid of corresponding concentration)

		Amount (mg.) of element left in HBr solution after 1 extraction									
		Concentration of HBr, *N*									
Element	Original amount, mg.	0.03	0.1	0.5	1.0	1.5	2.0	3.0	4.0	5.0	6.0
Tl (III)....	100	1 5	1 0	1.0	0 8	0 2	0.3	0.3	0.2	0.4	8
Tl (III)....	1	0	0	0	0	0	0	0	0	0	0
Fe (III)....	250			250.0	250.0	249.9	249.5	226.2	76.3	68.7	99.0
Ga.....	83			83	83	83	83	82.7	80.0	38.2	35.4
In.....	100			99	96.8		80.8	10 7	1		1
Au (III)...	60			0.5	0.5				0.5		16
Te.....	100			99.7	98		97		97		97
Hg (II)....	100			97	99		99.8		99.7		99.7

mercury, molybdenum, and antimony, but all of these are said to be removed from the ether layer by shaking the latter with 1 *N* hydrobromic acid. Gold (III) accompanies thallium quantitatively or almost so. It appears that ether extraction of thallic bromide provides a better separation of thallium than does extraction of the chloride.

II. Methods of Determination

The colorimetric methods for thallium are indirect.[6] The iodine method, A, is the one commonly used.

A. The Iodine Method

Thallic salts in acid solution are quantitatively reduced to thallous by iodide. The iodine liberated can be determined by extraction with an immiscible solvent such as carbon tetrachloride or disulfide, or by adding

Table 90

Determination of Thallium by the Iodine Method after Isolation with Dithizone[6]

Foreign metal	Thallium present γ	Thallium found γ
Cu, 0.5 g.	100	100
Cu, 1.0 g.	60	63
Cu, 1.0 g.	20	21
Ag, 1.0 g.	30	28
Fe, 0.5 g.	40	43
Sb, 0.5 g.	25	27
Mg, 0.5 g. (double Dz extraction)	70	75
Sn, 0.5 g. (double Dz extraction)	30	32
Hg, 0.1 g.	50	47
Zn, 0.1 g.	90	85
Ni, 0.1 g.	80	76
NaCl, 5 g.	70	68

starch suspension, and measuring the transmittancies. Bromine water is a suitable reagent for oxidizing univalent thallium to trivalent in hydrochloric acid medium (not in sulfuric). The excess bromine is removed by boiling, which, however, must not be prolonged for fear of reduction of some of the trivalent thallium. The safest procedure involves removal of most of the excess by boiling and destruction of any small remainder by the addition

[6] It seems likely that thallium can be determined with dithizone but no procedure has been described. Kamerman[2] determines thallium by extractive titration with dithizone at *p*H 9 (chloroform solution). Lead is first separated as sulfate in alcoholic medium.

of phenol.[7] Other oxidizing agents must of course be absent. Small amounts of ferric iron are made harmless by carrying out the reaction between thallic salt and iodide in a solution containing phosphate.

The following procedure includes directions for the isolation of thallium by ether extraction of thallic chloride,[8] or by dithizone extraction of a thallous solution according to Haddock (*loc. cit.*). Some results obtained in the dithizone extraction method, with final determination of thallium by the starch-iodine method, are given in Table 90.

Special Reagents

Bromine reagent. Dissolve 10 g. of sodium dihydrogen phosphate in a mixture of 90 ml. fresh bromine water and 10 ml. of concentrated hydrochloric acid.

Starch-glycerin. Make 1 g. of starch into a paste with 5 ml. of water and add the suspension slowly to 50 ml. of boiling water. Then add 50 ml. of glycerin and boil for 5 minutes.

Phenol solution, 25 g. of phenol in 100 ml. of glacial acetic acid.

Potassium iodide solution, 0.2 per cent in water. This solution should be freshly prepared from iodate-free iodide.

Ethyl ether, analytical reagent, or *dithizone solution*, 0.1 per cent in chloroform.

Hydrogen peroxide, 30 per cent.

Standard thallium solution. Prepare a 0.01 or 0.1 per cent Tl stock solution in 1 *N* nitric acid from thallous nitrate ($TlNO_3/Tl = 1.303$), and dilute this to 0.001 per cent. The latter solution should be prepared fresh at frequent intervals.

§ Procedure

Isolation of Thallium.[9] (*a*) *By ether extraction.* The sample solution should be 6 *N* in hydrochloric acid and should have a volume as small as feasible (not over 50 ml.). Add 5 ml., or more if necessary, of freshly pre-

[7] L. A. Haddock, *Analyst*, 60, 394 (1935).

[8] P. A. Shaw, *Ind. Eng. Chem., Anal. Ed.*, 5, 93 (1933). According to Shaw, 0.5 mg. of thallium can be determined to within ±0.01–0.02 mg. in the presence of 5 mg. of copper, lead, iron, arsenic, mercury, tungsten, and molybdenum (the carbon disulfide extraction method was applied in the determination of the liberated iodine after ether extraction of thallic chloride). A similar procedure for the determination of thallium in urine is described by H. H. Ackerman, *J. Ind. Hyg. Toxicol.*, 30, 300 (1948). After ether extraction of thallic chloride from 6 *N* hydrochloric acid, the starch-iodine reaction is applied. From 10 to 140 γ of thallium were determined with an accuracy of 95–99 per cent in the presence of 100 mg. of manganese, nickel, tin, zinc, mercury, lead, or copper, or less than 50 mg. of iron.

[9] *Samples of organic origin* (toxicological material) may be decomposed as follows according to Shaw (*loc. cit.*). A finely-divided sample of suitable size is treated with sufficient 1:1 hydrochloric acid to give a fluid mass, the mixture is heated to boiling and small amounts of potassium chlorate are added at intervals until the organic material is largely destroyed. The cool mixture is filtered to remove undecomposed fatty particles and the filtrate evaporated until it darkens slightly. The cold solution is treated with enough chlorine water to discharge the darkening and leave a considerable excess. Thallic chloride is then extracted with ether according to (*a*) above.

(*footnote continued on next page*)

pared chlorine water to oxidize thallium to the trivalent state. Shake for one minute in a separatory funnel with an equal volume of ethyl ether previously shaken with 6 *N* hydrochloric acid. Extract with two more portions of ether and combine the ether extracts. The latter may be washed with a little 6 *N* hydrochloric acid if the aqueous solution contained copper, bismuth, or other metal, which if not removed might interfere in the final determination. Evaporate the ether to dryness in a small Erlenmeyer flask, and add 1 ml. of water, a few drops of hydrochloric acid and 2 ml. of concentrated sulfuric acid. Heat to fumes of sulfuric acid and add nitric acid dropwise until any oxidizable substances are destroyed, and a colorless or light yellow solution remains.[10] Add 25 ml. of ammonium chloride (150 g. per liter), and evaporate to dryness (guard against spattering) to destroy nitrites.

(*b*) *By dithizone extraction.* To *ca.* 50 ml. of neutral sample solution containing thallium in the thallous state (reduce with sulfurous acid or hydroxylamine hydrochloride) add 0.5 g. of potassium cyanide and 0.5 g. of ammonium citrate (*cf.* p. 396). Extract with four 10–15 ml. portions of 0.1 per cent dithizone in chloroform. Wash the combined extracts with 20–50 ml. of 1:1000 ammonia, and shake the latter with a few milliliters of dithizone to recover any small amounts of thallium that may have gone into the ammoniacal solution. Evaporate the chloroform extracts to dryness in a 100 ml. Kjeldahl flask or a small Erlenmeyer. Add 1 ml. of concentrated sulfuric acid to the residue, heat, and add small amounts of 30 per cent hydrogen peroxide until all organic material has been destroyed.

Determination of Thallium. Add 20 ml. of water to the residue from (*a*) or (*b*) above, followed by 1 g. of ammonium chloride (if procedure *b* was used) and 25 ml. of the bromine reagent. Heat to boiling in a wide-mouthed flask and boil at such a rate that the solution becomes colorless in 3 minutes. Cool rapidly to 18° C., adjust the volume to about 35 ml., add 0.25 ml. of phenol solution, mix, and allow to stand for 3 minutes. Then add 5 ml. of freshly prepared 0.2 per cent potassium iodide and 1 ml. of starch-glycerin solution. Mix and allow to stand for 5 minutes at 18°. Then determine the transmittancy at about 600 mμ. The reference solution should contain iodide, starch-glycerin, etc. in the same concentration

If the dithizone extraction method is to be applied it is preferable to decompose an organic sample with sulfuric-nitric acid (or perchloric acid in conjunction with sulfuric or nitric acid). The acid mixture is diluted, nearly neutralized, and hydroxylamine hydrochloride is then added, followed by citrate and sufficient base to make the solution slightly alkaline. Cyanide is next added and the extraction with dithizone made as in (*b*).

[10] Hydrogen peroxide (30 per cent) may be used instead of nitric acid. The subsequent addition of ammonium chloride may then be omitted.

as the sample solution in order that there may be no error from the liberation of iodine by air-oxidation. It should be prepared at the same time as the sample solution.

B. The Thionalide Method[11]

In this method thallium is precipitated by thionalide in a tartrate-cyanide solution containing sodium hydroxide (no other metal is precipitated by thionalide in this medium). The washed precipitate is dissolved in acid and treated with phosphomolybdotungstic acid. On warming, the latter is reduced and the amount of thallium is found from the intensity of the blue color.

Reagents

Thionalide, 5 per cent solution in acetone (freshly prepared).
Potassium cyanide, 10 per cent (freshly prepared).
Sulfuric acid, 1 *N*.
Ethyl alcohol, 95 per cent.
Phosphotungstomolybdic acid. Reflux for 2 hours in a flask with a ground glass joint, a mixture of 1 g. phosphomolybdic acid, 5 g. sodium tungstate, 5 ml. concentrated phosphoric acid, and 18 ml. of water.
Formamide.

§ Procedure

The sample solution may have a volume of 3 to 5 ml., and should be neutral or very weakly acidic. Add 0.5 ml. of 2 *N* sodium hydroxide solution and 0.5 ml. of potassium cyanide solution to the sample in a centrifuge tube. Precipitate the thallium with 5–6 drops of thionalide solution. Heat on the water bath at 90° for about 5 minutes, stirring constantly, to convert the precipitate to the crystalline form. Cool, centrifuge, and remove the supernatant liquid with the aid of a capillary tube. Wash three times with 3 ml. portions of acetone, being careful that the whole interior of the tube is rinsed, centrifuging each time.

Dissolve the precipitate in two drops of sulfuric acid and 1 ml. of alcohol, heating gently if necessary. Transfer the solution to a color comparison tube and rinse the centrifuge tube with 1 ml. of warm alcohol and once or twice with 1 ml. of warm water. Depending upon the quantity of precipitate, add 1 to 3 drops of phosphotungstomolybdic acid and 1.5 to 2 ml. of formamide. Mix and allow to stand at 40° for 15 minutes. At the same time treat a series of standard thallium thionalate solutions, obtained in the same manner, with phosphotungstomolybdic acid. Dilute to volume

[11] R. Berg, E. S. Fahrenkamp, and W. Roebling, *Mikrochemie* (*Molisch Festschrift*), 44 (1936).

and compare the unknown solution in a colorimeter with the standard having the closest color intensity.

Notes. 1. Berg and his coworkers prepare a series of artificial standards from mixtures of aqueous solutions of Chicago blue, naphthylamine black and a trace of India ink by matching against the color developed by known amounts of thallium thionalate, and use these standards in the preliminary estimation of thallium in a sample with an accuracy of 20 per cent. For an exact determination a second portion of sample and a quantity of thallium equal to the estimated value are precipitated, phosphotungstomolybdic acid is reduced by the dissolved precipitates and the two solutions compared in a colorimeter.

2. Other metals precipitated by thionalide can be determined similarly to thallium, except that the precipitate is washed with hot water and dissolved in pyridine.

C. Other Methods

Thallium can be determined turbidimetrically or nephelometrically by adding phosphomolybdic acid solution (0.2 ml. of 5 per cent) to a 0.1 *N* nitric acid solution of a thallous salt (5 ml., containing 10–50 γ of Tl).[12] A stable yellow sol of thallous phosphomolybdate is formed, whose transmittancy can be determined after 5 minutes. Among the metals not giving precipitates with the reagent may be mentioned lead, cadmium, bismuth, and mercury (II). Mercury (I) gives a faint precipitate which dissolves on the addition of sufficient nitric acid. Potassium and ammonium salts should be absent, since they yield slightly soluble phosphomolybdates.

In pure solution, thallium can be determined as the sulfide by the addition of excess sodium sulfide to give a brown sol. The color is produced also in the presence of cyanide, and in this respect thallium behaves the same as lead and bismuth.

Traces of thallium (I) in 4 *N* hydrochloric acid, or still better in saturated sodium chloride solution, show a blue fluorescence when excited by short-wave ultraviolet radiation from an iron or aluminum spark.[13] Less than 0.02 p.p.m. of thallium in solution can be detected in this way.

[12] T. Pavelka and H. Morth, *Mikrochemie*, 11, 30 (1932).

[13] P. Pringsheim and H. Vogels, *Physica*, 7, 225 (1940); C. W. Sill and H. E. Peterson, *Anal. Chem.*, 21, 1266 (1949), have developed the test further.

CHAPTER XLIII

TIN

I. Separations

Precipitation with hydrogen sulfide in acid solution is an important method for the separation and concentration of traces of tin in the presence of iron and other elements not precipitated under these conditions. The precipitation should be made in the presence of tartaric acid if the solution contains tungsten, vanadium, and titanium. From copper and the other elements of the copper sub-group, tin can be separated by the precipitation of these with sulfide in basic solution, but this method is open to objection on the score of coprecipitation of tin. Tin can be precipitated and separated from copper in acid solution by hydrogen sulfide if sufficient thiourea is present to bind copper in a complex.[1]

When the nature of the sample permits, precipitation with ammonium hydroxide may be used to isolate traces of tin; a little ferric iron should be added to furnish iron hydroxide to collect the tin. Precipitation of tin with cupferron may be of value at times.[2] Ferric iron can be used as a collector. Presumably stannic cupferrate can be extracted by chloroform.

Tin has been isolated in the form of stannic acid by coprecipitation with hydrous manganese dioxide.[3]

Volatilization procedures are of importance in isolating small amounts of tin. Stannic chloride boils at 114° C. and stannic bromide at 202°. The volatilization of the former may be effected by leading dry hydrogen chloride through a hot (*ca.* 200°) solution in concentrated sulfuric acid.[4] Distillation of stannic bromide may be made from a sulfuric or perchloric acid medium.[5]

[1] N. Strafford, *Mikrochim. Acta*, **2**, 309 (1937).

[2] The solubility of stannic cupferrate in 1 *N* hydrochloric acid at 18° C. is reported to be 10^{-4} mole per liter (about the same as that of ferric cupferrate) by A. Pinkus and F. Martin, *J. chim. phys.*, **24**, 83, 137 (1927).

[3] S. K. Hagen, N. Hofman-Bang, and P. Gjertsen, *Acta Chemica Skand.*, **2**, 343 (1948).

[4] F. Leutwein, *Z. anal. Chem.*, **120**, 233 (1940). P. Klinger, E. Stengel, and H. Wirtz, *Metall u. Erz*, **38**, 124 (1941), dissolve the sulfides of tin and other metals in sulfuric acid and distil stannic chloride at 130–140°.

[5] See the table on p. 42. Regarding the separation of tin from arsenic and antimony by the distillation method see H. Biltz and W. Biltz, *Ausführung quantitativer Analysen*. Hirzel, Leipzig, 1930, p. 329.

The extractability of stannic diethyldithiocarbamate by carbon tetrachloride from ammoniacal citrate medium may possibly be put to use for the separation of tin in certain types of materials.

For the separation of tin from iron in the ash of materials of organic origin by fusion with a mixture of sodium cyanide and sodium carbonate followed by acidification to give insoluble Prussian blue see a paper by Stone.[6]

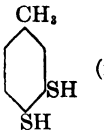
Stannic tin is not extracted by dithizone. Therefore, it is possible to remove various heavy metals by dithizone extraction from acidic or basic medium (in the latter case in the presence of citrate).

II. Methods of Determination

The colorimetric methods for the determination of tin available at present cannot be considered very satisfactory. More specific and sensitive reagents are needed.

A. The Dithiol Method

In acid solution, toluene-3,4-dithiol (4-methyl-1,2-dimercaptobenzene)



(m.p. 31° C.)

forms a magenta-red precipitate with stannous salts on warming.[7] Stannic tin also reacts, but more slowly than stannous. Thioglycolic (mercaptoacetic) acid may be used to reduce stannic tin to the stannous state. Many heavy metals react with the reagent to give more or less strongly colored precipitates. Bismuth gives a brick-red mercaptide; iron (III), copper, nickel, and cobalt give black precipitates, and silver, mercury, lead, cadmium, arsenic, etc. yield yellow precipitates. Molybdate and tungstate also react (pp. 459, 586).

The comparison of the unknown and standard suspensions must be made in reflected light according to Clark.[8] If the tin content of the solution is kept below 30 p.p.m. it is not necessary to add a protective colloid (agar). Among the non-interfering substances (2 per cent solutions) may be men-

[6] I. Stone, *Ind. Eng. Chem., Anal. Ed.*, **13**, 791 (1941); B. Glassmann and S. Barsutkiĭ, *Z. Untersuch. Lebensm.*, **56**, 208 (1928).

[7] R. E. D. Clark, *Analyst*, **61**, 242 (1936); **62**, 661 (1937). 4-Chloro-1,2-dimercaptobenzene may also be used as reagent.

[8] The method does not appear to have been studied photometrically. It may be mentioned that the dithiol complex of tin dissolves in some organic solvents with loss of its red color, the resulting solutions being pale yellow according to Bickford, Jones, and Keene (reference on p. 459).

tioned the alkali and alkaline earth metals, magnesium, zinc, aluminum, the halides, cyanide, thiocyanate, borate, oxalate, and tartrate. Fluoride delays the color development and phosphate decreases the color intensity. Iron has no effect up to 0.5 per cent, manganese none up to 1 per cent. Lead gives no color if the hydrochloric acid concentration is 7 per cent. Nitrites give a red color.

The reagent solution is not stable, being easily oxidized. The addition of thioglycolic acid increases its stability, but generally the reagent solution cannot be kept more than two weeks.

Special Solutions

Toluene-3,4-dithiol. Dissolve 0.2 g. of dithiol and 0.5 ml. of thioglycolic acid in 100 ml. of 1 per cent sodium hydroxide solution. Discard the solution when a white turbidity appears.

Standard tin solutions. (*a*) Dissolve 0.100 g. of tin in 10 ml. of concentrated hydrochloric acid, add 0.5 ml. of thioglycolic acid, and dilute to 100 ml. with water. (*b*) Dilute 10.0 ml. of solution (*a*) and 2 drops of thioglycolic acid to 100 ml. with water (1 ml. $\equiv$ 100 γ Sn). Do not keep this solution longer than a day.

§ General Procedure

Transfer 5 ml. of slightly acid sample solution (containing not more than 10 p.p.m. Sn) to a color comparison tube (p. 52) and add 0.5 ml. of concentrated hydrochloric acid and 0.5 ml. of dithiol reagent. Prepare a suitable series of similar standards at the same time. Immerse the tubes in a boiling water bath for 30 seconds and then allow to stand for 1 minute. Compare the tubes by examining from the side in reflected light.

Application of the Dithiol Method to the Determination of Tin in Foods

A number of procedures have been described for the determination of tin in food materials with dithiol as reagent. In one of these tin is isolated by precipitation as the sulfide,[9] and in another by volatilization as the bromide.[10] In still another,[11] tin is not isolated from the sulfuric acid digest of the sample, but interfering copper is removed by dithizone extraction. Iron does not interfere in small amounts. From 10 to 250 p.p.m. of tin in the sample can be determined within 15 per cent by visual comparison, even in the presence of 100 p.p.m. of iron and copper, according to the authors.

[9] R. De Giacomi, *Analyst*, 65, 216 (1940).

[10] N. H. Low, *Analyst*, 67, 283 (1942). For a similar method for determining tin in biological materials see J. Schwaibold, W. Borchers and G. Nagel, *Biochem. Z.*, 306, 113 (1940).

[11] H. Cheftel, F. Custot, and M. Nowak, *Bull. soc. chim. France*, 1949, 441.

§ Procedure

Take 10 to 20 g. of sample and decompose in the usual way with sulfuric and nitric acids. Limit the amount of sulfuric acid to not more than 4 ml. in order that the diluted solution will not be too acid for the succeeding determination. Make certain that all nitric acid has been removed at the end of the digestion.

Transfer the digest to a volumetric flask of suitable size, dilute to volume, and transfer to a separatory funnel an aliquot containing 10 to 35 γ of tin in 5 or 10 ml. Shake for 3 minutes with 5 ml. of a 0.02 per cent solution of dithizone in redistilled carbon tetrachloride. Draw off and discard the carbon tetrachloride and repeat the extraction if necessary until there is no change in the color of the dithizone.

Transfer the solution to a color comparison tube and add 2 or 3 drops of thioglycolic acid to reduce stannic tin and allow to stand for 5 to 10 minutes. Place the tube in a boiling water bath. After 3 minutes add 3 drops of fresh (not over 2 day-old) dithiol reagent (0.1 g. dithiol, 0.3 g. thioglycolic acid, 0.5 g. sodium hydroxide in 50 ml. of water). Compare the color against standards treated similarly.

B. The Phosphomolybdic and Silicomolybdic Acid Methods

Stannous tin, like many other strong reducing agents, reduces heteropoly molybdic acids to molybdenum blue, a compound of uncertain composition. The heteropoly acids are reduced more easily than molybdic acid itself and give a more stable product. Phosphomolybdic and silicomolybdic acids have been used as reagents. The respective methods are described below. These methods cannot be considered entirely satisfactory for the determination of traces of tin although they are no doubt useful at times. They are unspecific and the colored product is of the uncharacteristic type. Therefore, careful separations are frequently required. Moreover, the complete reduction of tin to the stannous state is by no means easy and the colored product is oxidized by air. It may be suspected that the tolerably good results obtained are due to cancellation of errors effected by treating the standards in the same manner as the sample.

1. Phosphomolybdic Acid as Reagent[12]

In this procedure the molybdenum blue formed in the reduction is extracted by amyl alcohol, in which it is relatively stable. A large excess of phosphomolybdic acid is required to give the maximum color intensity The law of Beer is obeyed. Tin may be reduced to the stannous state by aluminum in acid solution in a carbon dioxide atmosphere.

[12] N. Strafford, *Mikrochim. Acta*, 2, 306 (1937).

Copper and titanium are stated to be the only common metals giving the same reaction as tin under the conditions of the determination. Platinum, silver, mercury, lead, arsenic, antimony, bismuth, zinc, cadmium, nickel, cobalt, iron, and chromium do not interfere according to Strafford.

Special Solutions

Phosphomolybdate reagent. Solution A. Dissolve 2.5 g. of molybdic acid in 50 ml. of 1 *N* sodium hydroxide and dilute to 100 ml. with 2 *N* sulfuric acid. Solution B. Dissolve 0.44 g. of $NaH_2PO_4 \cdot H_2O$ in 100 ml. of water.

Shortly before use prepare the mixed reagent by mixing 10 ml. of solution *A* and 4 ml. of solution *B*, and diluting to 200 ml. with water.

Standard tin solution. 0.010 per cent Sn in 1:20 hydrochloric acid. This solution should be prepared fresh each day by dilution of a stronger (*e.g.*, 0.1 per cent) stannous solution.

§ Procedure

If the sample is of organic origin, decompose 5 g. (for <50 p.p.m. tin) with sulfuric and nitric acids according to the procedure on p. 584. Dilute the clear solution to about 100 ml. with water and add 5 g. of thiourea and also 2 g. of tartaric acid if appreciable amounts of titanium are present. Then add ammonium hydroxide until the solution is only slightly acid (pH 2–3, congo red paper). Cool, and saturate the solution with hydrogen sulfide. Heat on the steam bath for one-half hour and allow to stand for another half-hour. Filter through paper and wash three times with 10 ml. of hydrogen sulfide water. Transfer the paper and precipitate to a 100 ml. Kjeldahl flask, wash the precipitation vessel with 20 ml. of hot 1:1 nitric acid and add the latter to the flask. Add 1 ml. of concentrated sulfuric acid to the flask and digest the mixture. When oxidation appears complete add a little 30 per cent hydrogen peroxide. Then add 10 ml. of water to the cold mixture and evaporate to fuming.

Transfer the residue with the aid of 25 ml. 1:1 hydrochloric acid to a wide test tube (3.5 × 18 cm.) provided with a rubber stopper through which pass the stem of a 50 ml. funnel with stopcock and two tubes, also with stopcocks, for ingress and egress of carbon dioxide; the inlet tube should reach nearly to the surface of the solution, and the other should end at the bottom of the stopper. Drop 0.1 g. of aluminum foil into the tube, insert the stopper, and pass a fairly rapid current of carbon dioxide through the apparatus while gently heating. When the reaction subsides, raise the solution to boiling, close the stopcock of the exit tube, and cool in an ice bath. Then open the stopcock of the exit tube and allow 15 ml. of mixed phosphomolybdate reagent to run into the tube from the funnel. Close the exit tube stopcock and mix the contents of the tube by gentle shaking. After 5 minutes introduce 9.0 ml. of amyl alcohol and shake well to extract

the molybdenum blue. In all of these operations an atmosphere of carbon dioxide must be maintained in the tube.

Disassemble the apparatus and pour the contents of the tube into a small separatory funnel. Reject the lower aqueous phase and run the amyl alcohol into a 10 ml. volumetric flask, add 1 ml. of ethyl alcohol for clarification, and adjust the volume to 10 ml. Determine the transmittancy of the solution with the aid of a red filter. Construct the reference curve by carrying known amounts (0.02–0.25 mg.) of tin through the procedure.

2. Silicomolybdic Acid as Reagent[13]

The reduction of tin is effected by treatment with zinc. From 20 to 200 γ of tin can be determined with an error not exceeding 15 per cent as judged by the results reported.

Special Solutions

Silicate solution, 1 mg. silica per ml. Fuse 1 g. of pure silica with 5 g. of sodium carbonate, dissolve the melt in water, and dilute to 1 liter.

Molybdate solution. Dissolve 5.3 g. analytical reagent ammonium molybdate in 100 ml. of water, add 10 ml. of concentrated sulfuric acid, and dilute to 200 ml.

Silicomolybdate reagent. Dilute 10 ml. of molybdate solution to approximately 800 ml., add 2.5 ml. of silicate solution, and dilute to 1 liter. Allow to stand 1 hour before use; prepare fresh daily.

§ Procedure

To 6 ml. of boiling tin solution, 6 *N* in hydrochloric acid, contained in a 50 ml. Erlenmeyer flask, add 2 zinc shots (reagent grade, low in arsenic, lead and iron, and weighing 0.4–0.5 g. each). Shake while boiling for 1 minute and pour 20 ml. of silicomolybdate solution into the flask, mix, and decant immediately into a glass-stoppered flask. At the same time run a standard containing 0.1 mg. of tin. Compare the colors after 5 minutes (photometer or Duboscq colorimeter).

C. Other Methods

Cacotheline, a nitro derivative of brucine,

$$C_{12}H_{21}(OH)_2(NO_2)N_2O_2 \cdot HNO_3(?)$$

gives a violet color with an acid solution of stannous tin and other strong reducing agents such as antimony (III), titanium (III), uranium (III),

[13] I. Baker, M. Miller, and R. S. Gibbs, *Ind. Eng. Chem., Anal. Ed.*, 16, 269 (1944). The directions given above are part of a procedure for the determination of tin in ferrous and non-ferrous materials, in which tin is isolated by distillation after the addition of sulfuric acid, bromide and hydrochloric acid. Figures are given to show the generally satisfactory reproducibility of the results but the accuracy of the procedure is not established and therefore we do not give the method in full here.

rhenium (III), columbium (III), molybdenum and tungsten in lower valence states, sulfite, and thiosulfate. According to Strafford the color fades rapidly and the reaction is not suitable for quantitative purposes.[14]

Hematoxylin has been used for the determination of tin in the concentration range 0.3 to 2 p.p.m. of solution. Forty ml. of solution are neutralized (phenolphthalein as indicator), treated with 1 ml. of 1 per cent hematoxylin solution and 0.3 ml. of 1 *N* sodium hydroxide solution in excess, and compared after 10 minutes.[15] The method is not specific. Chromium (VI) and molybdenum (VI) give sensitive reactions under these conditions.

Quinalizarin gives a pink lake with stannic tin in weakly acid solutions. The reaction is not very sensitive. At *p*H 4.75 (acetate buffer) approximately 2 γ of tin can be detected in 10 ml. of solution (1.8 × 15 cm. tube). At a lower *p*H the sensitivity is less. The color develops slowly and an hour or more should be allowed for the attainment of full color intensity. Many metals react with quinalizarin in weakly acid medium, but since tin is readily separated by volatilization the reaction may prove of some value.

A semiquantitative method for the determination of small amounts of tin (IV) with anthraquinone-1-azo-4-dimethylaniline has been described.[16]

Purpurin and carminic acid give a fluorescence with stannic tin in a medium of *p*H 4.5; the reactions are sensitive (10^{-5} *M*) but not specific.[17]

α-Dinitrodiphenylamine sulfoxide[18] has been used for the colorimetric determination of tin but has little to recommend it.

Dithiocatechol is a possible reagent for tin.[19]

[14] *Cf.* A. M. Ribley and E. St. Clair Gantz, *Proc. Indiana Acad. Sci.*, **56**, 136 (1946); *Chem. Abst.*, **42**, 2543.

[15] V. Y. Tartakovskiĭ, *Zavodskaya Lab.*, **9**, 971 (1940); *Chem. Abst.*, **35**, 1342. The valence of tin is not mentioned in the abstract, but the standards are prepared from stannous chloride. According to G. Charlot,[17] stannic tin at *p*H 4.5 gives a reaction with hematoxylin which is sensitive to 10^{-5} *M*.

[16] V. I. Kuznetsov and I. M. Bender, *J. Applied Chem. U. S. S. R.*, **13**, 1724 (1940); V. I. Kuznetsov, *ibid.*, **13**, 769 (1940).

[17] G. Charlot, *Anal. Chim. Acta*, **1**, 218 (1946).

[18] G. S. Buchanan and S. B. Schryver, *Analyst*, **34**, 121 (1909).

[19] H. P. Brown and J. A. Austin, *J. Am. Chem. Soc.*, **62**, 673 (1946).

CHAPTER XLIV

TITANIUM

I. Separations

The separation of titanium from vanadium (V), molybdenum (VI), and phosphorus can be effected by double precipitation of titanium hydroxide with hot 1 *N* sodium hydroxide solution. The precipitation of titanium is not complete if iron is absent, but is quantitative when a little iron is present.[1] Titanium can also be separated from chromium in this way if the latter is first oxidized to the sexivalent state, as for example by the use of persulfate in sulfuric acid solution or sodium peroxide in basic medium. Fusion with sodium carbonate and leaching of the melt with water serves the same purpose as the sodium hydroxide precipitation; if relatively much chromium is present, a little sodium nitrate should be used with the sodium carbonate. In the absence of iron, titanium passes into the filtrate from the sodium carbonate leach. Zirconium is not a satisfactory collector for titanium in the sodium carbonate procedure.[2]

Separation of iron from titanium can be made by double precipitation of ferrous sulfide in ammoniacal medium in the presence of tartrate. Extraction of ferric chloride with ether from a 1:1 hydrochloric acid solution is a good method of separating most of the iron from titanium.

Occasionally precipitation of titanium with cupferron can be put to good use in the isolation of the element (*cf.* p. 580). A little iron (III) or zirconium may be used as a collector. Titanium may thus be separated from nickel, cobalt, chromium, uranium (VI), and phosphorus but not from vanadium. If much chromium and nickel is present (as in alloy steels) there may be some coprecipitation of these. A separation from the bulk of much iron (as in steel analysis) is achieved if it is present in the ferrous state. Since titanium cupferrate is soluble in chloroform it is to be expected

[1] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis.* Wiley, New York, 1929, p. 455.

[2] F. R. Bacon (private communication) found 0.004 per cent of TiO_2 in Bureau of Standards sample of glass sand No. 81 (certificate value 0.095 per cent) when 1 g. of sample was fused with 4 g. of sodium carbonate, the melt leached with 50 ml. of water, and the residue analyzed. When a 2 g. sample was fused with 8 g. of sodium carbonate and the melt leached with 200 ml. of water, 0.0005 per cent of TiO_2 was found; and when 40 mg. of zirconyl chloride were added and the fusion made under the same conditions, 0.034 per cent TiO_2 was obtained.

that it can be extracted from mineral acid medium by the use of this solvent.

p-Hydroxyphenylarsonic acid,[3] which yields slightly soluble salts with titanium and zirconium in dilute mineral acid medium, may perhaps be found useful in isolating small amounts of titanium and separating it from iron, vanadium, molybdenum, etc.

A great many metals can be separated from titanium by electrolysis with a mercury cathode (p. 31).

II. Methods of Determination

A. The Hydrogen Peroxide Method

The yellow color produced when hydrogen peroxide is added to an acid titanium (IV) solution has long been utilized for the determination of the

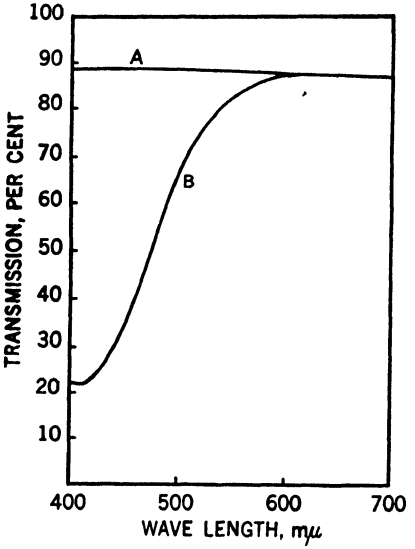


Fig. 73. Transmission curves of peroxidized titanium solution containing 8 p.p.m. Ti (B) and blank solution (A) in 5.3 cm. long quartz cell. (Michaelson and Liebhafsky, *Gen. Elec. Rev.*, **39**, 445 (1936).)

element. The colored substance formed in the reaction is probably $TiO_2(SO_4)^{-}_2$ or a similar ion.[4] The value of the equilibrium constant

[3] C. T. Simpson and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.*, **10**, 642 (1938).

[4] R. Schwartz, *Z. anorg. allgem. Chem.*, **210**, 303 (1933). M. Bendig and H. Hirschmüller, *Z. anal. Chem.*, **120**, 385 (1940); Y. Schaeppi and W. D. Treadwell, *Helv. Chim. Acta*, **31**, 577 (1948).

$$\frac{[Ti^{IV}][H_2O_2]}{[Ti^{IV}{\cdot}O]}$$

has been reported as 10^{-4} (Bendig and Hirschmüller[4]) and 10^{-6} (Schaeppi and Treadwell[4]). The determination is usually carried out in a sulfuric acid solution having a concentration ranging from about 1.5 to 3.5 *N*. The color is slightly weaker in 6 *N* sulfuric acid than in 1.5–2 *N* acid.[5] In perchloric acid solution the color intensity is independent of the acid concentration in the range 0 to 30 ml. of 70 per cent perchloric acid in a volume of 100 ml., *i.e.*, up to 3.5 *M*.[6] At higher concentrations the color is slightly weaker and the wave length of maximum absorption is shifted from 410 mμ to slightly longer wave lengths. The color is a little stronger in hydrochloric acid medium than in sulfuric acid. The use of hydrochloric acid is best avoided as a rule because of the stronger color of ferric iron in this medium.

TABLE 91

DETERMINATION OF TITANIUM BY THE PEROXIDE METHOD: THE EFFECT OF SOME FOREIGN SUBSTANCES

0.50 mg. titanium taken in each case; final volume 50 ml., containing 15 ml. 6 *N* sulfuric acid and 5 ml. 3 per cent hydrogen peroxide. Blue filter.

Foreign substance	Ti found, mg.
1.0 g. K_2SO_4	0.48
1.0 ml. 85% H_3PO_4	0.39
2.0 mg. NaF	0.40
1.0 g. tartaric acid	0.49
0.050 g. Fe^{III}	0.66
0.25 mg. V^{V}	0.61
2.5 mg. Mo^{VI}	0.56

A number of substances reduce the color intensity of peroxidized titanium solutions. Alkali metal sulfates show a slight bleaching effect (Table 91), which is stronger the lower the concentration of sulfuric acid in the solution.[7] In the presence of relatively much alkali sulfate the solution should contain 10 per cent by volume of sulfuric acid rather than the usual 5 per cent, and the standard should have the same acidity and preferably should contain about the same concentration of salt. Phosphate and especially fluoride form complexes with titanium and seriously reduce the

[5] A solution containing 0.50 mg. of titanium in 50 ml. of 6 *N* sulfuric acid was found to show the same color intensity as a solution of 0.47 mg. titanium in 50 ml. of 1.8 *N* acid (blue filter).

[6] A. Weissler, *Ind. Eng. Chem., Anal. Ed.*, **17**, 695 (1945).

[7] H. E. Merwin, *Am. J. Sci.*, **28**, 119 (1909).

color intensity. The magnitude of the bleaching effect of phosphoric acid is shown in Table 92. It will be noted that the effect depends upon the wave length. Citric and tartaric acid in moderate concentrations have practically no effect on the color intensity.

Iron interferes to a considerable extent because of its color. The color due to iron can be largely destroyed by the addition of phosphoric acid,

TABLE 92

EFFECT OF PHOSPHORIC ACID ON THE COLOR INTENSITY OF PEROXIDIZED TITANIUM SOLUTIONS[6]

(1 mg. Ti, 10 ml. 70 per cent perchloric acid and varying amounts of phosphoric acid in a final volume of 50 ml.)

H_3PO_4 (1.1), ml.	Optical Density (1 cm.)		
	400 mμ	410 mμ	460 mμ
0	0.288	0.303	0.205
2	0.290	0.292	0.160
4	0.287	0.285	0.149
6	0.287	0.283	0.148
8	0.286	0.281	0.147
10	0.285	0.277	0.145

which is added in like amount to the standard.[8] Vanadium and molybdenum also give yellow colors with peroxide; chromium (VI) gives an evanescent blue. The color given by vanadium[9] is comparable in intensity to that given by titanium (Table 91) but the molybdenum color is much weaker. It is possible to determine titanium in the presence of comparable amounts of vanadium by obtaining the extinction of the peroxidized solution at 410 and 460 mμ, the respective absorption maxima (Fig. 22). If molybdenum is also present an additional measurement at 330 mμ is required.[6] Columbium is said to interfere if iron is also present (p. 579).

When a spectrophotometer is used, the effect of iron, nickel, chromium (III), and other colored ions not reacting with peroxide may be compensated by using a solution of the sample, not treated with peroxide, in the comparison cell.

The color intensity of peroxidized titanium solutions increases slightly with a rise in temperature. The solutions show very little change with

[8] By the use of a green filter in the color comparison the error due to iron is largely eliminated but the titanium sensitivity is greatly reduced (M. Bendig and H. Hirschmüller, *Z. anal. Chem.*, 92, 1 (1933)).

[9] According to A. Thiel, *Absolutkolorimetrie* (1939), p. 77, the color produced by vanadium is destroyed by dihydroxymaleic acid. One ml. of fresh 1 per cent alcoholic solution of the acid is added to 100 ml. of the sample solution, which should contain not more than 0.2 mg. of vanadium.

the passage of time.[10] Beer's law holds for titanium concentrations as high as 50 p.p.m.[11]

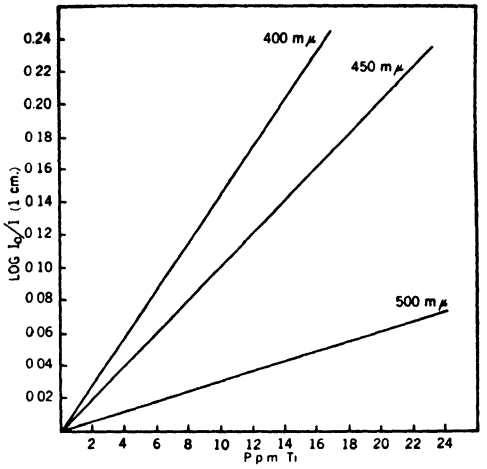


Fig. 74. Extinction of peroxidized titanium solutions at 400, 450, and 500 mμ. (From data of Michaelson and Liebhafsky.)

Standard Titanium Solution

(*a*) *Preparation from potassium titanium oxalate.*[12] Weigh 3.68 g. of recrystallized and air-dried $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ into a 500 ml. Kjeldahl flask, and add 8 g. of ammonium sulfate and 100 ml. of sulfuric acid. Gradually heat to boiling and boil for 5–10 minutes. Cool and pour the solution into 700–800 ml. of water. After cooling, dilute to 1000 ml. If the salt weighed out is pure and contains the proper amount of water, each milliliter of solution will contain 0.50 mg. of Ti. If it is not certain that these conditions are fulfilled, the solution should be standardized by precipitating the titanium with ammonia or preferably cupferron and igniting the precipitate to TiO_2.

To prepare a solution containing 0.50 mg. TiO_2 per ml. weigh out 2.21 g. of $K_2TiO(C_2O_4) \cdot 2H_2O$ and proceed as above.

(*b*) *Preparation from potassium fluotitanate.* Transfer 2.70 g. recrystallized and air-dried $K_2TiF_6 \cdot H_2O$ to a platinum dish, add 100 ml. of 1:1 sulfuric acid, heat until strong fumes are evolved, cool, carefully rinse down the sides of the dish with water and again heat to strong fuming. To be certain that all of the hydrofluoric acid has been expelled, it is advisable to heat to fuming for a third time after rinsing down the sides of the dish. Pour the cold solution into 700–800 ml. of water, add 50 ml. of concen-

[10] It has been stated that peroxidized titanium solutions show no change in color intensity for as long as two years (G. H. Ayres and E. M. Vienneau, *Ind. Eng. Chem., Anal. Ed.*, **12**, 96 (1940)). However, when iron is present the solutions are less stable because the excess hydrogen peroxide then slowly decomposes.

[11] H. Ginsberg, *Z. anorg. allgem. Chem.*, **211**, 401 (1933).

[12] W. M. Thornton, Jr., and R. Roseman, *Am. J. Sci.*, **20**, 14 (1930).

trated sulfuric acid, and dilute to 1000 ml. after cooling. Each milliliter of the solution should contain 0.50 mg. of Ti if the salt is pure and contains the proper amount of water. The strength of the solution may be checked by precipitating the titanium with ammonia or cupferron and igniting the precipitate to TiO_2.

To prepare a solution containing 0.50 mg. TiO_2 per ml., weigh out 1.62 g. of $K_2TiF_6 \cdot H_2O$ and proceed as above.

§ Procedure

Add 15 ml. of 6 *N* sulfuric acid to the sample solution (the final acidity may vary from 1.5 to 3.5 *N*) and, if iron is present in appreciable amounts, add dilute phosphoric acid from a buret or graduated pipet until the yellow color of ferric iron is destroyed. The same amount of phosphoric acid must be added to the standards. If the sample contains much sodium or potassium sulfate, add a like amount to the standards. Add 5 ml. of 3 per cent hydrogen peroxide and dilute the solution to 50 ml. in a volumetric flask.[13] Determine the transmittancy of the solution with the aid of a blue filter (maximum transmission at 420–430 mμ).

For the determination of very small amounts of titanium, the standard series method, or better the colorimetric titration technique (p. 53) is to be preferred. In a 1.8 × 15 cm. tube (internal cross-section about 2 cm.^{2}) 2 γ of titanium shows a faint color easily distinguishable from a blank.

B. Other Methods

Various phenolic compounds react with titanium to give colored products but they have the disadvantage that iron also reacts.

Disodium-1;2-dihydroxybenzene-3,5-disulfonate yields a strong yellow color with titanium (IV) in the *p*H range 4.3 to 9.6. The reagent has been applied for the determination of titanium by Yoe and Armstrong,[14] who prevent the interference of iron by reduction with sodium dithionite at *p*H 4.7. Beer's law is valid if a sufficiently high concentration of reagent is present. The coloration is stable. Among the metals that interfere badly by giving colors under the conditions of the determination are chromium, copper, molybdenum, vanadium, and tungsten (the latter gives an almost colorless complex absorbing strongly at 410 mμ). As much as 250 p.p.m. of iron is permissible. The limiting concentrations in p.p.m. for some of the common elements are: Al, 350; Ca, 20; F, 10; Ni, 25.

[13] The final concentration of titanium may conveniently be 2–25 p.p.m. if a photometer is used (1 cm. cell). A similar range of concentrations is suitable for comparison with a Duboscq type colorimeter.

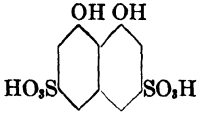
[14] J. H. Yoe and A. R. Armstrong, *Anal. Chem.*, 19, 100 (1947). See this paper for simultaneous determination of iron and titanium in limestone, feldspar, glass, etc. by the use of this reagent. The reagent has been used for the determination of titanium in nickel metal by C. V. Potter and C. E. Armstrong, *Anal. Chem.*, 20, 1208 (1948).

Aluminum, calcium, and some other elements interfere by consuming reagent and diminishing the titanium color; the effect can be counteracted by using a large quantity of reagent. The photometric determination is carried out as follows. Transfer the sample solution, containing up to 0.15 mg. of titanium, to a 50 ml. volumetric flask. Add 5 ml. of 4 per cent aqueous reagent solution and dilute ammonia until the mixture is neutral to Congo red paper. Add 5 ml. of buffer solution (equal volumes of 1 *M* acetic acid and sodium acetate) of *p*H 4.7 and dilute to the mark. Add 25 mg. of sodium dithionite and mix with a minimum of agitation. Obtain the transmittancy at 410 mμ within 15 minutes.

Thymol gives a reddish yellow color with titanium in concentrated sulfuric acid solution.[15] The reaction is more sensitive than the one with hydrogen peroxide. The reagent is prepared by dissolving 5 g. of thymol in 5 ml. of acetic acid and diluting to 100 ml. with concentrated sulfuric acid. The solution of titanium in concentrated sulfuric acid is treated with 20 ml. of the reagent, diluted to 100 ml. with sulfuric acid, and compared against a standard similarly prepared. Both solutions must be at the same temperature; the color intensity decreases with a rise in temperature. When the sulfuric acid content of the solution is less than 80 per cent the color intensity is markedly decreased. Tungsten interferes. Columbium also reacts.

Gallic acid produces a yellow to red-brown color in titanium solutions, particularly in the presence of acetate.[16] Salicylic acid has also been used for the colorimetric determination of titanium.[17]

Chromotropic acid



(or its sodium salt) gives a brown color with titanium in acid solution, and has been employed for the determination of titanium.[18]

Resoflavine (Color Index 1015) gives a yellow or orange color with titanium at *p*H 4.5, which is sensitive to 10^{-5} mole per liter.[19]

[15] V. Lenher and W. G. Crawford, *J. Am. Chem. Soc.*, **35**, 141 (1913).

[16] P. N. Das-Gupta, *J. Indian Chem. Soc.*, **6**, 855 (1929). Catechol reacts with titanium in weakly acidic solution to yield an orange-red color (J. Piccard, *Ber.*, **42**, 4343 (1909)). The reaction is more sensitive than the one with hydrogen peroxide, but iron and other metals also give a coloration.

[17] J. H. Müller, *J. Am. Chem. Soc.*, **33**, 1506 (1911).

[18] P. Klinger, E. Stengel, and H. Wirtz, *Metall u. Erz*, **38**, 124 (1941); A. V. Endredy and F. Brugger, *Z. anorg. allgem. Chem.*, **249**, 263 (1942).

[19] G. Charlot, *Anal. Chim. Acta*, **1**, 244 (1947).

III. Applications

A. Silicate Rocks

Ordinarily in a rock analysis, titanium is determined in the solution remaining after titration of total iron by permanganate. The following procedure may be used for the determination in a separate sample. It is assumed that enough iron is present to prevent titanium from going into the filtrate when the sodium carbonate melt is leached (p. 571).

§ Procedure

Weigh 0.3 g. of rock powder into a platinum crucible, mix with 1.5 g. of anhydrous sodium carbonate and fuse in the usual way. Leach the melt with about 50 ml. of water on the steam bath; add a few drops of alcohol to reduce manganate. Filter through a small paper, keeping as much as possible of the residue in the beaker. Wash with water and discard the filtrate and washings. Dissolve the insoluble material in 50 ml. of 1:20 sulfuric acid, pass the solution through the filter, and collect the filtrate in a 100 ml. volumetric flask. Wash with 1:20 sulfuric acid, add 5 ml. of 3 per cent hydrogen peroxide to the combined filtrate and washings, and dilute to 100 ml. with 1:20 sulfuric acid. Compare with a suitable standard in any convenient way.

Note. If sufficient iron is present to give an appreciable yellow color, add a regulated amount of phosphoric acid (see p. 576) to discharge the color. The transmittancy of the peroxidized solution is then best measured at 410 mμ.

B. Steel

Two procedures for titanium in ferro materials are given below, both based on the use of hydrogen peroxide as reagent. In Procedure A no separations are made. Iron is decolorized with phosphoric acid. By making extinction measurements at 400 and 460 mμ, one can determine titanium in the presence of reasonable amounts of vanadium. The color of nickel, chromium, and any unbleached iron is compensated by measuring the extinction against a portion of the sample solution which has not been treated with peroxide. Molybdenum interferes and a correction must be applied for its amount, as found from an independent determination. Columbium and tungsten do not appear to have much effect. The amount of titanium in the sample should be greater than 0.01 per cent. The general accuracy of the procedure can be judged from Table 93.

Procedure B was worked out for the determination of titanium in corrosion-resistant steels. Titanium is separated from the bulk of the iron (in the ferrous state), nickel, and chromium by cupferron precipitation. Small amounts of these metals accompany titanium and their effect is

corrected for by obtaining the transmittancy of the solution before and after adding hydrogen peroxide. Vanadium and molybdenum (the latter above 0.05 per cent) must be separated by treatment with sodium peroxide. Columbium interferes, apparently by forming a complex with ferric iron when hydrogen peroxide is added, and iron must then be removed as the sulfide (see the original). The average deviation in the determination of small amounts of titanium by this method is less than 0.001 per cent.

TABLE 93

DETERMINATION OF TITANIUM IN IRON AND STEEL BY THE PEROXIDE METHOD[a]

Sample	Ti present, %	Ti found, %
Bureau of Standards No.		
55a with added Ti and V (0.05%)	0.050	0.054
B. S. 55a with added Ti and V (0.40%)	0.050	0.052
B. S. 55a with added Ti and V (0.20%)	0.100	0.100, 0.104
B. S. 7c (cast iron, 0.042% V)	0.067	0.067, 0.068
B. S. 82 (cast iron, 0.011% V)	0.048	0.049, 0.049
B. S. 123a (stainless, 0.75% Cb, 0.11% W)	0.002	0.007
B. S. 123a with added Ti	0.202	0.210

[a] Selected figures from Weissler[20] mostly in lower Ti range

§ Procedure A[20]

Low-alloy steel and iron. Dissolve 1 g. of sample in 10 ml. of 1:1 nitric acid and 10 ml. of 70 per cent perchloric acid in a 125 ml. beaker. Evaporate to fumes of perchloric acid and continue to heat strongly until the fumes become transparent two-thirds of the way up the beaker. Cool rapidly in water to minimize peroxide formation. Dissolve the salts in 25 ml. of water and add 4.0 ml. of 1:1 phosphoric acid. Destroy any dichromic acid by adding a few drops of sulfur dioxide solution. Remove any silica or graphite by filtration through paper. Catch the filtrate in a 50 ml. volumetric flask, wash the filter with small portions of water, and dilute to volume. Add 0.10 ml. of 30 per cent hydrogen peroxide to a 5 ml. aliquot and obtain the extinction of the mixture at 400 and 460 mμ. As the reference solution use another 5 ml. aliquot to which has been added 0.10 ml. of water. Find the concentration of titanium by application of an expression analogous to the one on page 70. If vanadium and molybdenum are known to be absent, only the extinction at 400 mμ need be determined. Corrections can be applied to the reading at 400 mμ if the amounts of

[20] A. Weissler, *Ind. Eng. Chem., Anal. Ed.*, **17**, 775 (1945). When separation of titanium from iron, vanadium, molybdenum, and other elements seems desirable before its colorimetric determination see Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel*, p. 355, and T. R. Cunningham, *Ind. Eng. Chem., Anal. Ed.*, **5** 305 (1933).

vanadium and molybdenum present are known, by subtracting the extinctions due to these elements at this wave length as found from extinction-concentration curves established by the analyst for his conditions.

Stainless steel. Dissolve 0.5 g. of sample in 15 ml. of 1:1 hydrochloric acid and 2 ml. of concentrated nitric acid. Add 10 ml. of 70 per cent perchloric acid and evaporate, fume, and cool as described above. Dissolve the salts in 20 ml. of water and add 4.0 ml. of 1:1 phosphoric acid and 5 ml. of saturated sulfur dioxide solution to reduce chromium (VI) completely. Warm gently for 15 minutes to expel excess sulfur dioxide, filter through paper into a 50 ml. volumetric flask, wash, and make up to volume. Treat an aliquot of the solution with hydrogen peroxide and obtain the extinction of the mixture at 400 and 460 mμ as described above.

For the determination of metallic and combined titanium in steel see the original.

§ Procedure B[21]

Dissolve 5 g. of sample (Ti <0.05 per cent) in 80 ml. of acid mixture (310 ml. of concentrated hydrochloric acid, 95 ml. of concentrated sulfuric acid, and 600 ml. of water), warming gently. Evaporate almost to dryness, dilute to 150 ml. with hot water, and stir to dissolve salts.

Add a little filter paper pulp to the solution which has been cooled to room temperature or slightly below, followed by 6 per cent freshly prepared cupferron solution which is added dropwise until the precipitate assumes a deep reddish brown color. Usually 3–5 ml. of cupferron solution are required. Stir for a few minutes and allow the precipitate to settle. Filter on a fine paper containing a little filter paper pulp and wash about 10 times with cold 1:20 sulfuric acid. Transfer the paper to the original beaker and add 25 ml. of concentrated nitric acid, 10 ml. of concentrated sulfuric acid, and 10 ml. of 70 per cent perchloric acid. Evaporate to fumes of sulfuric acid. Cool, dilute to 75 ml., warm to dissolve salts, cool again, and add 25 per cent sodium hydroxide solution until the solution is alkaline. Add 0.5 g. of sodium peroxide in small portions with vigorous stirring. When reaction subsides, heat to boiling and boil for at least 10 minutes. (In the absence of vanadium or of appreciable molybdenum, omit the preceding sodium hydroxide-peroxide treatment.) Filter through a coarse paper, and wash with 1:100 ammonia until the washings are colorless. Return the paper to the beaker and destroy organic matter by adding 15 ml. each of concentrated nitric and sulfuric acids and 5 ml. of perchloric acid, and heating to fumes of sulfuric acid. Cool, dilute with 75 ml. of water, warm to dissolve salts, and cool somewhat. Add 3 ml. of saturated

[21] O. Milner, K. L. Proctor, and S. Weinberg, *Ind. Eng. Chem., Anal. Ed.*, 17, 142 (1945).

sulfur dioxide solution and boil for 5 minutes to expel the excess. Add 0.5 ml. of concentrated nitric acid to the boiling solution and boil for 1 or 2 minutes longer; allow to cool to room temperature. Any chromium present will now be in the trivalent state and iron in the ferric form.

Filter the solution into a 100 ml. volumetric flask and dilute to volume with water. Transfer 10 ml. of the solution to a 1 or 2 cm. absorption cell and find the transmittancy at or near 420 mμ. Then add 3 drops of 3 per cent hydrogen peroxide, mix, and again determine the transmittancy.

C. Bio Material (Animal Tissues)

§ Procedure[22]

Ash 50–100 g. of sample and dissolve the residue in concentrated sulfuric acid. Dilute the solution to give an acidity of about 2 *N*, and add sufficient tartaric acid to make its concentration 1–2 per cent and a few milligrams of ferric iron to act as a collector. Add an excess of cupferron (5 per cent solution), filter off the precipitate on paper, and wash with 0.2 per cent cupferron solution which is 2 *N* in sulfuric acid. Ignite the precipitate, fuse with a little potassium pyrosulfate and dissolve in dilute sulfuric acid. Add tartaric acid to make its concentration about 1 per cent, nearly neutralize with ammonia, and saturate with hydrogen sulfide. Make the solution ammoniacal, filter off the precipitate of ferrous sulfide, and wash with dilute ammonium sulfide solution. Make the filtrate about 2 *N* in sulfuric acid and boil to remove hydrogen sulfide.

Add a few milligrams of a zirconium salt to the solution and precipitate with cupferron. Filter off the precipitate, wash, ignite, and fuse the residue with 0.1 g. potassium pyrosulfate. Dissolve the melt in 5–10 ml. of 1:20 sulfuric acid, add 1 ml. of 3 per cent hydrogen peroxide, and compare against a standard containing the same amount of potassium sulfate as the sample solution.

[22] L. Maillard and J. Ettori, *Compt. rend.*, **202**, 594 (1936).

CHAPTER XLV

TUNGSTEN

I. Separations

Fusion of an oxide or silicate sample with sodium carbonate or hydroxide followed by leaching with water may be expected to separate tungsten (together with molybdenum, chromium, vanadium, arsenic, and phosphorus) from iron and other metals forming insoluble hydroxides. but little is known about the extent of retention of tungsten by the residue. Generally in such fusion procedures losses by coprecipitation are smaller than when precipitation is carried out in aqueous medium.

The separation of tungsten from iron and other metals by sodium hydroxide precipitation has received some study. Scobie[1] separates tungsten from much ferric iron by adding the almost neutral solution in a thin stream to boiling 20 per cent sodium hydroxide solution and keeping the mixture at the boiling point for one-half hour before diluting with water and filtering. The precipitate is dissolved in hydrochloric acid and the reprecipitation made in the same manner. According to Scobie as little as 0.2 mg. of tungsten can be separated satisfactorily in this way from as much as 10 g. of ferric chloride. In connection with the development of a method for the determination of tungsten in silicate rocks (p. 589), some experiments were run to find the approximate quantity of tungsten carried down by the hydroxides of ferric iron, titanium, calcium (carbonate), magnesium, and manganese under conditions similar to those that would exist in such a determination. Ten ml. of almost neutral sample solution were added dropwise to 15 ml. of hot 10 per cent sodium hydroxide solution. The results obtained (Table 94) show that there is little tendency for tungsten to be retained by the calcium, magnesium, or manganese precipitate, but that it is coprecipitated with iron and titanium.

Molybdenum can be separated from tungsten by precipitation with hydrogen sulfide in dilute mineral acid medium containing tartrate to prevent coprecipitation of tungsten. If a sharp separation is required, a collector must be used for the molybdenum sulfide, whose complete precipitation involves difficulties as well known. Because of similarity in size, quinquevalent antimony is a good collector for sexivalent molybdenum in the sulfide precipitation. A single hydrogen sulfide precipitation in 25 ml. of hot

[1] A. G. Scobie, *Ind. Eng. Chem., Anal. Ed.*, **15**, 79 (1943).

solution containing 20 γ of molybdenum, 1 mg. of Sb(V), 2 g. of sodium sulfate, and 0.5 ml. of 6 *N* sulfuric acid leaves from 0.1 to 0.3 γ of molybdenum in solution. Repetition of the precipitation under like conditions leaves less than 0.1 γ of molybdenum. This separation can be made successfully in the presence of small amounts of phosphorus, if hydrogen sulfide is first passed into a cold solution.

TABLE 94

RECOVERY OF TUNGSTEN IN SODIUM HYDROXIDE PRECIPITATION OF IRON, TITANIUM, AND OTHER ELEMENTS

(In each case 5.0 γ of tungsten were added as tungstate)

Elements present, g.	W found, γ
0 1 CaO	5.0
0.1 MgO	5.0
0.025 MnO	5.3
0.1 Fe_2O_3	4.2
0.1 Fe_2O_3, 0.12 Al_2O_3	4.4
0.015 TiO_2	4.0
0.015 TiO_2, 0.015 P_2O_5	4.0

Molybdenum can also be separated from tungsten by amyl acetate extraction of the dithiol complex of the former from hydrochloric acid of density 1.06 (*ca.* 3.7 *N*).[2] At 20–25° the tungsten complex is not formed at this acidity. The extraction is carried out in the presence of hydroxylamine to retard the decomposition of the reagent, which would otherwise lead to incomplete extraction of molybdenum because of the inhibiting effect of the decomposition products. This separation is applied preparatory to the determination of tungsten in steel by dithiol.

Small amounts of tungsten in a solution can be concentrated by adding a little ferric iron or aluminum[3] and precipitating with ammonia.

It may be expected that tungsten can be coprecipitated with suitable slightly soluble molybdenum compounds by mixed crystal formation, but since molybdenum would have to be removed before tungsten could be determined colorimetrically this is not an attractive possibility.[4]

[2] B. Bagshawe and R. J. Truman, *Analyst*, **72**, 189 (1947).

[3] In isolating tungsten from very dilute solution (that resulting from the sodium hydroxide precipitation described in the preceding footnote) Scobie (*loc. cit.*) adds enough aluminum ion to the acidified solution to make its concentration about 0.01 per cent and precipitates aluminum hydroxide at the boiling point by adding sodium bicarbonate solution until methyl orange shows its basic color.

[4] For coprecipitation of tungsten with the α-benzoinoxime compound of molybdenum prior to spectrographic determination see P. Fischer, R. Spiers, and P. Lisan, *Ind. Eng. Chem., Anal. Ed.*, **16**, 607 (1944).

It may be possible to isolate tungsten by coprecipitation in the slightly soluble compound that antimony (V) gives with rhodamine B in hydrochloric acid medium.

II. Methods of Determination

A. The Thiocyanate-Stannous Chloride Method

In strong hydrochloric acid medium, thiocyanate and stannous chloride produce a yellow color with tungsten (VI).[5] The method has recently been studied by Westwood and Mayer.[6] They found that the best concentration of sodium thiocyanate is 1.5 to 2.5 per cent in the final solution. Too high a concentration of thiocyanate gives a brown color in the absence of tungsten. The optimum concentration of hydrochloric acid is 8.5 to *ca.* 9.5 *N*. The maximum color intensity is obtained with 4.5 per cent stannous chloride in the mixture, above which the color remains constant. At these optimum concentrations the full color intensity is attained in 20 minutes and remains constant for at least 2 hours. Tartrate does not interfere with color development. The color intensity is the same in the presence of 0.1 g. of iron as ferric chloride and 1 g. of tartaric acid as in their absence. Moreover, the rate of color development is the same in the presence of these. There is no interference from aluminum, antimony, bismuth, lead, manganese, titanium,[7] and zirconium in milligram quantities. The color given by molybdenum fades on standing so that after 20 minutes it is about $^1/_{100}$ as strong as that produced by an equal weight of tungsten. Compounds of arsenic, selenium, and tellurium are reduced to the elements. More than small amounts of copper are precipitated as cuprous thiocyanate. Chromium, nickel, cobalt, and vanadium interfere to the extent that they are colored; their effect can therefore be compensated. Fluoride and nitrate inhibit color development, but phosphate does not interfere.

[5] The first procedure described (F. Feigl and P. Krumholz, *Angew. Chem.*, **45**, 674 (1932)) called for the addition of the reagents to a tungstate solution containing sodium hydroxide. The use of an alkaline solution is not necessary, however. An acidic tartrate solution can be used as well. In the absence of base or tartaric acid (or other complex former) the color development may be slower, especially if the hydrochloric acid concentration is not high, presumably because of the formation of colloidal particles of tungstic acid. It may be mentioned that titanous chloride gives more rapid color development than stannous chloride and is used in some procedures (S. Fernjančič, *Z. anal. Chem.*, **97**, 332 (1934)).

[6] W. Westwood and A. Mayer, *Analyst*, **72**, 464 (1947).

[7] Feigl and Krumholz[5] found that titanium gave a yellow color when more than 20 mg. was present in 50 ml. under their conditions (lower acidity than in the above procedure). F. S. Grimaldi and V. North, *Ind. Eng. Chem., Anal. Ed.*, **15**, 652 (1943), in investigating the thiocyanate method for tungsten in low-grade ores found no interference from titanium below 10 mg. in 25 ml.; above this concentration a yellow color was produced, which was stronger in the presence of phosphate.

The rate of color development is the same in the range 15–40°, but the final color intensity depends on the temperature, so that the latter should be controlled within ±2°. Beer's law holds to at least 17 p.p.m. Potassium thiocyanate cannot be used in place of sodium thiocyanate because of the precipitation of potassium bitartrate.

A departure from previous thiocyanate methods for tungsten has been made by Gentry and Sherrington who reduce tungsten to the trivalent

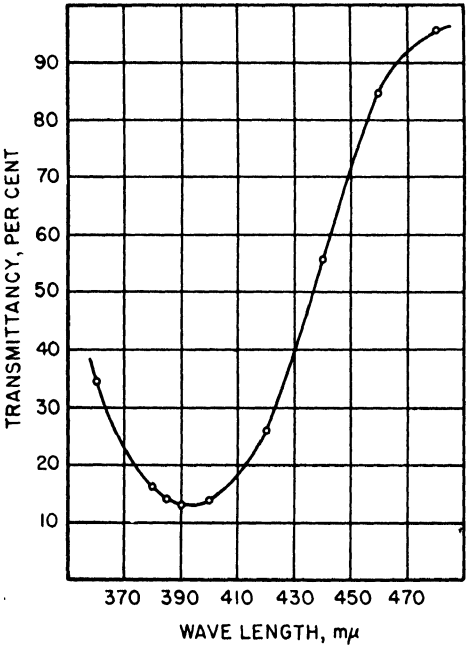


Fig. 75. Transmission curve of tungsten-thiocyanate complex in ethyl ether; 40 p.p.m. tungsten, 1 cm. cell. Spectrophotometer slit width 35 mμ. (Data of B. Warshowsky.)

state with tin amalgam in the presence of stannous chloride in 6 to 9 *N* hydrochloric acid solution before adding thiocyanate.[8] It does not matter whether the original sample solution is basic, neutral, or acidic (as with tartaric or citric acid). The reduced tungsten reacts with thiocyanate to give a definite compound, such as WOCNS as tentatively proposed by the authors. This compound is reported to exist in a purple and a yellow form; the latter is the stable form and is made the basis of the method. The interference of molybdenum is relatively small (the color is about $^1/_{40}$

[8] C. H. R. Gentry and L. G. Sherrington, *Analyst*. **73**, 57 (1948).

of that produced by tungsten). Unfortunately, vanadium and columbium give rather strong colors under the conditions, so that their amount must be less than that of tungsten. Vanadium interferes more strongly in this method than in the stannous chloride-thiocyanate method because of its reduction to the divalent state by tin amalgam. The presence of much iron requires a slight change in the optimum conditions. The variables in the procedure and the effect of foreign cations and anions have been investigated in detail. The method is sensitive. At 400 mμ an extinction of 0.001 is produced by 0.02 γ of tungsten in a column of solution having a cross-section of 1 sq. cm.

The tungsten thiocyanate complex can be extracted by various immiscible organic solvents (see p. 457). Isopropyl ether may be suggested as a suitable solvent to be used in conjunction with the procedure below, either for greater sensitivity or for the avoidance of the effect of such colored ions as nickel and chromium.[9] Special application has been made of ethyl ether extraction in the determination of minute amounts of tungsten in silicate rocks (p. 589).

Special Solutions

Sodium thiocyanate, 50 g. in 100 ml. of solution.

Stannous chloride, 70 g. of the dihydrate in 1 liter of concentrated hydrochloric acid. Prepare fresh every one or two days.

Standard tungsten solution, 0.0100 per cent W. Dissolve 0.0897 g. of $Na_2WO_4 \cdot 2\,H_2O$ in water and dilute to 500 ml. The solution may also be prepared by dissolving pure WO_3 in a slight excess of dilute sodium hydroxide.

Tartaric acid, 50 g. in 100 ml. of solution.

§ Procedure[10]

Transfer 10 ml. of neutral or weakly alkaline sample solution (containing up to 0.75 mg. of tungsten) to a 50 ml. volumetric flask and add 2 ml. of tartaric acid and 1.5 ml. of sodium thiocyanate solution. Dilute to the mark with stannous chloride at 20 ± 2° or other fixed temperature. Find the transmittancy at 420 mμ after 20 minutes.

B. The Dithiol Method

Toluene-3,4-dithiol forms a slightly soluble bluish green complex with

[9] A 1:1 mixture of isoamyl alcohol and chloroform and a 2:3 mixture of *n*-butyl alcohol and chloroform have also been used.

[10] Essentially the directions of Westwood and Mayer in generalized form. The procedure given by these authors for the determination of tungsten in cast iron is omitted here, since it is intended for larger than trace amounts.

tungsten, which can be extracted by butyl acetate or isoamyl acetate.[11] Molybdenum reacts similarly to give a yellow-green precipitate. Tin (p. 565), iron, and many other heavy metals also react with the reagent, but it appears that most of these do not give complexes soluble in organic solvents. The presence of such metals, except in very small amounts, is objectionable, because they yield precipitates and consume reagent.

The tungsten reaction is carried out in the *p*H range 1.5–2.5 in a method described by Bickford and others.[12] Heating facilitates the precipitation of tungsten before its extraction. Citric acid prevents the reaction. Molybdenum must be absent. Small quantities of molybdenum can be removed by extraction of its dithiol complex in the presence of citric acid. Tungsten can then be determined after destruction of citric acid. A number of heavy metals, such as copper, can be removed by dithizone extraction. Since the procedure proposed by Bickford and coworkers is intended for the determination of tungsten in organic materials, the directions are given under that heading (p. 593).

C. Other Methods

In strong sulfuric acid medium hydroquinone[13] produces a red color with tungsten (VI). Small amounts of water reduce the color intensity markedly. The higher the concentration of hydroquinone in the solution the larger the amount of water that may be present without affecting the color. Thus with 2 g. of hydroquinone, the color intensity begins to decrease when 2 ml. of water are present in 100 ml. of the sulfuric acid (*sp. gr.* 1.84) mixture; with 4 g. hydroquinone no decrease in color is noticed until 6 ml. of water are present in 100 ml.; and with 10 g. of hydroquinone in 100 ml., as much as 10 ml. of water in the mixture has no effect. Beer's law is obeyed. Chloride modifies the color produced (Fig. 76). Nitrate must be absent. Although the reaction product shows maximum absorption at 465 mμ, it is generally advisable to use light of wave length 570–580 mμ to avoid error due to traces of organic substances, nitrate, etc. which produce a yellow color.

Titanium gives a color very similar to that produced by tungsten, and

[11] C. C. Miller, *Analyst*, **69**, 109 (1944). The detection of tungsten in ferro alloys and in molybdenum and rhenium compounds is described. The interference of iron, copper, arsenic, gold, and tellurium is eliminated by addition of stannous chloride. Some semi-quantitative results of the determination of traces of tungsten in steel are reported. It is to be noted that Miller carries out the reaction in hydrochloric acid medium in contrast to the weakly acidic solution used by Bickford.

[12] C. F. Bickford, W. S. Jones, and J. S. Keene, *J. Am. Pharm. Assoc.*, **37**, 255 (1948).

[13] G. Heyne, *Z. angew. Chem.*, **44**, 237 (1931); G. Bogatzki, *Z. anal. Chem.*, **114**, 170 (1938). A number of phenolic substances (including phenol) react with tungstate in sulfuric acid. *Cf.* M. E. Defacgz, *Compt. rend.*, **123**, 308 (1896).

no way of preventing its interference is known. Ferric iron, but not ferrous, prevents the reaction of tungsten. Molybdenum (VI) may give a red, brown, or blue color depending upon conditions. The interference of molybdenum and ferric iron may be prevented by reduction with stannous chloride. To hinder the reduction of tungsten, phosphoric acid may be added according to Bogatzki. A low concentration of phosphoric acid has no effect, but larger amounts bleach the tungsten color. Aluminum, manganese, tantalum, and copper do not interfere. Vanadium (III), nickel, and chromium (III) do not give a color with the reagent but their own color may be slightly disturbing, unless compensated by the use of an aliquot of the solution in the reference cell.

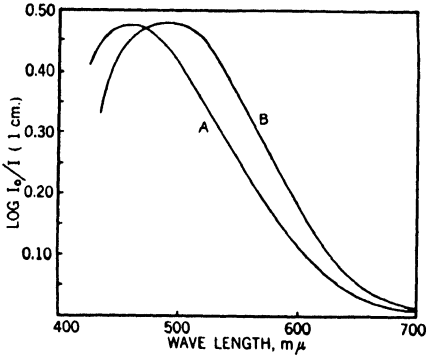


Fig. 76. Extinction curves of (A) 1 mg. tungsten and 2.5 g. hydroquinone in 100 ml. sulfuric acid, and (B) 1 mg. tungsten, 2.5 g. hydroquinone and 0.32 g. HCl in 100 ml. sulfuric acid. (According to Bogatzki.)

A number of methods for the determination of tungsten are based on its reduction to colored lower oxides by strong reducing agents. Titanous chloride[14] and stannous chloride reduce tungstates in acid solution to insoluble blue oxides remaining in colloidal suspension. Lead in phosphoric acid solution gives a red color.[15] These reactions are not very sensitive.

Phosphoric acid and vanadate give a yellow color with tungstate (phosphotungstovanadic acid, p. 607). Again the sensitivity is rather low, and even small amounts of iron hinder the development of the color.

Rhodamine B reacts with tungsten (VI) in dilute hydrochloric acid. The color change is from yellow-red to violet. A rough quantitative

[14] A. Travers, *Compt. rend.*, **165**, 408 (1917); **166**, 416 (1918).
[15] A. Petrovskii, *J. Chem. Ind. Moscow*, **7**, 905 (1930).

method (± 20 to 30 per cent) has been worked out by Heyne.[16] Relatively much molybdenum may be present.

III. Applications

A. Silicate Rocks[17]

In the following method, iron, titanium, etc. are separated by double sodium hydroxide precipitation, and molybdenum by hydrogen sulfide precipitation with antimonic sulfide as collector. Tungsten is then determined by the stannous chloride-thiocyanate method with ether extraction of the complex. Visual color comparison is preferred to photometric measurement because of the very faint color obtained with the minute quantities of tungsten normally present in igneous rocks. Satisfactory results are obtained with silicic and intermediate rocks. Subsilicic rocks containing large amounts of iron and titanium give low results, as much as half of their tungsten content being lost in the separations. Useful results (approximately 80 per cent recovery of tungsten) can still be obtained with a sample containing 6 per cent total iron oxides, 0.9 per cent titanium dioxide, 3 per cent magnesium oxide, and 5 or 6 per cent calcium oxide as well as 0.25 per cent phosphorus pentoxide.

Under the conditions of the procedure below, vanadium gives a yellow-brown coloration, about $^1/_{500}$ as strong as that produced by an equal weight of tungsten. The amount of vanadium in silicic rocks is too small to affect the determination of tungsten appreciably. Uranium, columbium, tantalum, phosphorus, boron, and platinum (from the utensils) in small amounts do not interfere.

Special Solutions

Sodium hydroxide, 10 grams in 100 ml. of water.

Tartaric acid, 50 grams in 100 ml. of solution.

Antimony pentachloride, 0.5% antimony in 4 *N* hydrochloric acid. This solution may be prepared by adding saturated potassium bromate solution to a hot antimony trichloride solution containing 0.5% antimony in 4 *N* hydrochloric acid until the color of bromine appears.

Potassium thiocyanate, 10 grams in 100 ml. of water.

Stannous chloride, 5 grams of the dihydrate in 100 ml. of concentrated hydrochloric acid. The solution should not be older than a month.

Ethyl ether. Only the reagent grade product should be used. The best quality ether need not be subjected to any purification procedure before use.

Salt solution for standards. Dissolve 50 grams of sodium hydroxide and 10.0 grams of tartaric acid in 250 ml. of water and add to the cold solution 225 ml. of 6 *N* sulfuric acid and 10 ml. of antimony pentachloride solution. Pass a rapid stream of hydrogen

[16] E. Eegriwe, *Z. anal. Chem.*, **70**, 400 (1927); G. Heyne, *Z. angew. Chem.*, **44**, 237 (1931).

[17] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **18**, 163 (1946).

sulfide into this solution, cooled to room temperature, for 0.5 hour. Allow the mixture to stand overnight and filter off the precipitate on a retentive paper.

Color Comparison Tubes

These should have a capacity of 5 ml. with the dimensions 1.2 × 8 cm., and should be provided with glass stoppers. A narrow strip of millimeter graph paper is glued to the back of each tube to serve as a scale for reading the height of the liquid column. The paper strip should be waterproofed with paraffin or other suitable material.

§ Procedure

Transfer 1.0 gram of 100-mesh silicic rock or 0.8 gram of mediosilicic rock to a platinum dish and add 5 ml. of 6 *N* sulfuric acid, 2 ml. of concentrated nitric acid, and 5 ml. of 48% hydrofluoric acid. Evaporate to dryness and heat the residue until fumes of sulfuric acid cease to come off. Add 1 ml. of 6 *N* sulfuric acid and a few milliliters of water to the dish and warm with stirring to bring as much as possible of the salts into solution. Then evaporate to dryness and fume off the excess of sulfuric acid at approximately 350° C. Add 1 ml. of 6 *N* sulfuric acid and 10 ml. of water and digest slightly below the boiling point for 15 or 30 minutes while stirring at intervals. Disregard undissolved material.

Sodium Hydroxide Precipitation. Add the mixture dropwise with stirring to 15 ml. of hot sodium hydroxide solution in a 50-ml. beaker. Pour the liquid back into the platinum dish and digest slightly below the boiling point for about 15 minutes. Filter the mixture through a sintered-glass crucible (Jena 1G4 or equivalent), catching the filtrate in a vial or test tube hung inside the suction flask. Wash the precipitate, which has been sucked dry, with 2 or 3 ml. of water. Transfer the filtrate to a 50-ml. beaker and place on a steam bath to reduce the volume by evaporation.

By means of a stirring rod transfer most of the precipitate in the crucible to the beaker in which the precipitation was made. Clean the platinum dish with about 5 ml. of 1 to 1 hydrochloric acid and pour the solution into the crucible. Without applying suction, allow the precipitate remaining in the crucible to dissolve and then pour the solution into the beaker containing the solution of the major part of the precipitate. Now apply suction and wash the crucible with a few milliliters of water. Add the washings to the solution of the precipitate and evaporate the whole to a volume of a few drops. Dilute with 5 ml. of water and add the solution dropwise to 10 ml. of hot sodium hydroxide solution. Keep the mixture slightly below the boiling point for 10 or 15 minutes and then filter through a sintered-glass crucible. Wash with two portions of water totaling 5 ml. Combine the filtrate and washings with those from the first precipitation and evaporate the whole to a volume of 15 ml.

Hydrogen Sulfide Precipitation. Cool the evaporated solution to room temperature and add 6 *N* sulfuric acid dropwise with stirring until a slight permanent precipitate of aluminum hydroxide is formed. Then add 1.0 ml. of tartaric acid solution, 0.5 ml. of 6 *N* sulfuric acid, and 0.2 ml. of antimonic chloride solution. If necessary allow the solution to stand until it becomes clear. Cover the beaker and pass in a rapid stream of hydrogen sulfide for 10 minutes. Then heat the solution to the boiling point while continuing the passage of hydrogen sulfide, keep at the boiling point for a few minutes, remove the beaker from the heat, and pass in the gas for another 5 or 10 minutes. Stirring during this interval aids in the coagulation of the precipitate. Allow the precipitate to stand for 2 hours or preferably overnight.

Filter off the sulfide precipitate on a small (5-cm.) filter paper of fine texture and wash with a few milliliters of hydrogen sulfide water containing a drop of 6 *N* sulfuric acid. Evaporate the combined filtrate and washings to 15 ml. Cool the solution to room temperature and add 5 drops of bromine water (a yellow color should persist for a minute or two) and 0.2 ml. of antimonic chloride solution. Precipitate with hydrogen sulfide as before. Allow the precipitate to stand overnight and filter it off on a small retentive filter paper which has been washed with a little dilute (0.5 *N*) sulfuric acid. Wash the precipitate with 2 or 3 ml. of cold water containing a drop of 6 *N* sulfuric acid.

Determination of Tungsten. Evaporate the combined filtrate and washings from the second sulfide precipitation to a volume of 15 ml. in a 50-ml. beaker. At the same time evaporate 25-ml. portions of the salt solution for the standards to which have been added 1, 2, and 3 micrograms of tungsten, respectively. If the vanadium content of the sample is equal to, or greater than, 0.02% (0.03% vanadium sesquioxide), add an amount of ammonium metavanadate equivalent to the quantity of vanadium in the sample to each of the standards.

Cool each solution to room temperature (20° C.), transfer to a small separatory funnel, and extract with 5 ml. of ether. Draw off the aqueous solution in each case and wash the ether layer in the funnel with 1 or 2 ml. of water, adding the latter to the extracted aqueous solution. If the ether extract from the sample solution shows an appreciable coloration (compare in a small vial against the ether from one of the standard solutions), extract the aqueous solution once more with 2 to 3 ml. of ether. Discard the ether extracts.

Treat the extracted sample and standard solutions with 1.0 ml. of potassium thiocyanate and 10 ml. of stannous chloride solution. If necessary adjust the volumes to equality by adding water until the heights of the solutions in the beakers are the same. The volume should lie between 25

and 30 ml.; if it is less than 25 ml., salt is almost certain to crystallize out. After mixing, set the solutions aside at 25° to 30° C. for an hour.

Cool the solutions to 20° C. or slightly less and transfer to separatory funnels. Extract each solution with 5.0 ml. of ether by shaking for 15 seconds. Allow the phases to separate, drain off the aqueous solutions, and run the ether layers into the color comparison tubes. If desired the funnels can be rinsed with 1 ml. of ether. Compare the tubes axially against a white background in good light. Pick out the standard having a color intensity closest to the sample. By means of a glass tube remove small volumes of ether from the standard or the sample tube, as the case requires, until the two solutions show the same color intensity. Usually it is best to note the heights of the solution being withdrawn at which it is just perceptibly darker and lighter, respectively, than the solution against which comparison is made. The intermediate height is then taken as the matching height. This operation should be carried out in a cool environment (20° C.) to avoid undue loss of ether by evaporation. Find the tungsten content of the sample from the ratio of the matching height to the original height of the solution whose depth is varied. Run a blank through all steps of the procedure.

TABLE 95

DETERMINATION OF TUNGSTEN IN SYNTHETIC SILICIC ROCK[a]

W present, γ	3.7	5.7	10 7	10.7[b]	5 7[c]
W found, γ	3 3	6 4	10 6	10.8	6.2

[a] 1 g. sample; only one sodium hydroxide precipitation made to separate Fe, Ti, etc.
[b] 10 p.p.m. Mo present.
[c] 15 p.p.m. Mo and 300 p.p.m. V_2O_5 present.

B. IRON AND STEEL

Procedures for the determination of tungsten in ferro materials by the thiocyanate[6,8] and dithiol[2] methods have been described but since these are intended for amounts above the trace range the detailed directions will not be given here. The dithiol procedure of Bagshawe and Truman comes closest to trace requirements, and it appears that a few hundredths of a per cent of tungsten can be determined by their procedure. Hydroquinone has been used by Bogatzki[13] for the determination of tungsten in steel.

C. BIO MATERIALS

§ Procedure A (Thiocyanate-Reducing Agent)[18]

Transfer 2 ml. of blood, 10 ml. of urine or 2 g. of organ to a Kjeldahl flask and add 4 ml. of concentrated sulfuric acid, 5 ml. of nitric acid, and

[18] J. C. Aull and F. W. Kinard, *J. Biol. Chem.*, **135**, 119 (1940).

5 ml. of 70 per cent perchloric acid. Heat gradually and if charring occurs add more nitric-perchloric acid (equal volumes of each) until the solution clears. Heat until white fumes are no longer evolved, cool the mixture, and dilute with water. Make distinctly alkaline with 40 per cent sodium hydroxide. Boil vigorously for several minutes, cool, and dilute to a suitable volume. Filter the solution and take a 5 or 10 ml. aliquot for analysis according to the general procedure above.

Alternatively (the procedure used by Aull and Kinard) carry out the determination with titanous chloride as reducing agent in place of stannous chloride as follows. To a 5 ml. aliquot (up to 0.1 mg. W) add 1 ml. of 15 per cent potassium thiocyanate, 4 ml. of concentrated hydrochloric acid, and 1 ml. of titanous chloride (boil 1 ml. of 10 per cent titanous chloride with 2 ml. of hydrochloric acid to expel traces of hydrogen sulfide and dilute to 80 ml. with hydrochloric acid). Determine the transmittancy of the solution after 10 minutes, using a filter showing maximum transmission at 420 mμ.

§ Procedure B (Dithiol)[12]

Take a weight of sample that will contain about 25 γ of tungsten and destroy organic matter in the usual way with sulfuric-nitric acid. After removal of nitrosyl sulfuric acid by addition of water and evaporation (p. 385), cool the solution in an ice bath and add 5 ml. of ammonium hydroxide. Evaporate until salts crystallize out and heat gently to fuse these. Dissolve the cooled solid in water, add 5 ml. of ammonium hydroxide, evaporate, and again fuse the salts. Add 3 ml. of concentrated nitric acid and boil until essentially all of the nitric acid has been removed, as indicated by cessation of effervescence.

Add 8 ml. of ammonium sulfate-phosphoric acid solution (300 g. of ammonium sulfate, 40 ml. of 85 per cent phosphoric acid, sufficient ammonia to give a *p*H of 1.8, in a total volume of 1 liter) for each milliliter of sulfuric acid originally added in the digestion. Boil and cool the solution. Adjust the pH of the solution to 1.5–1.8 with the aid of a glass electrode. Bring the volume to about 18 ml. and add 2 ml. of dithiol solution (0.2 g. dithiol and 0.5 ml. of thioglycolic acid in 100 ml. of 0.25 *N* sodium hydroxide solution, prepared fresh daily). Heat in a boiling water bath for 30 minutes. If much precipitate forms, add 2 ml. more of the reagent solution.

Cool the solution and extract the tungsten complex with a 15 and a 10 ml. portion of redistilled butyl acetate. Filter the butyl acetate solution through a small paper filter, dilute to 25 ml. if necessary, and obtain the transmittancy with a red filter (640 mμ). Prepare a 25 γ tungsten standard by adjusting the *p*H and volume of 13 ml. of ammonium sulfate-phos-

phoric acid mixture as described above, precipitating with dithiol, and extracting with butyl acetate. It is advisable to check the *p*H of the aqueous phase after the extraction to be sure that it lies in the range 1.5 to 2.5.

See the original for a modified method for the determination of very small amounts (0–10 γ) of tungsten. When molybdenum is present in small amounts, tungsten can be determined by first removing the molybdenum complex by extraction from citric acid solution, destroying citric acid, and proceeding as above.

CHAPTER XLVI

URANIUM

The colorimetric methods for uranium are relatively insensitive and not well suited for the determination of very small amounts of the element. However, a fluorimetric method is available which can be used for the determination of extremely minute amounts.

I. Separations

Uranium may be separated from the metals of the hydrogen sulfide group by the precipitation of these in an acid solution containing tartrate. Ammonium sulfide does not precipitate uranium from a solution containing ammonia and tartrate, and a separation may thus be effected from iron and other metals yielding sulfides under these conditions.

Uranium (VI) forms a soluble complex with alkali metal carbonates. Ferric iron, aluminum, and other metals may be precipitated with ammonium carbonate, and uranium left in solution. Traces of iron remain in solution and may give rise to difficulties when very small amounts of uranium are to be determined, because iron reacts with some of the colorimetric reagents for uranium.[1] A fusion with sodium carbonate followed by leaching with water will presumably separate uranium from iron and other metals yielding slightly soluble precipitates under the conditions. The extent of retention of uranium by the residue is problematical.

Electrolysis with a mercury cathode in sulfuric acid solution serves to separate iron, and has the advantage over other methods of not being subject to loss of uranium by coprecipitation. Cupferron precipitates iron, vanadium, titanium, etc., but not sexivalent uranium in dilute sulfuric acid solution; quadrivalent uranium is precipitated. The insoluble cupferrates can be extracted by chloroform.

Large amounts of iron (III) can be removed by ether extraction of its chloride from 1:1 hydrochloric acid.

Very small amounts of uranium can be isolated by coprecipitation with

[1] Probably the small amounts of iron (and aluminum) remaining in solution can be removed by addition of 8-hydroxyquinoline followed by chloroform extraction. The hydroxyquinolates of many heavy metals are precipitated in ammonium carbonate solution but uranium (VI) oxinate is not.

ferric or aluminum hydroxide,[2] or with the phosphates of iron and aluminum.[3] See p. 599.

It has long been known that solid uranyl nitrate is soluble in ether. In recent years use has been made of the extractability of uranium nitrate by ethyl ether from aqueous solution.[4] The extraction is best made from a solution containing both nitric acid and ammonium nitrate (the latter to increase the nitrate ion concentration). The partition coefficient reaches

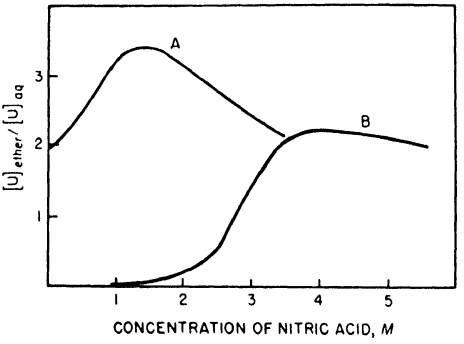


Fig. 77. Distribution of uranyl nitrate between ethyl ether and aqueous nitric acid solutions: (A) in the presence of ammonium nitrate (saturated solution), (B) in the absence of ammonium nitrate. (According to A. Norström and L. G. Sillén, *Svensk Kem. Tids.*, **60**, 232 (1948).)

a maximum of *ca.* 3.5 in a solution saturated with ammonium nitrate which is about 1.5 *M* in nitric acid (the latter figure is the acid concentration of the aqueous layer after shaking with ethyl ether, the nitric acid distributing itself roughly equally between the two phases). The maximum partition coefficient with nitric acid alone is about 2.3 in 4 or 5 *M* nitric acid medium (the concentration of nitric acid in the ether is approximately 3 to 4 *M*).[5]

Uranyl thiocyanate can be extracted from slightly acidic medium by ethyl acetate; ether is less suitable as an extractant.[6]

[2] W. D. Urry, *Am. J. Sci.*, **239**, 191 (1941).

[3] Uranium can be separated from vanadium (V) by precipitation as phosphate from a nearly neutral (very slightly acid) solution. Aluminum phosphate may be used as collector. See J. A. Tschernichow and E. Guldina, *Z. anal. Chem.*, **96**, 257 (1934).

[4] F. Hecht and A. Grünwald, *Mikrochem. ver. Mikrochim. Acta*, **30**, 279 (1943). A continuous extraction apparatus is used. *Cf.* P. Misciatelli, *Phil. Magazine*, **7**, 670 (1929); W. F. Hillebrand, *U. S. Geol. Survey Bull.*, **78**, 47 (1891). T. R. Scott, *Analyst*, **74**, 486 (1949), adds ferric nitrate to aid the extraction of uranyl nitrate; see this paper for the colorimetric determination of uranium with hydrogen peroxide following the extraction.

[5] A. Norström and L. G. Sillén, *Svensk Kem. Tid.*, **60**, 227 (1948).

[6] R. Vanossi, *Anales soc. cient. argentina*, **137**, 3 (1944).

II. Methods of Determination

A. The Fluorescence Method

Uranium (VI) shows rather weak fluorescence in aqueous medium. The fluorescence intensity is stronger in the presence of phosphoric or hydrofluoric acid and use is made of this behavior in a method for the sensitive detection of uranium.[7] A phosphoric acid concentration of 5 to 50 per cent is recommended; in this range the fluorescence remains approximately constant. Under these conditions stannous tin shows a pink fluorescence, stannyl tin a yellowish green much like that of uranium, and cerium (III) a white fluorescence. These elements, as well as many others which inhibit the fluorescence of uranium, can be removed by suitable treatment as described by Sill and Peterson; chief reliance is placed on the carbonate separation. It may be possible to base a quantitative method on such or a similar procedure. With radiation of 253.7 mμ wave length, less than 1 γ of uranium can be detected in a column of solution having a cross-section of 1 square centimeter.

A solid solution of uranium in sodium fluoride shows strong yellowish fluorescence[8] in ultraviolet light. Minute amounts of uranium may be determined by evaporating the sample solution with a known weight of sodium fluoride, mixing the dry residue by grinding in an agate mortar, fusing a portion of the powder in a platinum loop, and comparing the bead so obtained against standard beads in ultraviolet light. The comparison may be made more accurately by photographing the fluorescence spectra of the sample and standard beads, and measuring the darkening with a microphotometer.[9] A micro pastil press may be used to obtain beads constant in weight to 5 per cent. The intensity of the fluorescence is proportional to the amount of uranium present in the range 10^{-6} to 5×10^{-3} mg. of U (25 mg. bead). As little as 10^{-7} mg. of uranium can be detected.

The solution in which uranium is to be determined by this method should in general be free from foreign elements, because some of these may seriously reduce the intensity of the fluorescence. Silica, titanium, thorium, iron, and sulfate all interfere; the effect of manganese is less serious. Potassium, magnesium, and barium in small amounts are without effect, but calcium interferes seriously. As little as 6 per cent of calcium fluoride in the bead nearly completely extinguishes the fluorescence, 2 per cent reduces

[7] C. W. Sill and H. E. Peterson, *Anal. Chem.*, **19**, 646 (1947).

[8] L. Papish and L. E. Hoag, *Proc. Natl. Acad. Sci. U. S.*, **13**, 726 (1927); E. L. Nichols and M. Slattery, *J. Optical Soc. Am.*, **12**, 449 (1926); M. K. Slattery, *ibid.*, **19**, 175 (1929).

[9] F. Hernegger and B. Karlik, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt.* **IIa, 144**, 217 (1934).

it 83 per cent, and 1 per cent reduces it 45 per cent. In the presence of calcium the hue of the fluorescence is green; as little as 1 per cent of calcium suffices to produce a change in hue visible to the eye and gross errors can thus be avoided.[10]

Some observations made by Northup[11] in an investigation of the qualitative test for uranium by the above fluorescence reaction may be recorded here as having a bearing on its quantitative application. With an argon lamp as the source of ultraviolet radiation, the sensitivity is approximately 1 p.p.m. of uranium in fused sodium fluoride. When the fluorescence is very faint the test is made more certain by the use of Corning filter 9860 (3 mm. thickness) to eliminate visible light. An argon bulb is preferred to other sources of ultraviolet because it supplies radiation down to 310 mμ only and does not excite the fluorescence of certain of the rare earths.[12] The only other element found to fluoresce under the conditions is columbium, which however gives a much less sensitive reaction. Relatively high concentrations of silica, titanium dioxide, vanadium pentoxide, germanium oxide, sodium phosphate, and sodium arsenate were found to decrease the fluorescence intensity if the sodium fluoride bead was heated for only a short time, but the inhibiting effect of these was reduced or eliminated by longer heating (3 to 5 minutes in the case of silica). Columbium and tantalum pentoxides, and especially the rare earths, inhibit the fluorescence of uranium; magnesium, and the alkaline earths to a lesser extent, show a similar behavior. Aluminum also inhibits the fluorescence. Longer heating of the bead does no good with these. Manganese and other elements which color the bead reduce the fluorescence intensity, but sometimes the effect can be diminished by continuing the ignition under either oxidizing or reducing conditions depending upon the foreign substance. Tungstate, molybdate, sulfate, and the halides and nitrates of the alkali metals are said to be without effect. (It will be noted that some of these observations are not in accord with those of Lahner, possibly because of a difference in conditions.) Northup separates uranium from columbium, the rare earth metals, and other foreign substances by ether extraction of its solid hydrated nitrate. This separation is imperfect quantitatively.

In the following paragraphs the application of the fluorescence method to the determination of uranium in various natural samples will be briefly described.[13]

[10] I. Lahner, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt.* **IIa, 148,** 149 (1939).

[11] M. A. Northup, *Ind. Eng. Chem., Anal. Ed.*, **17,** 664 (1945).

[12] E. L. Nichols and H. L. Howes, *J. Optical Soc. Am.*, **13,** 573 (1926).

[13] See T. R. P. Gibb and H. T. Evans, Jr., *Science*, **105,** 72 (1947), for a semiquantitative field method for the determination of uranium by the fluorophotometric method.

1. *Sea Water*[9]

The sample (1–20 liters) is weakly acidified and concentrated by evaporation, the calcium sulfate separating being filtered off. The concentrated solution of salts is boiled to remove carbon dioxide, ferric chloride is added as collector, and ferric hydroxide is precipitated with carbonate-free ammonia. About 90 per cent of the uranium is carried down with the iron precipitate. The filtrate is acidified with hydrochloric acid, ferric chloride added, and ferric hydroxide precipitated as before. In most cases a third precipitation is unnecessary. The combined iron precipitates are dissolved in hydrochloric acid and the iron precipitated with ammonia to eliminate salts of the alkali metals. Iron is then separated from uranium by triple precipitation with ammonium carbonate. The filtrates are evaporated to dryness, and ammonium salts expelled by ignition in platinum. The residue, consisting mostly of silica, is treated with hydrofluoric and sulfuric acids and the latter volatilized. The residue is dissolved in a little hydrochloric acid and the solution evaporated to dryness. A weighed amount (*e.g.*, 1 g.) of sodium fluoride together with water and a drop or two of hydrofluoric acid are added and the mixture evaporated to dryness. The powder is mixed by grinding in an agate mortar and a bead of about 25 mg. obtained by heating the sodium fluoride in a platinum wire loop. Excessive heating should be avoided in the formation of the bead. It suffices to heat just to the point where the globule appears clear.

The procedure was tested by adding a known amount of uranium to a sample in which uranium had been determined. The added amount was recovered within the limits of error.

The uranium content of sea water is 1 to 2 γ per liter.

2. *Carbonate Rocks*[10,14]

The sample (2–5 g.) is dissolved in dilute hydrochloric acid. Any residue remaining is treated with hydrofluoric and sulfuric acids, the latter evaporated, the residue dissolved in hydrochloric acid, and this added to the main solution. Uranium is then coprecipitated with ferric hydroxide and the iron separated with ammonium carbonate as in the case of sea water.

3. *Silicates, Silicate Rocks, and Glass*[15]

The sample (1 g.) is fused with sodium carbonate and silica separated by treating the melt with hydrochloric acid and evaporating to dryness on

[14] Amounts of uranium varying from 10^{-6} to 10^{-4} per cent were found in limestones and dolomites of the Austrian Alps.

[15] J. Hoffmann, *Sprechsaal*, **73**, 153 (1940); *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse, Abt.* **IIa**, **148**, 189 (1939).

the water bath. The silica residue is volatilized with hydrofluoric acid and any remaining material is decomposed by fusion with a 10:3 mixture of sodium carbonate and borax; the solution of this melt is combined with the filtrate from the silica. The metals of the hydrogen sulfide group are separated in the usual manner; a pressure bottle is used in the hydrogen sulfide precipitation if molybdenum is present. Metals such as chromium and nickel which interfere in the fluorescence determination are separated by repeated precipitation with ammonium sulfide. Uranium is then precipitated with other metals by the addition of pure carbonate-free ammonium hydroxide; in the second precipitation a little ferric chloride is added to insure complete precipitation of uranium. Next uranium is separated from the other hydroxides by treating the hydrochloric acid solution with ammoniacal ammonium carbonate. This precipitation is repeated, and the solution heated a long time in the second precipitation to make certain the precipitation of any calcium carbonate. The uranium-containing solution is evaporated in a platinum dish in the presence of hydrofluoric acid. One-half to one gram of sodium fluoride is added together with water, the solution evaporated, and the residue ignited. The latter is transferred to an agate mortar and ground well to assure homogeneous distribution of uranium in the sodium fluoride. A bead of sodium fluoride is then obtained on a platinum wire and comparison made against standard beads. The uranium content of igneous rocks may be expected to fall in the range 10^{-3} to 10^{-6} per cent. A series of beads containing from 5×10^{-3} to 10^{-6} mg. U per 25 mg. bead may be used in the comparison.

4. Organic Materials

The following is a résumé of the method used by Hoffmann[16] in determining uranium in animal tissues. The sample is ashed, the ash dissolved in nitric acid, and phosphate removed by precipitation with tin. The excess tin is precipitated with hydrogen sulfide and the filtrate treated with hydroxylamine hydrochloride and an excess of ammonia. The filtrate is evaporated and the residue treated with fuming nitric acid. Uranium is then precipitated with pure ammonia after the addition of a little ferric chloride. The precipitate is dissolved in acid and iron precipitated with an ammoniacal solution of ammonium carbonate. The precipitation is repeated, the filtrate evaporated to dryness and the residue ignited. Sodium fluoride solution is then added, evaporated, and a bead of fused sodium fluoride obtained as described above.[17]

[16] J. Hoffmann, *Wien. tierärztl. Monatsschr.*, **28**, 561 (1941); *Bodenkunde u. Pflanzenernähr.*, **26**, 318 (1942).

[17] The minute amounts of uranium that can be determined in this way are indicated by the uranium contents found in cattle (Hoffmann): blood, 1.6×10^{-13} g./ml.; muscle, 4×10^{-11} g./g.; bones 1.3×10^{-8} g./g.

A procedure for the determination of uranium in bio material by the fluorescence method following isolation by adsorption on serum albumin has been described.[18] As little as 0.005 γ of uranium per gram of tissue can be determined.

B. The Thiocyanate Method[19]

Thiocyanate produces a yellow coloration with uranium (VI) in acidic solution. The color intensity depends greatly upon the thiocyanate concentration and to a lesser extent upon the acid concentration. A *p*H of 1.5 is satisfactory. Interference from iron is prevented by reduction with stannous chloride, which does not reduce uranium (VI); a few milligrams of iron in 25 ml. can be made harmless in this way. Copper in amounts up to 10 mg. in 25 ml. has no effect. Larger amounts produce a precipitate, but if this is filtered off, as much as 50 mg. of copper does no harm. As much as 0.25 g. of thorium has no effect; 1.25 g. weakens the uranium color slightly. Molybdenum interferes badly by giving a much stronger color under the conditions, and even traces must be absent.

§ Procedure

To 10 ml. of solution (0.05 to 0.75 mg. of uranium), whose *p*H has been adjusted to 1.0 with potassium hydroxide solution, add 2 ml. of stannous chloride solution (50 g. of the dihydrate in 500 ml. of 1:9 hydrochloric acid) and 7 ml. of ammonium thiocyanate solution (500 g. in 1 liter). Dilute the mixture to 25 ml. and centrifuge if turbid. Obtain the transmittancy at 365 mμ, using a blank solution in the reference cell.

The blank solution and the known uranium solutions for the establishment of the standard curve should contain roughly the same amount of acid as the sample originally and should be brought to *p*H 1.0 by addition of potassium hydroxide. The amount of thorium in the blank and standards should be within 0.25 g. of that in the sample.

C. The Hydrogen Peroxide Method

Hydrogen peroxide gives a yellow color with uranium (VI) in sodium or ammonium carbonate solution. The reaction is not very sensitive but may be of value on occasion, since it may be applied to the filtrate of a sodium carbonate precipitation or fusion. It has been suggested as the basis of a method for the determination of uranium in silicate rocks[20]; the lower limit

[18] W. F. Neuman, R. W. Fleming, A. B. Carlson, and N. Glover, *J. Biol. Chem.*, **173**, 41 (1948).

[19] J. E. Currah and F. E. Beamish, *Anal. Chem.*, **19**, 609 (1947).

[20] O. Hackl, *Z. anal. Chem.*, **119**, 321 (1940). *Cf.* E. A. Arnold and A. R. Pray, *Ind. Eng. Chem., Anal. Ed.*, **15**, 294 (1943).

of such a method would lie in the neighborhood of 0.01 per cent U. The effect of chromium (VI) can be compensated by using an aliquot of the sample in the comparison cell of a photoelectric photometer. Molybdenum (VI) and vanadium (V) also give yellowish colors with hydrogen peroxide but these are much less intense than that given by uranium. Cerium (III, IV) gives a strong yellow color with hydrogen peroxide in carbonate solution (p. 255). Fluoride and phosphate have no effect in small amounts, but larger quantities (in the neighborhood of 0.1 g. of the ammonium salt in 50 ml.) diminish the color intensity. Silicate has practically no effect.

§ Procedure

Add 5 ml. of 10 per cent sodium carbonate solution and 2 ml. of 3 per cent hydrogen peroxide (prepared by dilution of 30 per cent solution) to an

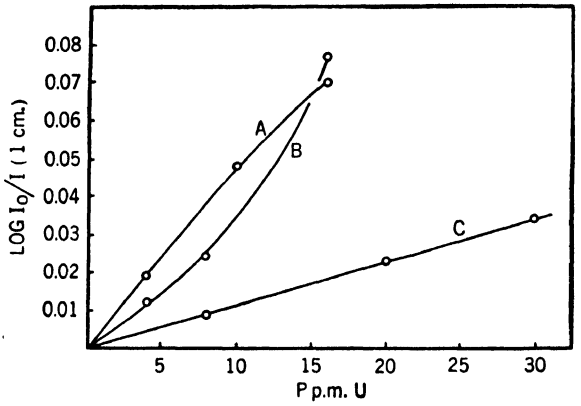


Fig. 78. Determination of uranium. A. Diethyldithiocarbamate method. B. Ferrocyanide method (neutral solution). C. Hydrogen peroxide method. Blue filter (Wratten 47) used in each case.

approximately neutral uranium solution containing a suitable amount of uranium (*cf.* Fig. 78) and dilute to 25 ml. with water. Use a blue filter (450 mμ) in determining the transmittancy of the solution. The standard uranium solution can be prepared from uranyl nitrate ($UO_2(NO_3)_2.6H_2O$/U = 2.11).

D. The Ferrocyanide Method

Ferrocyanide ion yields slightly soluble brown uranyl ferrocyanide in neutral or slightly acid medium which may be used for the colorimetric determination of uranium. In the writer's limited experience with the method, reproducible results are not easily obtained with low concentra-

tions of uranium in dilute mineral acid medium.[21] The color develops slowly, and frequently turbid solutions result. In neutral solution the color is more reproducible although less strong and the liquid does not readily become turbid. Beer's law is not followed (Fig. 78, curve B obtained with a green filter). The addition of ammonium acetate to yield an approximately neutral solution is not permissible because the color then is greatly weakened. A final potassium ferrocyanide concentration of 2 per cent is satisfactory. The solution may be read 10 or 15 minutes after the addition of ferrocyanide. Traces of iron and copper interfere seriously in this method.

§ Procedure

To 10–15 ml. of sample solution (0.1 to 0.5 mg. U) as nearly neutral as possible (not more than 0.02 *N* in mineral acid) add 5 ml. of potassium ferrocyanide (10 per cent solution containing 1 per cent of sodium sulfite) dilute to 25 ml., and determine the extinction after 15 minutes, using a blue filter. The standards must have the same acidity and salt concentration as the sample solution.

E. The Diethyldithiocarbamate Method

The addition of sodium diethyldithiocarbamate to a neutral uranyl solution produces a stable yellow color which is suitable for the determination of uranium if iron and copper are absent. It is very important that the sample solution be neutral before addition of the reagent. A slightly acid reaction (*p*H 6) causes the yellow color to fade quite rapidly. The initial color intensity is greater in slightly acid than in neutral solution. The addition of a little sodium carbonate discharges the color.

§ Procedure

Add 5 ml. of 20 per cent ammonium acetate solution and then 1 ml. of 1 per cent sodium diethyldithiocarbamate to the sample solution which should contain less than the equivalent of 0.1 ml. of 6 *N* sulfuric or hydrochloric acid. Dilute to 25 ml. with water and determine the extinction after 5 minutes (use a blue filter).

F. Other Methods

Sodium salicylate produces a red-brown color in neutral uranyl solutions.[22] The reaction is not particularly sensitive and minute amounts

[21] Five ml. of 10 per cent potassium ferrocyanide were added to about 15 ml. of uranium solution containing 1 ml. of 1 *N* sulfuric acid and the solution diluted to 25 ml. A protective colloid was not added.

[22] Müller, *Chem. Ztg.*, **43**, 739 (1919).

of iron interfere. Various phenolic acids such as tannic and gallic yield brown colorations with uranium in solutions containing sodium acetate (the latter should be added after the acid).[23] Again the color intensity is not strong and iron interferes badly. Thioglycolic acid gives a coloration with uranium (p. 379).[24]

[23] P. N. Das-Gupta, *J. Indian Chem. Soc.*, **6**, 763 (1929).

[24] A procedure has recently been described by W. H Davenport, Jr., and P. F. Thomason, *Anal. Chem.*, **21**, 1093 (1949).

CHAPTER XLVII

VANADIUM

I. Separations

A useful method for the separation of vanadium from iron, titanium, etc. involves fusion of the sample with sodium carbonate (together with a little potassium nitrate if necessary) or sodium peroxide and leaching of the melt with water. Molybdate, tungstate, phosphate, arsenate, chromate, and a trace of iron accompany vanadate into the filtrate.

Cupferron in dilute (1:10) sulfuric acid medium precipitates quinquevalent vanadium as well as iron, titanium, zirconium, and some other metals. Aluminum, chromium, uranium (VI), arsenic, and phosphorus are not precipitated.[1] If chromium is present in the sexivalent condition it should be reduced by the addition of hydrogen peroxide followed by boiling to destroy the excess of the latter. For the isolation of vanadium from highly dilute solutions, iron may be added to serve as a collector if it is not already present.[2] From the standpoint of trace analysis it is worth noting that vanadium cupferrate, like most other cupferrates, can be extracted with ether and chloroform.[3]

In a slightly basic solution, vanadate, chromate, molybdate, tungstate, arsenate, and phosphate can be precipitated with mercurous nitrate.[4] This separation has been used in the determination of small amounts of vanadium in silicate rocks.

Vanadium in the quinquevalent state is coprecipitated with ammonium phosphomolybdate.[5]

[1] Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 110. According to M. G. Raeder and T. Aakre, *Kgl. Norske Videnskab. Selskab., Forh.*, **15**, 75 (1942), vanadium (V) can be precipitated quantitatively from solutions containing up to 2 g. of sulfuric acid in 100 ml. Separation from aluminum in this way is said to be impossible. Vanadium (IV) is reported to require a lower acidity than this for complete precipitation.

[2] L. W. Strock and S. Drexler, *J. Optical Soc. Am.*, **31**, 167 (1941), found that the precipitation of vanadium (1:2,000,000) by cupferron was complete in the presence of iron at acidities ranging from *p*H 7 to 15 per cent HCl. A high neutral salt concentration (20 per cent K, Na, Ca, Mg chlorides) did not interfere.

[3] D. Bertrand, *Bull. soc. chim.*, **9**, 121 (1942), extracts the cupferrate with chloroform from a solution having a *p*H of 1.8.

[4] W. F. Hillebrand, *J. Am. Chem. Soc.*, **20**, 454 (1898).

[5] J. R. Cain and J. C. Hostetter, *J. Ind. Eng. Chem.*, **4**, 250 (1912); *J. Am. Chem. Soc.*, **43**, 2552 (1921).

Electrolysis with a mercury cathode in dilute sulfuric acid solution serves to separate vanadium from iron, chromium, molybdenum, copper, nickel, etc. Uranium and phosphorus remain in the aqueous solution with vanadium.

Small amounts of vanadium (IV and V) are coprecipitated with ferric iron and aluminum in an ammonium hydroxide precipitation.[6] Iron is a better collector than aluminum. Because of the similarity in the ionic radii of phosphorus (V) and vanadium (V), it may be expected that ferric phosphate will be a good collector for vanadate.

A good method for the isolation of minute amounts of quinquevalent vanadium in certain cases is based on the extraction of its 8-hydroxyquinoline compound,[7] $V_2O_3(C_9H_6ON)_4$, with chloroform from a weakly acid solution (*p*H 4–5); chromium (VI) is not extracted.[8] After evaporation of the chloroform the residue can be fused with sodium carbonate and the vanadium transformed into vanadate. Ferric iron and molybdenum (VI) are also extracted. This method of separation is therefore not applicable to ferrous materials. Aluminum, silicate, phosphate, fluoride, etc. do not hinder the extraction of vanadium. Tungsten gives a precipitate with oxine (insoluble in chloroform), except when present in very small amounts, and should therefore be absent. For the behavior of other metals with oxine see p. 114. Some results showing the satisfactory separation of vanadium in the presence of 100–200 times as much chromium in the analysis of silicates are given on p. 613.

Chromium can be separated from vanadium by ethyl acetate extraction of perchromic acid from very slightly acidic solution as follows.[9] Add 2 drops of 1:1 sulfuric acid to 40 ml. of neutral sample solution in which chromium is present in the sexivalent state, followed by 80 to 150 ml. of ethyl acetate depending upon the amount of chromium present. Then add 0.5 ml. of 3 per cent hydrogen peroxide and shake for a few seconds. Separate the layers and extract the aqueous phase with 15–20 ml. of ethyl acetate (or more if the Cr_2O_3 content exceeds 3 mg.). Wash the combined ethyl acetate extracts with 10–20 ml. of water. This method for the removal of chromium is suitable for small quantities only, since the solubility of perchromic acid in ethyl acetate corresponds to only 1 mg. of Cr_2O_3 in 15 ml. Molybdenum remains with vanadium in this separation.

[6] T. Ernst and H. Hörman, *Nach. Ges. Wissen. Göttingen*, N. F., **1**, 205 (1936), isolate vanadium in sea water by ammonia precipitation after adding about 100 mg. of ferrous ammonium sulfate to 1 liter of sample.

[7] R. Montequi and M. Gallego, *Anales soc. españ. fis. quim.*, **32**, 134 (1934).

[8] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 336 (1936).

[9] M. D. Foster, *U. S. Geol. Survey Bull.*, **950**, 16 (1946).

II. Methods of Determination

A. The Phosphotungstate Method[10]

A sensitive and selective method for the determination of vanadium is based on the formation of yellow soluble phosphotungstovanadic acid by the addition of phosphoric acid and sodium tungstate to an acid vanadate solution. The strongest color is obtained when the molecular ratio of phosphoric acid to sodium tungstate lies in the range 3:1 to 20:1, and the tungstate concentration in the sample solution is 0.01 to 0.1 *M*. A final concentration of phosphoric acid equal to 0.5 *M* and of sodium tungstate equal to 0.025 *M* is recommended (Wright and Mellon[10,11]).

The acidity of the solution may vary over a fairly wide range. A solution 2.4 *N* in sulfuric, nitric, or hydrochloric acid, and containing 50 γ of vanadium per ml. gives virtually the same color intensity as a solution containing no acid, provided it is boiled. In the cold, a brownish color is obtained which after several hours goes over into the normal yellow color of phosphotungstovanadic acid. The higher the acid concentration the stronger is the brownish color. Boiling hastens the attainment of equilibrium. More dilute vanadium solutions—less than 10 γ of V per ml.—need not be boiled if the acidity is in the neighborhood of 0.5 *N* and iron is absent; the maximum color is not developed immediately in the cold, but the difference is not great enough to be of importance in visual comparison.

The following substances, in the amount indicated per 100 ml. of sample solution, have no appreciable effect on the vanadium color: NaCl (3 g.); $NaNO_3$ (5 g.); Mg, Ca, Sr, Ba, Zn, Cd, Hg^{II}, Al, Pb, As^{V}, acetate, Br^- (all 0.5 g.); Ag (0.1 g); Th (0.01 g.); SiO_2 (0.05 g. as Na_2SiO_3); tartrate, citrate, oxalate (0.1 g. of anion); CN^- (0.02 g.); H_3BO_3, F.

In addition to ions which are themselves colored, such as chromate, copper, cobalt, etc., the following interfere:

1. Potassium and especially ammonium ions give slightly soluble phosphotungstates.
2. Titanium, zirconium, bismuth, antimony, and tin give slightly soluble phosphates or basic salts except in very low concentrations.
3. Molybdenum (VI) gives a yellow color with the reagent, which however only becomes serious at relatively high concentration (>500 γ per ml. when vanadium concentration is 2.5 γ per ml.) *Cf.* Table 96.
4. Iodide, thiocyanate, etc. reduce phosphotungstic acid.

[10] A. P. Vinogradov, *Compt. rend. acad. sci. U. R. S. S.*, **1931A**, 249; E. B. Sandell[8]; E. R. Wright and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 251 (1937). *Cf.* H. H. Willard and P. Young, *Ind. Eng. Chem.*, **20**, 764 (1928).

[11] The statements in the discussion following above are based on the findings of these authors in a comprehensive study of the phosphotungstate method.

Ferric ion in small amounts is not harmful if the solution is boiled. Ten milligrams of iron (III) in 100 ml. of cold solution imparts a brownish hue, but this disappears if the solution is boiled. However in a concentration greater than 100 mg. per 100 ml. iron begins to interfere even if more phosphoric acid is added.

Phosphotungstovanadic acid is quite stable in solution. No change in the color intensity takes place in 24 hours, but after 2 weeks a diminution of about ten per cent occurs.

Some figures obtained by the phosphotungstic acid method in the determination of vanadium by colorimetric titration are given in Table 96.

Special Solutions

Sodium tungstate, 0.5 *M*. Dissolve 16.5 g. of $Na_2WO_4 \cdot 2H_2O$ in water and dilute to 100 ml.

Standard vanadium solution. Dissolve 1.785 g. of pure V_2O_5, previously ignited at 500° C., in a slight excess of sodium hydroxide, then add a slight excess of sulfuric acid and dilute to 1 liter. This solution will contain 1.00 mg. of vanadium per ml. If there is any doubt about the purity of the vanadium pentoxide, acidify a 50 ml. portion of the solution with sulfuric acid, reduce with sulfur dioxide in the usual manner, expel the excess of sulfur dioxide by boiling and titrate with 0.05 or 0.1 *N* potassium permanganate.

Dilute the above vanadium solution further, conveniently to give a solution containing 0.01 mg. V per ml.

TABLE 96

DETERMINATION OF VANADIUM BY THE PHOSPHOTUNGSTIC ACID METHOD

(Colorimetric titration in 1.8 × 15 cm. flat-bottomed tubes; 10-15 ml. of solution)

Addition	Vanadium taken γ	Vanadium found γ	Error γ
	3	3	0
	5	4	−1
	12	12	0
	20	21	+1
	50	51	+1
0.5 mg. Mo (VI)	20	22	+2
1.0 mg. Mo (VI)	20	23	+3
10.0 mg. Mo (VI)	20	26	+6

§ Procedure

Make the solution approximately 0.5 *N* in sulfuric, nitric, or hydrochloric acid, and add 1.0 ml. of 1 : 2 phosphoric acid and 0.5 ml. of sodium tungstate solution for each 10 ml. of sample solution. Heat to boiling (this is not necessary if only small amounts of vanadium are present and iron is

absent—see p. 613), cool, dilute to volume, and determine the extinction of the solution at 400 mμ (Fig. 79). If small amounts of colored ions such as nickel, cobalt, and dichromate are present use an aliquot of the original sample solution in the reference cell (p. 74). At 400 mμ, an extinction of

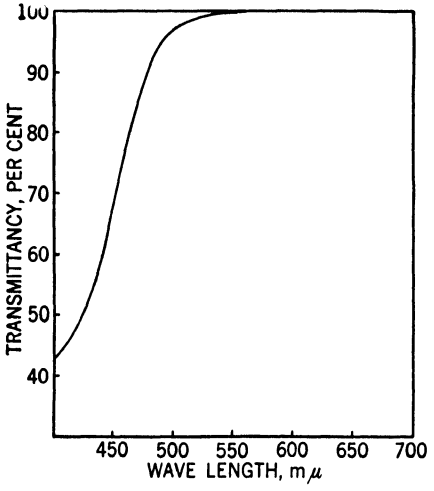


Fig. 79. Transmission curve of phosphotungstovanadic acid (10 p.p.m. V, 1 cm. cell). (According to Wright and Mellon.)

0.001 corresponds to approximately 0.03 γ V per cm.^{2} In visual colorimetry the solution should contain more than 5 γ V per cm.^{2} cross-section.

B. The Peroxide Method

The red-brown color produced when an acid solution of vanadium (V) is treated with hydrogen peroxide is thought to be due to the formation of a compound of the type O_2VX_3 or possibly $(O_2VX_5)^=$. Vanadium and hydrogen peroxide react in equimolecular amounts as shown by Schaeppi and Treadwell,[12] who formulate the reaction as follows in sulfuric acid medium:

$$OV(SO_4)_{3/2} + H_2O_2 \rightleftharpoons O_2V(SO_4)_{3/2} + H_2O.$$

These authors report the value 1.2×10^{-5} for the equilibrium constant

$$\frac{[OV(SO_4)_{3/2}][H_2O_2]}{[O_2V(SO_4)_{3/2}]}.$$

A large excess of hydrogen peroxide changes the color of the solution from

[12] Y. Schaeppi and W. D. Treadwell, *Helv. Chim. Acta*, 31, 577 (1948).

red-brown to yellow and reduces the color intensity, supposedly by a shift in the equilibrium:[13]

$$\underset{\text{red-brown}}{(VO_2)_2(SO_4)_3} + 6\ H_2O \underset{H_2SO_4}{\overset{H_2O_2}{\rightleftharpoons}} \underset{\text{yellow}}{2\ VO_2(OH)_3} + 3\ H_2SO_4.$$

Other metals giving colors with hydrogen peroxide are titanium and molybdenum (VI). The titanium color can be bleached by fluoride, which in moderate amounts does not affect the vanadium color, but the presence of fluoride is of course often objectionable in glass vessels. When comparable amounts of titanium and molybdenum[14] are present, vanadium can be determined by measuring the extinction of the peroxidized solution at

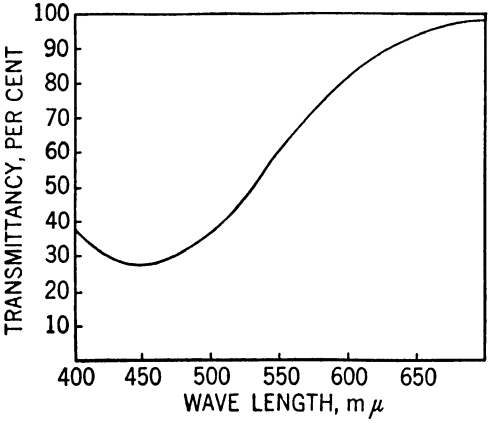


Fig. 80. Transmission curve of peroxidized vanadium in sulfuric acid solution (20 p.p.m. V, 5 cm. cell). (According to Wright and Mellon.)

three suitable wave lengths (p. 579); the accuracy of such a procedure is not likely to be very satisfactory. The interference of iron (III) may be prevented by the addition of phosphoric acid or fluoride. Chromium (VI) gives a blue color which soon fades, leaving an almost colorless solution when small amounts are present. Iodide and bromide must be absent.

Wright and Mellon[15] in their study of the peroxide method for vanadium found that with a hydrogen peroxide concentration of 0.03 per cent, the sulfuric acid concentration could vary between 0.6 and 6 *N* without any appreciable effect on the color; below 0.6 *N* acidity the full color is not

[13] J. Meyer and A. Pawletta, *Z. anal. Chem.*, **69**, 15 (1926).

[14] It has been stated that oxalic acid, especially together with boric acid, bleaches the molybdenum peroxy color. On the contrary, Foster[9] found that oxalic acid intensifies the color due to molybdenum; this is in accord with the writer's observations.

[15] E. R. Wright and Mellon, *Ind. Eng. Chem., Anal. Ed.*, **9**, 375 (1937).

developed and above 6 N it fades. With higher peroxide concentrations the acidity must be increased to permit development of maximum color intensity. In the range 0.006 to 0.09 per cent hydrogen peroxide concentration the color intensity remains constant (solutions 1.5 N in sulfuric acid).[16] Neutral salts such as sodium sulfate or sodium chloride have little effect on the color. The color is fairly stable; under the condition recommended below there should be no appreciable change in color intensity in 2 or 3 days. Beer's law is obeyed.

§ Procedure

The solution should be free from the interfering elements mentioned above. The effect of metals such as nickel, cobalt, etc. and very small amounts of chromium can sometimes be compensated by adding like amounts to the comparison solution; when a photometer is used, an aliquot of the sample solution can be put in the reference cell. Vanadium must be present in the quinquevalent form.

Make the solution 1 to 2 N in sulfuric acid and add 0.25 ml. of 3 per cent hydrogen peroxide for each 10 ml. of sample, and compare at 450 mμ against a standard vanadium solution having the same acidity and containing the same amount of peroxide. If titanium is present add hydrofluoric acid (say 1 ml. for 10–20 ml. of solution). This will decolorize ferric iron also. If titanium is absent, phosphoric acid may be used in place of hydrofluoric acid for the decolorization of iron. If hydrofluoric acid is added, the comparison should be made in inexpensive tubes by the standard series method.

C. Other Methods

8-Hydroxyquinoline reacts with quinquevalent vanadium as already mentioned to give a strongly colored violet-black compound which can be extracted by various organic solvents. It has been proposed to utilize this reaction in the determination of vanadium in water as follows.[17] The sample (50 ml.) is made acid to Congo red with sulfuric acid and 5 drops of a 2.5 per cent solution of 8-hydroxyquinoline in 20 per cent citric acid are added. The solution is shaken with 10 ml. of isoamyl alcohol to extract the quinolate. Copper, but not iron, interferes. Beer's law is followed.

[16] Foster[9] found that in the range 10 to 15 per cent by volume of sulfuric acid or 10 to 20 per cent of nitric acid, the color is independent of the concentration of hydrogen peroxide when this varied from about 0.01 per cent to 0.3 per cent in the mixture. In 25 per cent hydrochloric acid solution the color intensity is independent of the hydrogen peroxide concentration. The intensity of the color is largely independent of the kind of acid present.

[17] J. M. Bach and R. A. Trelles, *Bol. obras sanit. nacion Buenos Aires*, **5**, 127 (1941); *Chem. Abstracts*, **36**, 859 (1942); *ibid.*, **35**, 545 (1941).

8-Hydroxyquinoline-5-sulfonic acid gives a brown color with metavanadate and has been used for determining concentrations of vanadium of the order 1 p.p.m.[18] Iron reacts similarly.

A mixture of molybdate and phosphoric acid gives a yellow color with vanadate.[19] The reaction is analogous to the phosphotungstate reaction described above. Molybdate alone gives a yellow color with vanadate in neutral solution.[20]

In concentrated sulfuric acid vanadate reacts with strychnine to yield a violet color passing into orange.[21] Iron must be absent, but titanium, molybdenum, and tungsten do not interfere.

Diphenylamine, diphenylamine sulfonic acid, etc. are oxidized by vanadate to blue compounds in acid solution.[22] Many oxidizing agents give the same color. Ferric iron does not react in the presence of phosphoric acid.

Benzidine gives a strong yellow color with vanadium (V) in 10 per cent phosphoric acid solution. The reaction has been applied in the determination of vanadium in rocks, minerals, and ores. The interference of chromium and manganese in higher valence forms is eliminated by addition of ferrous salt and nitrite.[23]

Vanadium has been determined by the color of its cupferrate in chloroform,[3] and as thiovanadate (red) in iron ores, slags, etc. by addition of sodium sulfide to an alkaline vanadate solution.[24]

III. Applications

A. Silicate Rocks

The phosphotungstate method may be applied with advantage in the determination of the small amounts of vanadium occurring in silicate rocks. Vanadium is isolated from the solution of the sodium carbonate melt by the 8-hydroxyquinoline-chloroform extraction procedure mentioned above. As much as 1 per cent Cr_2O_3 and several per cent fluorine do not interfere. Molybdenum is normally not present in sufficiently large amounts to affect the results (*cf.* Table 96). The following results show the reliability of the method (first figure gives the percentage of V_2O_3 added to a synthetic basic rock, the second the percentage found): 0.0021, 0.0027; 0.004, 0.005;

[18] J. Molland, *Compt. rend.*, **210**, 144 (1940); *Tids. Kjemi Bergvesen*, **19**, 119 (1939).
[19] G. Bogatzki, *Arch. Eisenhüttenw.*, **12**, 539 (1939).
[20] A. G. Woodman and L. L. Cayvan, *J. Am. Chem. Soc.*, **23**, 105 (1901).
[21] A. W. Gregory, *Chem. News*, **100**, 221 (1909).
[22] V. L. Meaurio, *Ann. chim. anal.*, **23**, 47 (1918).
[23] I. P. Alimarin, *J. Applied Chem. (U. S. S. R.)*, **17**, 83 (1944); *Chem. Abst.*, **39**, 1115.
[24] E. Stengel, *Tech. Mitt. Krupp Forschungsber.*, **2**, 93 (1939); *Chem. Abstracts*, **33**, 9189 (1939).

0.015, 0.014; 0.042, 0.040; 0.006, 0.005 (1% Cr_2O_3); 0.0120, 0.0115 (1% Cr_2O_3).

§ Procedure

Fuse 1 g. of 100-mesh rock powder with 5 or 6 g. of anhydrous sodium carbonate in platinum in the usual way. After complete decomposition allow the crucible to cool to room temperature, add a few milliliters of water and heat to boiling to loosen the cake. Transfer the latter to a small Pyrex beaker, rinse the crucible, and add a few drops of alcohol and 30–40 ml. of water to the beaker. Heat on the steam bath, and hasten disintegration of the cake by crushing and grinding with a flattened glass rod. When the residue has been entirely disintegrated and manganate reduced, filter the solution through a fine grained paper and wash with hot 1 per cent sodium carbonate solution. Dilute the filtrate and washings to 100 ml. in a volumetric flask.

Pipet 10 or 25–50 ml. (the former volume for basic rocks, the latter for siliceous rocks) of the mixed solution into a small Erlenmeyer flask and add a drop or two of methyl orange indicator solution. Then add 4 *N* sulfuric acid from a buret until the solution assumes the intermediate color of the indicator. Swirl the solution to liberate carbon dioxide and transfer to a small separatory funnel. Add 2–3 drops of 8-hydroxyquinoline solution (2.5 per cent in 1:8 acetic acid) for 10–25 ml. of sample and 2–3 ml. of reagent quality chloroform. Shake for 1 minute to extract the blackish vanadium-oxine compound, allow the chloroform to settle, and draw it off into a platinum crucible. Rinse out the stem of the funnel with a milliliter of chloroform. Then repeat the extraction with 8-hydroxyquinoline and chloroform as before until the last portion of chloroform shows only a faint yellow color due to the reagent itself.

Add 0.1 g. of anhydrous sodium carbonate to the crucible containing the combined extracts, and evaporate off the chloroform at a low temperature. Heat the crucible with a flame to destroy organic matter and finally apply the full heat of the burner for 1 or 2 minutes to fuse the sodium carbonate. Vanadium is thus converted into sodium vanadate. Dissolve the melt in a few milliliters of water. The solution should be clear; if it is not, filter through a small porous porcelain or sintered glass crucible. If the vanadium is to be determined by colorimetric titration or the standard series method, transfer the solution to a flat-bottomed tube having a cross-section of about 2 cm.^{2} and a volume of about 25 ml. (p. 52). The volume of the solution may be 5–10 ml. Add 1.0 ml. of 4 *N* sulfuric acid, 1.0 ml. of 1:2 phosphoric acid, and 0.5 ml. of 0.5 *M* sodium tungstate solution. Compare against standards similarly treated.

If a photometer is used, transfer the solution to a 10 or 25 ml. volumetric flask and treat as described in the general procedure, p. 608.

Notes. 1. Vanadium can be determined with fair accuracy directly without previous separation with 8-hydroxyquinoline if its amount is not too small and chromium is absent. The results tend to be low as shown by the following figures obtained on various rocks (the first figure is the percentage of V_2O_3 obtained by 8-hydroxyquinoline separation, the second the percentage obtained by direct colorimetric determination in the filtred sodium carbonate extract); 0.042, 0.036; 0.026, 0.023; 0.029, 0.031; 0.062, 0.055; 0.044, 0.039; 0.245, 0.245 (magnetite-ilmenite).

2. There appears to be no appreciable retention of vanadium in the leached residue. Thus in a basic rock containing 0.060 per cent V_2O_3, re-fusion of the washed residue from the first sodium carbonate fusion yielded an additional 0.001 per cent V_2O_3.

3. The addition of potassium nitrate in the fusion is usually not necessary.

B. Iron and Steel

In the following method, vanadium is first separated from the bulk of the iron by addition of sodium bicarbonate to the acid solution of the sample[25]; the relatively small precipitate of iron contains the vanadium as well as chromium, titanium, etc. The washed precipitate is fused with sodium peroxide, the melt is extracted with water and the solution boiled to precipitate titanium completely. The filtrate contains vanadate together with chromate. Vanadium can then be determined by the peroxide or phosphotungstate method, a separation from chromate first being made if necessary.

§ Procedure[26]

Transfer 5 g. of sample to a 250 ml. Erlenmeyer flask, add 60 ml. of 1:9 sulfuric acid and boil until reaction is complete. Dilute the solution with about 50 ml. of hot water and add an 8 per cent sodium bicarbonate solution from a buret until a permanent precipitate is produced, and then 2 ml. in excess. Boil for 1 minute, allow the precipitate to settle, filter through a fast filter, and without delay wash the flask and precipitate twice with hot water. Disregard any cloudiness in the filtrate. Ignite the residue in a nickel crucible, mix it with about 10 times its volume of sodium peroxide, and fuse. Cool and dissolve the melt in 50 ml. of cold water. Add 0.5 g. of sodium peroxide to the solution, heat to boiling and boil for 10 minutes; allow to stand on the steam bath for one-half hour. Filter through as-

[25] G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, *Chemical Analysis of Iron and Steel.* Wiley, New York, 1931, p. 74.

[26] The directions for the sodium bicarbonate precipitation are those of Lundell, Hoffman, and Bright, *loc. cit.*, p. 300. For other procedures for vanadium in iron ore and slags, see H. Pinsl, *Arch. Eisenhüttenw.*, 11, 293 (1937); *Giesserei*, 27, 441 (1940).

bestos and wash with a cold solution containing 2 per cent sodium hydroxide and 1 per cent sodium sulfate. Dilute the filtrate and washings to 100 ml.

If the chromium content of the solution is low, vanadium may be determined directly in a suitable aliquot by the peroxide or phosphotungstate method according to the directions given on p. 611 or p. 608. If chromium is present in appreciable amounts, isolate the vanadium with 8-hydroxyquinoline as described on p. 613.

Note. The above procedure is especially intended for samples with low vanadium contents. If the percentage of vanadium is greater than 0.1, other procedures may be used. For example, the steel may be dissolved in sulfuric acid, and nitric acid added to oxidize iron. Vanadium may then be oxidized by adding ammonium persulfate and boiling, and determined by the peroxide method by comparison against a similar standard solution. If titanium is present, both vanadium and it can be determined by obtaining the extinction at two suitable wave lengths (see p. 578). Molybdenum should not be present in appreciable amounts. Much chromium will make necessary a separation of it and vanadium. See also the procedure given by Wright and Mellon (*loc. cit.*) for the determination of vanadium in steel.

C. Bio Materials

The determination of minute amounts of vanadium in this class of materials is best made by ashing the sample and then treating the ash as described under "Silicate Rocks," p. 613.

Bertrand[27] has described a method for vanadium in plant material, in which it is isolated by chloroform extraction of the cupferrate and finally determined by its color in the same solvent. As little as 2 γ of vanadium in 100 g. of sample is reported to be determinable in this way.

[27] D. Bertrand, *Bull. soc. chim. biol.*, **23**, 391 (1941).

CHAPTER XLVIII

ZINC

I. Separations

A. Sulfide Precipitation

Isolation of zinc by precipitation as sulfide is sometimes of value in trace analysis; this method was commonly used before the introduction of dithizone. In ammoniacal solution the precipitation of zinc sulfide is easily effected, and if tartrate is present, separation can be made from aluminum, titanium, and similar metals; iron, manganese, nickel, cobalt, and other sulfide-forming metals accompany the zinc. Precipitation of zinc sulfide in very dilute acid solution, the procedure so useful in ordinary analysis, is incomplete for traces unless a collector is used. By using 0.5 mg. of copper as collector, quantities of zinc of the order 0.01 mg. can be completely precipitated from 10 ml. of an acetic acid-acetate solution neutral to methyl orange.[1] Mercuric sulfide may also be used as collector; it is easily eliminated by ignition. Small amounts of copper (some milligrams) can be precipitated in 0.2–0.3 *N* hydrochloric acid solution without serious loss of zinc from the solution, but with large amounts, an appreciable fraction of the zinc will be removed from the solution by co- or post-precipitation.[2]

B. Dithizone Extraction

The use of dithizone (p. 87) provides an easy way of isolating zinc prior to its determination in silicates, bio materials, water, etc. The simplest procedure involves the extraction of zinc from a weakly ammoniacal solution containing citrate or tartrate to prevent the precipitation of iron, aluminum, and other metals. Other metals reacting with dithizone should not be present in large amounts, for an impractically large volume of dithizone will then be required for extraction.[3] This condition is fulfilled in the

[1] R. E. Lutz, *J. Ind. Hygiene*, **7**, 273 (1925). For the separation of zinc from much iron by hydrogen sulfide precipitation in citrate medium at *p*H 2.5 see H. A. Bright, *Bur. Standards J. Research*, **12**, 383 (1934).

[2] O. R. Alexander and L. V. Taylor, *J. Assoc. Official Agr. Chem.*, **27**, 325 (1944), separate zinc from lead, cadmium, bismuth, antimony, tin, mercury, and silver by hydrogen sulfide precipitation of the latter metals from a solution of *p*H 2 (2 mg. copper ion in 50 ml. as collector). See further Taylor and Alexander, *ibid.*, **28**, 271 (1945).

[3] When relatively large amounts of such metals as copper, silver, and mercury are present, it is preferable to remove them by an initial dithizone extraction from *ca.* 0.1 *N* mineral acid solution (carbon tetrachloride solution of dithizone).

case of the samples mentioned. The alkalinity of the solution from which zinc is to be extracted is of importance because of the formation of zincate. The optimum *p*H for the extraction with dithizone in chloroform from a citrate-buffered solution is 8.3 as shown in Fig. 81.[4] The data represented were obtained by extracting 100 ml. of zinc solution (containing 30 ml. of 20 per cent ammonium citrate and some extraneous salts) with one 10 ml. portion of a chloroform solution of such strength that 150 per cent dithizone in excess of the amount required to combine with the zinc was present.

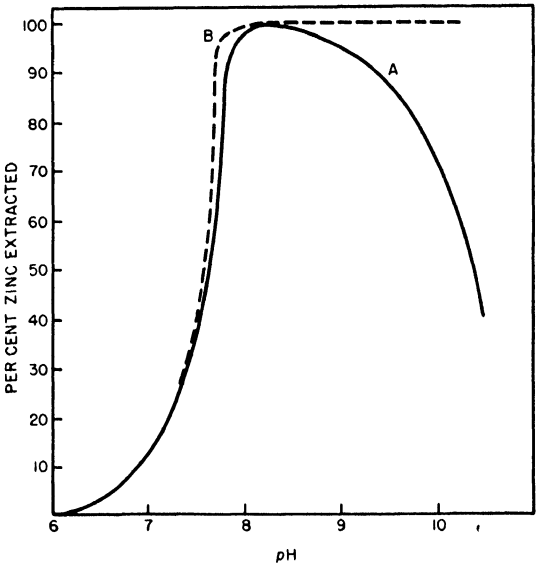


Fig. 81. Extraction of zinc by dithizone (A) and dinaphthylthiocarbazone (B) in chloroform solution as a function of the *p*H. (After Cholak, Hubbard, and Burkey.)

The extraction is 90 per cent complete at *p*H 7.8 and 9.3. These may be taken as the approximate *p*H values at which virtually complete extraction of zinc is obtainable if *two* portions of 0.01 per cent dithizone are used. With a carbon tetrachloride solution of dithizone these *p*H values are shifted downward slightly.

The simplest way of recovering the zinc from the carbon tetrachloride or chloroform solution consists in shaking the latter with dilute mineral acid (0.01–0.02 *N*) to decompose zinc dithizonate and transfer zinc to the aqueous phase. The value of the equilibrium constant of zinc dithizonate in chloroform is approximately 3 (p. 93). If a 0.0002 *M* zinc dithizonate

[4] J. Cholak, D. M. Hubbard, and R. E. Burkey, *Ind. Eng. Chem., Anal. Ed.*, **15**, 754 (1943).

solution (corresponding to 0.01 per cent or 0.0004 *M* dithizone) is shaken with 0.01 *N* hydrochloric acid, the ratio of concentration of zinc in the chloroform and aqueous phases at equilibrium will be:

$$\frac{[ZnDz_2']_{CHCl_3}}{[Zn^{++}]_{H_2O}} = K\frac{[Dz]^2_{CHCl_3}}{[H^+]^2} = \frac{3 \times 16 \times 10^{-8}}{10^{-4}} = 0.005.$$

Accordingly if the volume of acid is somewhere near that of the chloroform, most of the zinc will be found in the aqueous phase. The small remaining fraction of zinc in the chloroform can be virtually completely removed by shaking with a fresh portion of acid. This conclusion has not been verified experimentally in the case of a chloroform solution of zinc dithizonate but it has been shown that a carbon tetrachloride solution of zinc dithizonate can be decomposed quantitatively in this way. Cupric dithizonate in carbon tetrachloride is hardly affected by shaking with 0.01 *N* acid, which is in accord with the large value (*ca.* 10^{10}) for the equilibrium constant of this complex (see further p. 297). Lead, cadmium, and, to some extent, bismuth accompany zinc into the acid phase. Cobalt dithizonate is but slightly decomposed by dilute hydrochloric acid and practically all of it remains in the carbon tetrachloride. Nickel dithizonate is partially decomposed by weak mineral acids.

Di-β-naphthylthiocarbazone has some advantages over dithizone for the separation of zinc by extraction. Because of the insolubility of the naphthyl compound in basic solutions the extraction of zinc is complete at a *p*H as high as 10.5 (Fig. 81). Moreover it is possible to add sodium diethyldithiocarbamate to convert copper, nickel, cobalt, and bismuth into the corresponding carbamate complexes; zinc still reacts quantitatively with naphthylthiocarbazone in the presence of carbamate in basic medium (difference from dithizone). When the chloroform solution of the carbamate complexes and zinc naphthylthiocarbazonate is shaken with 0.2 *N* hydrochloric acid, zinc is brought into the aqueous phase, whereas copper, nickel, and cobalt remain in the chloroform. Bismuth carbamate is partially decomposed by the acid treatment and some of it is thus transferred to the aqueous phase. For details see p. 634.

C. Other Separations

Diethylammonium diethyldithiocarbamate has been used as an extraction reagent for zinc (p. 636).

Nickel and cobalt in small amounts can be separated from zinc by simultaneous chloroform extraction of the dimethylglyoxime and α-nitroso-β-naphthol complexes respectively from a citrate-buffered solution at *p*H *ca.* 8.[5] The excess of the nitrosonaphthol is removed by extracting with chloroform.

[5] O. R. Alexander and L. V. Taylor, *J. Assoc. Official Agr. Chem.*, **27**, 326 (1944).

The separation of much copper from zinc is perhaps most expeditiously accomplished by electrolysis. Large amounts of iron can be separated by ether extraction of ferric chloride from a hydrochloric acid solution.[6]

II. Methods of Determination

Dithizone and its analogs are the only reagents known at present which permit a satisfactory direct colorimetric determination of traces of zinc. Di-β-naphthylthiocarbazone has certain advantages over dithizone (pp. 112, 633) but very satisfactory results can also be obtained with the latter. The procedure involving the use of the naphtyl reagent has been worked out for the determination of zinc in bio material and it will be found described in the section on special applications (p. 634).

Zinc occurs in small amounts in many materials, including reagents, and care should be taken to avoid contamination of the sample. Rubber stoppers and "ties" of separatory funnels are sources of extraneous zinc. Pyrex glass contains about 10 p.p.m. of zinc.

A. The Dithizone Method

Zinc reacts readily with dithizone in weakly alkaline medium to form the keto complex which is soluble in carbon tetrachloride or chloroform, giving a solution of bright red color. In weakly acid solution the reaction is more or less complete, depending upon the concentration of dithizone in the organic solvent according to the relation given above.

Since many other metals react with dithizone under the same conditions as zinc, it is necessary to use a complex-forming agent to prevent the interference of these.[7] At a *p*H of 4 to 5.5, sodium thiosulfate largely prevents the reaction of copper, mercury, silver, gold, bismuth, lead, and cadmium while permitting that of zinc to proceed.[8] In the presence of much nickel

[6] H. A. Bright, *Bur. Standards J. Research*, 12, 383 (1934).

[7] The alternative would be to remove all other metals reacting with dithizone under the conditions of the zinc determination by the use of hydrogen sulfide and special reagents. Such a method is not entirely safe because too much reliance is placed on the completeness of such separations. It is preferable to make such separations as are required, but to employ a complex-forming reagent in the final determination to prevent the reaction of any small amounts of other metals that may be present at this stage.

[8] H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **107**, 241 (1937). G. Kortüm and Finckh, *Die Chemie*, **57**, 73 (1944), modify this procedure by extracting zinc at *p*H 6 from a medium containing oxalate, cyanide, and thiosulfate to prevent reaction of other metals. It is stated that zinc in alloys can be determined within ±1.5 per cent, but the kind and amount of foreign metals are not specified. These authors claim that the extraction of zinc is as complete in the presence of the complex-forming substances mentioned as it is in the presence of the buffer alone at *p*H 6, although the rate of extraction is much smaller when thiosulfate-cyanide is present.

and cobalt it is necessary to use potassium cyanide as a complex forming agent.

Sodium diethyldithiocarbamate has also been used as a general complex former in ammoniacal solution in the determination of zinc after removal of copper.[9] It has been extensively applied in procedures for zinc in bio materials and appears to be more popular than thiosulfate as a complexing agent in the United States. Further studies are needed to establish the merits of these two complexers. It is known that thiosulfate is more effective than carbamate in preventing the interference of cadmium. Both thiosulfate and carbamate form weak complexes with zinc and thus reduce the color intensity given by dithizone. Sodium bis-(2-hydroxyethyl) dithiocarbamate has been proposed as a superior substitute for sodium diethyldithiocarbamate.[10] It complexes cadmium more effectively.

Zinc, like other heavy metals, can be determined by the mixed-color or mono-color method, and depending on conditions one or the other may be preferable. If only traces of other metals reacting with dithizone are present so that relatively little thiosulfate or carbamate need be added, then the mixed color procedure may be applied to advantage. But if high concentrations of interfering metals are present this method cannot readily be applied directly because there may be slight reaction between the foreign metals and dithizone which can be prevented in the mono-color method.

1. The Mixed-Color Method

This method with thiosulfate as complexing agent is readily applied in the determination of zinc in rocks, bio samples, water, etc., and as already mentioned, is used in preference to the mono-color method whenever possible, *i.e.*, whenever relatively large amounts of dithizone-reacting metals are

TABLE 97

DETERMINATION OF ZINC BY THE MIXED COLOR METHOD IN THE PRESENCE OF SOME FOREIGN METALS (RED FILTER)

2.00 γ zinc taken in each determination

Foreign metal, γ.....	500 Pb	1000 Fe^{III}	5 Cu	250 Bi	250 Cd
Zn found, γ.....	2.1	2.18	2.2	3.0	3.1
Foreign metal, γ.....	300 Co, 300 Ni		500 Ni	(2.0 ml. $Na_2S_2O_3$)	
Zn found, γ.....	5.1		2.8	1.35	

[9] E. B. Holland and W. S. Ritchie, *J. Assoc. Official Agr. Chem.*, **22**, 333 (1939); H. Cowling and E. J. Miller, *Ind. Eng. Chem., Anal. Ed.*, **13**, 145 (1941); R. L. Shirley, D. R. Waldron, E. D. Jones, and E. J. Benne, *J. Assoc. Official Agr. Chem.*, **31**, 285 (1948).

[10] E. J. Serfass and W. S. Levine, *Chemist Analyst*, **36**, 55 (1947). See the same authors, *Monthly Review Am. Electroplaters' Soc.*, **34**, 1046 (1947), for the use of this reagent in the determination of zinc in nickel plating baths.

not present or appropriate separations have been made. If copper is first separated, the mixed-color method may be used for the materials mentioned with assurance of correct results. The effect of some foreign metals in this method is indicated in Table 97. It will be noted that lead has practically no effect, nickel and cobalt considerably more, while copper may be present in very small amounts only (about twice that of zinc). By the addition of more thiosulfate the permissible limits of these metals can be increased, but then the sensitivity of the zinc reaction is decreased.

The concentration of zinc dithizonate in the carbon tetrachloride solution may be found directly by measuring the transmittancy with a green filter (*ca.* 530 mμ) or alternatively indirectly by obtaining the concentration of the remaining dithizone from the measurement of the transmittancy with a red filter (620 mμ). The deviation from linearity shown in Fig. 83 is at least in part to be attributed to the use of insufficiently selective filters.

Carbon tetrachloride or chloroform solutions of zinc dithizonate and dithizone should be exposed to light as little as possible. The use of amber glassware has been recommended for prevention of the fading of the color.

Reagents

Dithizone, 0.001 per cent (weight/volume) in pure carbon tetrachloride.

Acetate buffer, *p*H *ca.* 4.75. Mix equal volumes of 2 *N* sodium acetate and 2 *N* acetic acid, and remove reacting heavy metals by shaking with 0.005 or 0.01 per cent dithizone solution. Filter through a small quantitative paper to remove droplets of carbon tetrachloride.

Sodium thiosulfate, 25 g. of $Na_2S_2O_3 \cdot 5H_2O$ in 100 ml. of water.

Standard zinc solution, 0.01 per cent in *ca.* 0.1 *N* hydrochloric acid. Dissolve reagent-grade 30-mesh zinc in a slight excess of hydrochloric acid and dilute to volume. From this solution prepare by dilution with pure water a 0.001 per cent zinc solution in 0.01–0.02 *N* hydrochloric acid.

§ Procedure

To 10 ml. of solution[11] only slightly acidic (0.01–0.03 *N*) and containing less than 5 γ of zinc, which has been transferred to a small separatory funnel, add 5.0 ml. of buffer solution (*p*H 4.75) and 1.00 ml. of sodium thiosulfate solution. Mix and shake vigorously for 2 minutes with 5.0 ml. of 0.001 per cent dithizone in carbon tetrachloride. Dry the stem of the funnel with filter paper and run the clear carbon tetrachloride solution into a covered cell. Obtain the transmittancy of the solution with light of either 520–540 or 620 mμ wave length (*cf.* Figs. 82 and 83).

[11] The volume of the sample may be larger—say 20 ml.—but then correspondingly larger volumes of buffer and thiosulfate should be added. The volume should be known within 1 or 2 ml. so that the standards for the construction of the calibration curve can be diluted to the same volume (the concentration of thiosulfate affects the zinc ion concentration and therewith the color given with a constant amount of dithizone).

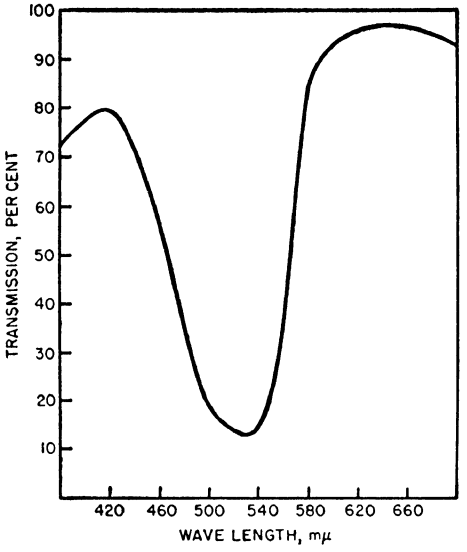


Fig. 82. Transmission curve of zinc dithizonate in carbon tetrachloride (0.6 p.p.m. of zinc). (After Cowling and Miller.)

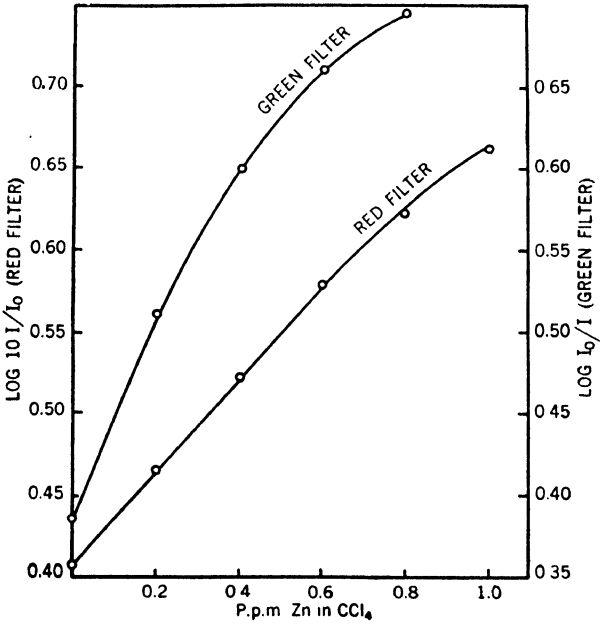


Fig. 83. Determination of zinc with dithizone by the mixed-color method (1 cm. layer of solution).

Visual Comparison. The procedure is very similar to that just described. It is advantageous to determine first the approximate amount of zinc in the sample solution which has been diluted to a definite volume (conveniently 25 ml.). To do this, transfer 1 or 2 ml. of the solution to a flat-bottomed glass-stoppered tube (Fig. 10), add 2–3 ml. of water, enough acetate buffer to make the *p*H 4.5–4.75 and 5 drops of sodium thiosulfate solution. Shake for a minute with 5 ml. of 0.001 per cent dithizone. The colors given by various amounts of zinc are approximately the following: 1 γ, blue; 2 γ, purple-violet; 3 γ, violet; 4–5 γ, red-violet.

Transfer an aliquot containing 2–4 γ of zinc to a color comparison tube, add sufficient acetate buffer to maintain the *p*H practically constant, and 1.00 ml. of sodium thiosulfate (for a total volume of 10–15 ml.). Shake well for 2 minutes with 5.0 ml. of 0.001 per cent dithizone and compare against a series of standards, each having the same volume and containing the same amount of thiosulfate and acetate buffer as the sample solution. Examine the carbon tetrachloride layers transversely against a white background in good light. The adjacent members of the standard series may conveniently differ by 0.5 γ of zinc.

When the sample contains less than 1–2 γ of zinc, reduce the volume of dithizone to 1 or 2 ml. A few tenths of a microgram of zinc can then be determined with considerable precision.

2. The Mono-Color Method

This method does not rest on an entirely sound foundation because it is not possible to wash out completely the excess dithizone from the organic solvent without decomposing some of the zinc dithizonate.[12] By preparing the standards under the same conditions as the sample itself, the error can be largely compensated. Moreover, if conditions are so arranged that a very little dithizone is left in the organic solvent, little zinc will be lost and absorption by the remaining dithizone will be relatively small at the wave length of maximum absorption by zinc dithizonate.

A solution of sodium sulfide, instead of ammonia or other base, is used to remove the excess of dithizone in this method, because traces of zinc in the sulfide solution will not react with the excess of reagent, as would happen if ammonia were used (zinc is a common impurity in ammonia and other alkalies). Before removal of the excess dithizone, the carbon tetrachloride extract is washed with sodium thiosulfate solution to decom-

[12] Kortüm and Finckh[8] obtained values that were 4 to 6 per cent low when applying the mono-color procedure for zinc. Shirley *et al.*[9] report favorably on a monocolor procedure for zinc in plant materials; sodium diethyldithiocarbamate is used as complexing agent and excess dithizone is removed with 0.01 *N* ammonium hydroxide.

pose any small amounts of dithizonates of foreign metals. Zinc dithizonate in carbon tetrachloride obeys Beer's law.

The directions given below for the mono-color method are those of Fischer and Leopoldi. Some representative results obtained in the application of the procedure are contained in Table 98. Traces of zinc are readily determined in this way in the presence of iron, lead, silver, etc., even at ratios of foreign metal to zinc of 10,000:1. The determination is more difficult in the presence of copper, bismuth, and mercury, because of the large amount of thiosulfate required to prevent these metals from reacting (*cf.* below). Still it is possible to determine 10 γ of zinc in the presence of 10 mg. of these metals. Relatively little cadmium (*ca.* 0.1 mg.) may be present. Tin interferes in the stannous state but not in the stannic; large amounts of tin are best eliminated by volatilization as the bromide (see p. 626).

Reagents

Dithizone, 0.005 per cent (weight/volume) in carbon tetrachloride.

Sodium acetate solution, 0.5 *M*. Free the solution from heavy metals by shaking with successive small portions of 0.005 or 0.01 per cent dithizone solution, and filter through a small moistened filter paper to remove droplets of carbon tetrachloride.

Sodium thiosulfate solution, 50 g. $Na_2S_2O_3 \cdot 5H_2O$ in 100 ml. of water.

Sodium thiosulfate-acetate wash solution. Mix 225 ml. of 0.5 *M* sodium acetate solution, 10 ml. of 50 per cent sodium thiosulfate solution, and 40 ml. of 10 per cent nitric acid, and add water to make 500 ml. Remove traces of zinc by shaking with dithizone.

Potassium cyanide, 5 g. in 100 ml. of water.

Sodium sulfide wash solution. Dilute 40 ml. of a 1 per cent sodium sulfide stock solution with 1 liter of water.

Standard zinc solution. See p. 621.

§ Procedure

The solution may have a volume of 10–25 ml. and should preferably contain 5 γ or more of zinc. The sample should be only slightly acid (say 0.1 *N* in hydrochloric acid). If much acid is present it is preferably removed by evaporation (best in a silica dish); neutralization is usually less advisable because it may introduce appreciable quantities of zinc.

Add sodium acetate solution to give a *p*H of 5 to 5.5 (bromcresol green may be used as indicator). Next add sufficient sodium thiosulfate to form complexes with the interfering metals. The amount of thiosulfate to be added depends on the interfering element and its quantity. For each milligram of foreign metal the following amounts (milligrams) of $Na_2S_2O_3 \cdot 5H_2O$ are required:

Cu	500–600
Hg	650–750
Bi	300–350
Ag	50–60
Pb	32–40

Shake the solution vigorously with 2–3 ml. of 0.005 per cent dithizone for about a minute, draw off the extract into another separatory funnel, and wash the first with 0.5–1 ml. of carbon tetrachloride. Repeat the extraction until the last portion of dithizone remains unchanged in color after shaking for 2 to 3 minutes.

Wash the combined carbon tetrachloride extracts two or three times with 5 ml. portions of sodium thiosulfate-acetate wash solution. Then wash once with water and two or three times with 5 ml. portions of sodium sulfide solution. The last portion of sulfide wash solution must remain colorless.

Dilute the washed zinc dithizonate solution to a definite volume with carbon tetrachloride and obtain the transmittancy of the solution at 535 mμ, or compare against a similar standard solution obtained in the same way. Run a blank through the whole procedure.

TABLE 98

DETERMINATION OF ZINC WITH DITHIZONE BY THE MONO-COLOR METHOD[a]

Foreign Metal	Zn taken γ	Zn found γ	Error γ
	6.2	6.0	−0.2
	4.1	4.1	0.0
	37.4	36.8	−0.6
50 mg. Fe (III)	6.2	7.3	+1.1
100 mg. Mn	6.2	6.3	+0.1
10 mg. Cu	8.3	8.8	+0.5
100 mg. Ag	16.6	16.2	−0.4
125 mg. Pb	8.3	8.7	+0.4
0.07 mg. Cd	12.4	12.8	+0.4
150 mg. Sn[a]	16.6	16.9	+0.3
100 mg. Al[b]	6.2	7.0	+0.8
100 mg. Ni[c]	6.3	6.0	−0.3
100 mg. Co[c]	6.4	6.8	+0.4

[a] Sn volatilized with Br_2 + HBr.
[b] Double extraction.
[c] In the presence of KCN.

Notes. 1. In the presence of appreciable amounts of nickel and cobalt proceed as follows. Approximately neutralize the solution with pure ammonia and add enough 5 per cent potassium cyanide solution to dissolve the precipitate first formed. Add

dilute hydrochloric acid dropwise until the *p*H is 3 to 4, and then adjust the *p*H to 5–5.5 with sodium acetate. Extract the clear solution with dithizone as described above. Fourteen ml. of 5 per cent potassium cyanide are sufficient to tie up 100 mg. of either nickel or cobalt.

It is also possible to carry out the determination of zinc in the presence of nickel (Zn:Ni > 1:1000) by making a double extraction as follows. Extract the thiosulfate-containing solution with dithizone until a brownish-green color is obtained (due to nickel which reacts after zinc), and then shake the combined extracts, which have been washed with water, with two 5 ml. portions of 0.1 *N* hydrochloric acid to bring zinc into the aqueous phase. Adjust the *p*H of the acid extract to 5–5.5 and determine zinc in the usual way. In the presence of much thallium a similar double extraction should be made.

2. If tin is present in the sample volatilize it by adding 5 ml. of bromine-hydrobromic acid mixture (20 ml. Br_2 + 100 ml. HBr) and evaporating to dryness on the steam bath. Treat the residue with 1 ml. of aqua regia, evaporate to dryness, and dissolve the residue in 0.5 ml. of 10 per cent nitric acid.

3. Aluminum hinders the extraction of zinc from slightly acid solution, and if it is present in amounts greater than 100 mg., it is necessary to extract zinc from a faintly ammoniacal solution containing citrate or tartrate. Large amounts of other reacting heavy metals can then not be present, for too much dithizone would be required for extraction. The extract containing zinc and other reacting metals is shaken with dilute hydrochloric acid (*e.g.*, 0.1 *N*) to bring zinc into the aqueous phase, in which it is then determined according to the above procedure. See further p. 631.

4. Large amounts of cadmium will react with dithizone in spite of the presence of thiosulfate. As much as 70 γ of cadmium may be present however if the zinc dithizonate extract is washed 5–6 times with sodium sulfide to remove cadmium completely (Table 98).

5. Instead of using thiosulfate to prevent the reaction of copper, mercury, and silver (and probably gold and palladium), these metals may be precipitated with hypophosphite in acid solution. Add 1 or 2 ml. of 10 per cent sodium hypophosphite solution to 10 or 20 ml. of sample solution acidified slightly with mineral acid, heat to boiling, and keep at the boiling point for a few minutes until the precipitate has coagulated. Filter the solution, wash with water, and extract the filtrate and washings with dithizone solution to remove traces of unprecipitated metals. Then determine zinc, after adjusting the acidity of the solution, by either the mono- or mixed-color method. The results with 10 mg. of copper, 15 mg. of mercury, and 100 mg. of silver are low to the extent of 5–10 per cent for zinc quantities ranging from 6 to 33 γ, owing to slight coprecipitation of zinc.

B. The 8-Hydroxyquinoline Method (Fluorimetric)

There are various possibilities in the use of oxine for the photometric determination of zinc. Zinc hydroxyquinolate can be determined indirectly after precipitation (p. 114). It can also be extracted with chloroform and the transmittancy determined, or the fluorescence of the resulting solution can be measured. Details regarding the last two methods are lacking. However, another fluorimetric method has been described, in which zinc hydroxyquinolate is precipitated from weakly acidic aqueous medium and the fluorescence of the suspension, stabilized by gum arabic,

is measured.[13] The sensitivity of such a method is much less than that of one in which the zinc hydroxyquinolate is extracted with an organic solvent and accordingly less valuable in trace analysis. From 1 to about 10 p.p.m. of zinc can be determined by the fluorescence of the suspension; the precision is about 0.4 p.p.m. or better. Other metals, such as iron and aluminum, which are precipitated in acetic acid-acetate medium, will, of course, interfere. Because of its dark color, ferric hydroxyquinolate in traces reduces the fluorescence of the zinc to zero. Aluminum produces high results since its quinolate also fluoresces. Extraneous salts affect the fluorescence of the zinc compound to the extent shown by the following figures, which represent the error in milligrams of zinc produced by 1 mg. of the salt (procedure as below): ammonium tartrate 0.0005, sodium chloride 0.00004, potassium dihydrogen phosphate 0.0002, potassium iodide 0.00015, potassium nitrate 0.00007, magnesium sulfate 0.0008, barium chloride 0.0001, calcium nitrate 0.0003, hydrogen fluoride 0.0034, trisodium silicate 0.0004. The salts were investigated in various concentration ranges, usually from 25 mg. or more to 100–500 mg. (hydrogen fluoride 2 to 20 mg.), and the amount of zinc present was about 0.2 mg. The sign of the error is not stated except for magnesium which gives low results.

With a sufficient quantity of gum arabic, readings are constant for 25 minutes or longer. The temperature should be kept constant within 2°; the fluorescence intensity increases with temperature. A complicating factor in the method is the absorption of the exciting light by the excess 8-hydroxyquinoline below 500 mμ, so that the amount of the latter must be regulated. Light with a wave length above 460 mμ produces practically no fluorescence. Light in the neighborhood of 420 mμ is best for excitation.

Reagents

8-Hydroxyquinoline, 5 g. in 11.5 ml. of glacial acetic acid diluted to 100 ml. with water.

Gum arabic, 2 per cent in water. Filter if not clear.

Ammonium acetate, 154 g. in 1 liter.

Dichlorofluorescein or fluorescein. Add a 0.1 per cent alcoholic solution to 1 liter of water until the resulting solution has a fluorescence approximately as strong as that given by 0.3 mg. of zinc in the procedure. About 0.35 ml. will be required. The solution is stable for weeks.

§ Procedure

To the approximately neutral zinc solution (0.05 to 0.5 mg.) in a 50 ml. flask add 5 ml. of ammonium acetate, 2 ml. of gum arabic solution, enough water to make the volume approximately 45 ml., and 0.20 ml. of 8-hydroxyquinoline solution. Dilute to the mark with water. Measure the strength

[13] L. L. Merritt, Jr., *Ind. Eng. Chem., Anal. Ed.*, **16**, 758 (1944).

of the fluorescence photoelectrically, using a 420 mμ filter in the primary beam. A secondary filter cutting off most of the radiation below about 500 mμ should be used to absorb any scattered or reflected primary light. The reading of standard dichlorofluorescein solution may be adjusted to 50. At room temperature (25° and below) the standard curve is a straight line, not necessarily passing through the origin however.

C. Other Methods

In weakly alkaline alcoholic solution, urobilin or stercobilin gives a strong green fluorescence with zinc. As little as 1 γ of zinc can be detected in ultraviolet light. Many metals interfere, even if present in minute amounts only, but after isolation zinc can be determined satisfactorily with urobilin.[14] Benzoin has been used as a qualitative fluorescence reagent for zinc.[15]

Zinc can be determined nephelometrically or turbidimetrically as the ferrocyanide[16] or the sulfide.[17]

In an indirect method, zinc is precipitated with 5-nitroquinaldic acid and the precipitate is reduced with stannous chloride to give an orange water-soluble compound.[18]

A color reaction for zinc with methylene blue and thiocyanate has been described.[19]

III. Applications of the Dithizone Method

A. Silicate Rocks

The mixed-color dithizone method is the most suitable one for the determination of zinc in rocks. All the reacting metals of the sample are first isolated by extracting the ammoniacal citrate solution of the decomposed rock with dithizone in carbon tetrachloride. The extract is then shaken with very dilute hydrochloric acid (0.01–0.02 *N*) to obtain zinc, lead, etc., in the aqueous phase; copper, and most of the cobalt and nickel remain in the carbon tetrachloride. Zinc can then be determined in the aqueous solution after adjusting the *p*H and adding thiosulfate.[20]

[14] R. E. Lutz, *J. Ind. Hygiene*, **7**, 273 (1925).

[15] C. E. White and M. H. Neustadt, *Ind. Eng. Chem., Anal. Ed.*, **15**, 599 (1943).

[16] L. T. Fairhall and J. R. Richardson, *J. Am. Chem. Soc.*, **52**, 938 (1930); H. M. Boggs and A. O. Alben, *Ind. Eng. Chem., Anal. Ed.*, **8**, 97 (1936).

[17] L. W. Winkler, *Z. angew. Chem.*, **26**, 38 (1913); L. Pincussen and E. Brück, *Biochem. Z.*, **265**, 58 (1933).

[18] W. L. Lott, *Ind. Eng. Chem., Anal. Ed.*, **10**, 335 (1938).

[19] V. I. Kuznetsov, *Doklady Akad. Nauk, S. S. R.*, **41**, 113 (1943); *Chem. Abst.*, **38**, 3925 (1944).

[20] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **9**, 464 (1937).

TABLE 99

DETERMINATION OF ZINC IN SILICATE ROCKS BY THE DITHIZONE METHOD

Sample	Zinc present per cent	Zinc found per cent
Acid rock (synthetic)	0.0024	0.0026
Acid rock (synthetic)	0.004	0.0045
Acid rock (synthetic)	0.007	0.007
Acid rock (synthetic)	0.0115	0.012
Basic rock (synthetic)	0.0105	0.010
Basic rock (synthetic)	0.015	0.015
Basic rock (synthetic)[a]	0.005	0.006

[a]Contained 0.05% Cu, 0.1% Pb, 0.2% Ni, and 0.05% Co.

Reagents

See p. 404.

§ Procedure

Decompose 0.25 g. of sample with perchloric and hydrofluoric acids as described on p. 405, and if any appreciable amount of insoluble material remains treat as there described. Extract the dithizonates from the ammoniacal citrate solution[21] and shake the extract with 0.02 *N* hydrochloric acid (p. 406).

Make up the hydrochloric acid solution containing the zinc to 25 ml. in a volumetric flask. Take 5 ml. (for less than 0.01 per cent zinc) or 2 ml. (for 0.01–0.025 per cent) of the solution for analysis. Add 2 ml. of acetate buffer and 0.5 ml. of sodium thiosulfate (see p. 621) and shake with 5 ml. of 0.001 per cent dithizone for 2 minutes. Determine the transmittancy of the carbon tetrachloride solution (p. 621) or compare against a series of standards prepared in the same manner as the sample solution (p. 623). Correct the result for zinc in the reagents.

B. SOILS[22]

For the determination of *total* zinc in soils, a procedure very similar to that given above for silicate rocks may be used. If much organic matter

[21] When much nickel is present it can be removed before the dithizone extraction by addition of dimethylglyoxime to the ammoniacal citrate solution followed by chloroform extraction of nickel dimethylglyoxime.

[22] See also G. D. Sherman and J. S. McHargue, *J. Assoc. Official Agr. Chem.*, **25**, 510 (1942). These authors recommend fusion of the soil sample with sodium-potassium carbonate (3 g. of mixed carbonates for 0.5 g. sample). Silica is dehydrated and separated in the usual manner. Another dithizone procedure is described by R. S. Holmes, *Soil Sci.*, **59**, 77 (1945).

is present it may be advisable to treat the finely ground sample first with a few milliliters of concentrated nitric acid, evaporate to dryness and then decompose with perchloric and hydrofluoric acids. The rest of the procedure is the same as in A above, except that a smaller aliquot may be necessary, since the zinc content of soils may rise to 500 p.p.m.

C. Water

§ Procedure

Add 5 ml. of 10 per cent sodium (or ammonium) citrate to 50 ml. of sample and if the solution is not already basic, make it weakly ammoniacal. Shake with small portions of 0.01 per cent dithizone in carbon tetrachloride until the latter does not turn violet or bluish but remains green. Combine the extracts, wash the carbon tetrachloride with a few milliliters of water and shake thoroughly with 10 ml. of 0.02 *N* hydrochloric acid to transfer the zinc to the aqueous phase. Draw off the carbon tetrachloride into another separatory funnel and shake with a fresh 5 or 10 ml. portion of 0.02 *N* acid to be certain that all the zinc has been removed. Dilute the acid extracts to 25 or 50 ml. in a volumetric flask, and determine zinc in a 10 ml. aliquot according to the mixed color method, p. 620.

Note. If copper does not greatly exceed zinc (Cu/Zn < 2) and excessive amounts of iron are not present, zinc may be determined directly in 10 ml. of the sample after adjustment of the *p*H and addition of thiosulfate as described on p. 621.

When very minute traces of zinc are to be determined in water, a suitable amount of acidified sample should be evaporated to a small volume in a silica or platinum dish. Sodium citrate is then added and zinc isolated as described above.

D. Chromium-Nickel Steels

In the procedure below,[23] chromium is eliminated as CrO_2Cl_2 (trivalent chromium leads to low results)[24] and a chloroform solution of dithizone is used in preference to a carbon tetrachloride solution to reduce the amount of nickel extracted in the isolation of zinc. Copper need not be separated by sulfide precipitation unless it exceeds 0.5 per cent.

§ Procedure

Dissolve 0.5 g. of steel in 3 ml. of concentrated hydrochloric acid and 2 ml. of concentrated nitric acid. Add 3 ml. of 70 per cent perchloric acid and 1 drop of hydrofluoric acid and evaporate until perchloric acid vapors condense in the neck of the flask and all the chromium has been oxidized.

[23] L. G. Bricker, S. Weinberg, and K. L. Proctor, *Ind. Eng. Chem., Anal. Ed.*, **17**, 661 (1945).

[24] Private communication, L. G. Bricker.

Pass in dry hydrogen chloride to volatilize chromium and tin. Cool and dilute with 10 ml. of water.

Add 5 ml. of citric acid solution (20 g. in 100 ml.), neutralize with ammonia to litmus paper, and add 2–3 drops in excess (*p*H 8–8.5). Extract the cold solution with 10 ml. of dithizone (0.01 g. in 100 ml. chloroform) and then with 5 ml. portions until the chloroform remains greenish purple after shaking for 20 seconds. If the copper content is less than 0.5 per cent, 20–30 ml. of dithizone should be sufficient.

Shake the combined chloroform extracts with 10 ml. of 0.1 *N* hydrochloric acid for at least 1 minute. Discard the chloroform layer and wash the aqueous phase with a few milliliters of chloroform to remove any remaining dithizone, repeating the treatment if necessary. Add 1 drop of methyl orange solution and titrate the hydrochloric acid solution with 0.1 *N* ammonium hydroxide to the yellow color. Add 1.0 ml. of sodium thiosulfate solution (15 g. in 100 ml. water) and 5 ml. of phthalate buffer of *p*H 6 (79 ml. of 0.1 *N* sodium hydroxide and 2.00 g. of potassium biphthalate in a total volume of 100 ml.).

Shake the solution with 25 ml. of dithizone (0.01 g. in 500 ml. of carbon tetrachloride) for 1 minute, allow the layers to separate, and remove the aqueous phase by means of a siphon. Add 25 ml. of sodium sulfide solution (0.05 g. in 100 ml. of water) and shake for 15 seconds to remove excess dithizone; repeat with another 25 ml. portion of sodium sulfide after siphoning off the first portion. Obtain the transmittancy of the carbon tetrachloride solution at 520 mμ. A blank must be run.

TABLE 100

DETERMINATION OF ZINC IN CHROMIUM-NICKEL STEELS BY THE DITHIZONE METHOD[23]

Zn present, per cent.....	0 007[a]	0.012[a]	0.011[b]	0.015[c]	0.030[c]
Zn found, per cent.....	0.004	0.011	0.011	0.014	0.032

[a] 18% Cr, 8% Ni. [b] 20% Cr, 10% Ni. [c] 25% Cr, 20% Ni.

E. COBALT

A procedure for the determination of 0.005–0.05 per cent of zinc in metallic cobalt has been described.[25] The isolation of zinc is accomplished by fractional extraction from a solution containing cyanide and thiosulfate at *p*H 4.5–5.5.

F. ALUMINUM ALLOYS

Fischer and Leopoldi[26] have applied the mono-color dithizone method (p. 623) to the determination of zinc in aluminum. The interference of

[25] R. S. Young, *Metallurgia*, **36**, 347 (1947).

[26] H. Fischer and G. Leopoldi, *Aluminum*, **25**, 356 (1943).

aluminum hydroxide in the extraction is minimized by the addition of ammonium oxalate to the solution of the sample. The cobalt content of the sample must not exceed the zinc content. For typical results see Table 101.

TABLE 101

DETERMINATION OF ZINC IN ALUMINUM ALLOYS[26]

Present, %								Found, %	
Si	Cu	Co	Ni	Fe	Mn	Mg	Pb	Zn	Zn
—	3.0	—	0.9	0.5	0 9	1.0	—	0.102	0.099 0.098
—	3.0	0.16	0 9	0.5	0.9	1.0	—	0.102	0.107 0.097
—	6.0	0.32	1.8	3.0	1.5	5 0	2.0	0.53	0.525 0.53
0.6	4.5	—	—	0.6	0.9	3.2	—	0.097	0.100
10.0	4.0	—	—	0.5	0.6	0.9	—	0.104	0.095

The authors' directions are for amounts of zinc above the trace range, but the procedure is nevertheless given here because it has some features of interest and probably can be used for lower concentrations.

Special Solutions

Dithizone, about 5 mg. purified reagent (p. 107) in 100 ml. of carbon tetrachloride. The dilute solution is unstable and is best prepared fresh by dilution of a stronger solution (p. 109).

Ammonium hydroxide, 12.5 per cent NH_3.

Ammonium oxalate, 5 per cent.

Potassium cyanide, 5 per cent.

Sodium acetate, 5 per cent.

Sodium thiosulfate, 50 g. in 100 ml. of water.

Sodium sulfide, 5 g. in 500 ml. Dilute 25 ml. of this solution to 500 to obtain the *wash solution*.

Complex-forming solution. Add successively, with shaking, to a 500 ml. separatory funnel, 15 drops ammonia, 1.5 ml. ammonium oxalate, 15 ml. potassium cyanide, 35 ml. hydrochloric acid (1 *N*), 85 ml. sodium acetate, and a mixture of 120 ml. sodium thiosulfate and 150 ml. of sodium acetate. Shake the solution with small portions of dithizone until the latter remains green. Since the extraction of zinc proceeds slowly, it is best to use a shaking machine and allow 10 minutes for the reaction. Droplets of dithizone should finally be removed by washing with carbon tetrachloride. A slight separation of sulfur in the aqueous solution does no harm.

§ Procedure

Dissolve 0.5 g. of sample in 25 ml. of 1:1 hydrochloric acid, add 0.2 g. potassium chlorate, and boil 5 minutes. Dilute the solution to 250 ml. in

a volumetric flask and filter through a coarse paper, rejecting the first portion of the filtrate. Pipet a suitable aliquot (5 ml. for 0.1 to 0.2 per cent zinc) into a 100 ml. separatory funnel, and add 30 ml. of the complex-forming solution and 10 ml. of dithizone. Shake in a shaking machine. If the carbon tetrachloride becomes red or red-violet in a short time, draw off the extract into a graduated glass-stoppered 25 ml. cylinder, and shake with a 5 ml. portion of dithizone. If after 5 minutes the carbon tetrachloride is only a dark violet, separate it, add 1 ml. of dithizone and shake for 1 minute. The last extract must remain green. If any flocs are visible on the surface of the carbon tetrachloride do not draw these off, but wash the last extract with carbon tetrachloride. Add 5 ml. of sodium sulfide wash solution to the combined extracts and dilute the latter to 25 ml. with carbon tetrachloride. Shake a few times with the wash solution and draw off the carbon tetrachloride phase. Repeat the washing 3 or 4 times with 5 ml. portions of wash solution. The last portion of wash solution must remain colorless. Filter the carbon tetrachloride extract through an acid-free filter paper of coarse texture to remove water droplets.

Obtain the transmittancy of the carbon tetrachloride solution of zinc dithizonate at 530 mμ. A 1 cm. cell is suitable for 6–27 γ of zinc. A reagent blank should be run.

G. Bio Materials

Procedures involving the use of di-β-naphthylthiocarbazone and dithizone respectively as reagents are given below. The use of the former has been investigated more thoroughly. It has certain advantages over dithizone (*p*H adjustment less critical, quantitative extraction of zinc in the presence of the complexing agent sodium diethyldithiocarbamate) but unfortunately it cannot be applied in the presence of appreciable amounts of cadmium.

There is no unanimity of opinion concerning the best method of destroying organic matter. Some workers claim that dry oxidation may lead to incomplete recovery of zinc. Others[27] have found that dry ashing gives entirely satisfactory results. No doubt wet oxidation is free from the objections that may be raised against oxidation by ignition (*cf.* the remarks on p. 317). One advantage of dry ashing is the smaller blank associated with a procedure based on it. The digestion method requires the neutralization of the acid in the mixture with ammonia or other base, and appreciable amounts of zinc may thus be introduced unless the ammonia is redistilled and stored in a wax-lined bottle. Moreover, it is claimed by some that the oxidizing acids (nitric acid) required contain appreciable quantities of zinc. A combination of acid digestion and ashing is described below.

[27] R. E. Lutz, *J. Ind. Hygiene*, **7**, 279 (1925); P. K. Thompson, *ibid.*, **7**, 358 (1925).

1. Di-β-naphthylthiocarbazone as Reagent[4]

An initial separation of zinc from copper, nickel, cobalt, iron, and most of the bismuth is made as described on p. 618, diethyldithiocarbamate being used as a complexer. The final extraction of zinc is made from an ammonia solution containing carbamate. All of the excess naphthylthiocarbazone

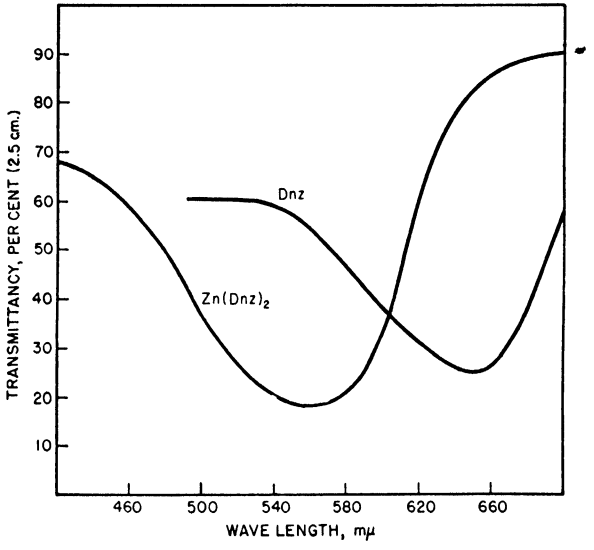


Fig. 84. Transmission curves of dinaphthylthiocarbazone and its zinc complex in chloroform (2 p.p.m. of reagent in each case). (After Cholak, Hubbard, and Burkey.)

remains in the chloroform phase and the concentration of zinc can be determined by measuring the absorption by the zinc complex or by the remaining reagent.

Special Reagents

Ammonium hydroxide. Absorb the tank gas in cooled water or (less preferably) distil the reagent-quality solution. Preserve the solution in a wax-lined bottle.

Ammonium citrate. Dissolve 400 g. of citric acid in water and add enough ammonia to make just alkaline to thymol blue. Dilute to 1 liter. Before use, dilute with an equal volume of water and shake with successive portions of dinaphthylthiocarbazone in chloroform until the latter retains its original color.

Sodium diethyldithiocarbamate, 1.25 g. in 100 ml. of water. Prepare fresh daily.

Di-β-naphthylthiocarbazone. Solution A: 20 mg. of the pure reagent in 1 liter of redistilled chloroform containing 10 ml. absolute alcohol. Solution B: 200 mg. in 1 liter of redistilled chloroform containing 10 ml. of absolute alcohol. Keep both solutions in brown bottles and store in a refrigerator.

§ Procedure

Transfer 10–20 g. of tissue or other material, or 100 ml. of urine, to a 200 ml. glazed silica evaporating dish. Add 10 ml. of redistilled nitric acid and evaporate to dryness on the hot plate. Then ignite in a muffle furnace at 500°. Complete destruction of organic matter may be hastened by moistening the residue with nitric acid from time to time, evaporating, and igniting. Do not use more nitric acid than actually necessary, in order to keep the blank as low as possible. Take up the carbon-free ash in a little hydrochloric acid and water. Do not filter off any insoluble material, but carry it along through the procedure.

Initial extraction of zinc. Transfer the entire solution or an aliquot of it to a graduated 150 ml. separatory funnel, and add 30 ml. of 20 per cent ammonium citrate solution, 4 drops of thymol blue indicator solution, and sufficient ammonium hydroxide to give a *p*H of 9.5. Next add 4 ml. of the carbamate solution and dilute to 100 ml. with water. Shake for 1 minute with 5 ml. of naphthylthiocarbazone solution A. A faint violet color indicates less than 5 γ of zinc. Then add 5 ml. of naphthylthiocarbazone solution B and again shake for 1 minute. Draw off the chloroform layer and extract with additional 5 ml. portions of solution B if necessary until the original blue-green color does not change. The color is most easily recognized when the solution is being shaken. Shake the combined chloroform extracts with 50 ml. of water, drain the chloroform into another separatory funnel, and shake the aqueous layer with a few milliliters of chloroform to recover droplets of the thiocarbazone.

Shake the chloroform solution (or an aliquot of it containing not more than 50 γ of zinc) with 50 ml. of 0.2 *N* hydrochloric acid for 1 minute. Discard the chloroform phase and remove any entrained thiocarbazone in the aqueous layer by shaking with a few milliliters of pure chloroform and drawing off. The acid solution contains the zinc, freed from copper, nickel, cobalt, iron, mercury, silver, and most of the bismuth.

Colorimetric determination. Shake 45 ml. of dilute ammonium hydroxide (50 ml. of concentrated ammonium hydroxide diluted to 1 liter) and 1 ml. of sodium diethyldithiocarbamate solution with 5 ml. of naphthylthiocarbazone solution A to remove traces of zinc which may have been taken up from the glass. Draw off the chloroform layer and wash the aqueous layer with a few milliliters of chloroform. Allow the chloroform floating on the surface of the ammonia solution to evaporate and add the solution to the 0.2 *N* hydrochloric acid extract of the zinc. Shake for 1 minute with 10 ml. of naphthylthiocarbazone solution A (0–5 γ of zinc) or solution B (0–50 γ of zinc). For the determination of zinc in the 0–5 γ range, dilute 5 ml. of the chloroform extract to 25 ml. with pure chloroform and obtain

the transmittancy at 550 or 650 mμ, preferably in a 2.5 cm. cell. In the 0–50 γ range dilute 5 ml. of the extract to 100 ml. with chloroform and use a 1 cm. cell.

Obtain the standard curves by carrying known amounts of zinc in 0.2 *N* hydrochloric acid through the procedure described in the last paragraph. A linear relation should be obtained between concentration and extinction.

TABLE 102

RECOVERIES OF ZINC FROM SYNTHETIC URINE ASH REPRESENTING 100 ML.[a]

Zinc taken, γ.....	1.0	5.0	30	50	0[b]	50[b]	50[c]
Zinc found, γ.....	0.8	4.8	30.8	49.8	0	50	62

[a] Partial data of Cholak, Hubbard, and Burkey, *loc. cit.*
[b] 100 γ each of Hg, Pb, Cu, Bi present.
[c] 100 γ each of Hg, Pb, Cu, Bi, Cd present.

2. Dithizone as Reagent

A number of procedures for the determination of zinc in samples of biological origin by the use of dithizone have been described.[28] In the simple procedure given below, all the dithizone-reacting metals are first extracted from an ammoniacal citrate solution and the carbon tetrachloride extract is shaken with 0.02 *N* hydrochloric acid. As already mentioned, copper, mercury, cobalt, and most of the bismuth and nickel[29] remain in the carbon tetrachloride, whereas zinc, lead, and cadmium are transferred to the aqueous phase. In the latter the zinc is easily determined by mixed-color photometry after the adjustment of the *p*H and addition of thiosulfate to prevent the reaction of the metals accompanying zinc into the acid layer. The metal most likely to interfere is cadmium. However, 250 parts of cadmium are required to produce as much color as *ca.* 1 part of zinc (Table 97), so that the method should be satisfactory in the great majority of cases.

Special Solutions

Dithizone, 0.01 per cent in carbon tetrachloride.
Hydrochloric acid, 6 *N*. Redistilled acid is preferable but not essential.

[28] See references in footnotes 2 and 9; N. Strafford, P. F. Wyatt, and F. G. Kershaw, *Analyst*, **70**, 232 (1945) (zinc and other heavy metals in medicinals). In a procedure for the isolation of zinc described in *Analyst*, **73**, 304 (1948), the solution of the sample obtained by wet oxidation is extracted at *p*H 7.5–8.0 with a chloroform solution of diethylammonium diethyldithicarbamate. The carbamates of lead, copper, silver, cadmium, mercury, nickel, cobalt, bismuth, and zinc pass into the chloroform phase; ferric iron is partially extracted. The chloroform extract is shaken with 10 per cent sodium hydroxide solution containing citrate to transfer zinc to the aqueous phase.

[29] Much nickel can be removed before the dithizone extraction by extracting its dimethylglyoxime complex with chloroform, but this will hardly ever be necessary.

Hydrochloric acid, 0.02 *N*. Use redistilled water in diluting.

Ammonia, concentrated aqueous solution.

Sodium citrate, 10 per cent. Dissolve 10 g. of the citrate in 100 ml. of water, make faintly ammoniacal, and remove reacting heavy metals by shaking with small portions of 0.01 per cent dithizone until the carbon tetrachloride remains green. Filter through a small paper previously washed with dilute hydrochloric acid to remove droplets of carbon tetrachloride. Keep the purified solution in a ceresin-coated bottle.

§ Procedure

If the material contains more than 2–3 p.p.m. of zinc, a 1 gram sample is sufficient. Ash[30] in a silica or platinum dish at a temperature below 500° (see p. 410). Add a mixture of 2–3 ml. 6 *N* hydrochloric acid and an equal volume of water to the ash and heat at the boiling point until all soluble material has been brought into solution. Filter through a small paper which has previously been washed with hot dilute hydrochloric acid to remove traces of zinc. Wash with warm water. If particles of carbon are visible in the residue, ignite the paper and its contents as before and extract the residue with a little dilute hydrochloric acid.[31]

Add 5 ml. of sodium citrate to the filtrate and washings (volume about 20 ml.), make ammoniacal (litmus), and add an excess of 0.2–0.3 ml.[32] Extract in a separatory funnel with a few milliliters of 0.01 per cent dithizone solution and transfer the carbon tetrachloride to another separatory funnel. Repeat the extraction with more dithizone until the last portion remains green after shaking for at least one-half minute.

Wash the combined carbon tetrachloride extracts with a few milliliters of water and then shake for 2 minutes with 10 ml. of 0.02 *N* hydrochloric acid, transfer the latter to a 25 ml. volumetric flask, and shake the carbon tetrachloride solution with a fresh 10 ml. portion of the dilute hydrochloric acid to insure the removal of all the zinc. Add the aqueous solution to the flask and make up to 25 ml. with water. Depending upon the amount of zinc expected, take a 10 ml. aliquot (1–5 γ) or less, and proceed as described in the general procedure, p. 621.

[30] If it is desired to use a digestion method in destroying organic matter, follow the directions on p. 385.

[31] If an appreciable amount of residue insoluble in hydrochloric acid remains, it should be hydrofluorized or otherwise treated (fusion with sodium carbonate) to bring it into solution. L. H. Rogers and O. E. Gall, *Ind. Eng. Chem., Anal. Ed.*, 9, 42 (1937), have shown that zinc may be present in hydrochloric acid-insoluble material.

[32] If the solution becomes appreciably turbid, allow it to stand for half an hour, filter off the precipitate, fuse it with sodium carbonate, and treat further as described on p. 405.

CHAPTER XLIX

ZIRCONIUM

I. Separations

The very low solubility of zirconium dihydrogen phosphate in 1:10 hydrochloric or sulfuric acid enables small quantities of zirconium to be precipitated as such and separated from most metals.[1] When titanium is present, hydrogen peroxide must be added to prevent its precipitation. The precipitate can be fused with sodium carbonate[2] and the melt leached with water to separate phosphate. All traces of phosphate must be eliminated by thorough washing before dissolving the residue in hydrochloric or dilute perchloric acid.

Phenylarsonic and other arsonic acids yield slightly soluble precipitates with zirconium in acid solution,[3] but their value for the separation of traces of zirconium remains to be proven.

Cupferron is a useful precipitant for zirconium in certain cases. Ferric iron can be used as a collector.[4] Presumably zirconium cupferrate can be extracted by chloroform.

Large amounts of iron can be separated from zirconium by ether extraction of ferric chloride or by electrolysis with a mercury cathode.

II. Methods of Determination

A. The Alizarin Method

Under suitable conditions it is possible to determine small amounts of

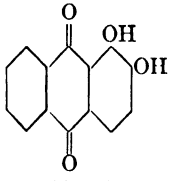
[1] According to G. von Hevesy, *Chemical Analysis by X-rays and Its Applications*, Cornell Univ. Press, Ithaca, 1932, p. 211, the solubility of zirconium phosphate, $ZrO(H_2PO_4)_2$, in 6.0 *N* hydrochloric acid corresponds to 3.3 mg. ZrP_2O_7 or 1.1 mg. Zr per 100 ml. at room temperature. It may be inferred that in 1:10 hydrochloric acid in the presence of excess phosphate the solubility will be much smaller. *Cf.* O. Hackl, *Z. anal. Chem.*, **122**, 1 (1941). T. R. Cunningham and R. J. Price, *Ind. Eng. Chem., Anal. Ed.*, **5**, 334 (1933), have described the precipitation of zirconium phosphate in the presence of much iron (steel analysis); iron is first reduced to the ferrous state with sulfite.

[2] Direct fusion of silicate and other samples with sodium carbonate provides a separation from phosphate, sulfate, and fluoride, which interfere in the colorimetric determination of zirconium.

[3] See, for example, F. Feigl, *Specific and Special Reactions*. Nordeman, New York. 1940; p. 120.

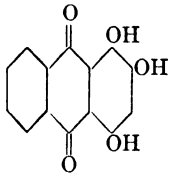
[4] See the reference on p. 605.

zirconium (and hafnium) by the use of various hydroxyanthraquinones such as:



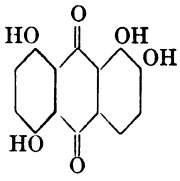
Alizarin

1,2-Dihydroxyanthraquinone



Purpurin

1,2,4-Trihydroxyanthraquinone



Quinalizarin

1,2,5,8-Tetrahydroxyanthraquinone

These dyes (or their sulfonic acids) form slightly soluble, strongly colored lakes with most cations at the proper acidities; the color of the lake is different from that of the dye itself. The zirconium lake is stable at relatively high acidities in contrast to most of the other metal lakes. The molar ratio of zirconium to alizarin sulfonic acid in the lake formed by this reagent is close to 1:1, especially at acid concentrations above 0.1 *N*.[5] It appears that zirconium reacts in the zirconyl form and that both hydroxy group hydrogens are replaced in the reagent.

The use of alizarin, purpurin, and quinalizarin for the determination of small amounts of zirconium has been described by Liebhafsky and Winslow.[6] These authors form the lake in an alcoholic, very slightly acidic solution. They report that for general use alizarin is the most suitable of the three hydroxyanthraquinones mentioned. It gives a red lake which follows Beer's law rather closely up to a concentration of at least 4 p.p.m. of zirconium. The other two reagents (especially quinalizarin) give colored products which show large deviations from Beer's law. Quinalizarin, however, is 2–3 times as sensitive a reagent as alizarin. The failure of the purpurin lake to conform to Beer's law has been attributed to scattering of light by the relatively large particles composing it. The alizarin lake has the smallest particle size of the three, and when first formed may exist in true solution. Eventually the alizarin lake settles out, but it can be redispersed by shaking, and the transmission curve of such a suspension is but little different from one freshly prepared.

Other workers have described methods in which alizarin sulfonic acid is used as reagent and the lake is formed in an aqueous medium, and at a

[5] In 0.1 *N* hydrochloric acid medium the lake appears to contain more alizarin sulfonic acid than demanded by the 1:1 ratio, as shown by Brita Hök, M.S. Thesis, University of Minnesota, 1949.

[6] H. A. Liebhafsky and E. H. Winslow, *J. Am. Chem. Soc.*, **60**, 1776 (1938).

higher acidity than specified by Liebhafsky and Winslow. Green carries out the reaction in 0.1 *N* hydrochloric acid.[7] Hök[5] recommends an acidity of 0.2 *N* to minimize the effect of other metals. There is very little difference in the color intensity of the lake in 0.1 and 0.2 *N* hydrochloric acid solutions. The effect of various substances is shown in Table 103. Moderate amounts of calcium, magnesium, manganese, aluminum, and titanium do not interfere. Large amounts of sodium chloride and divalent metal chlorides cause low results. This may be due in part to the effect of electrolytes on the particle size of the lake and therewith on the light scattering, and in part to the formation of a weak zirconyl chloride complex.

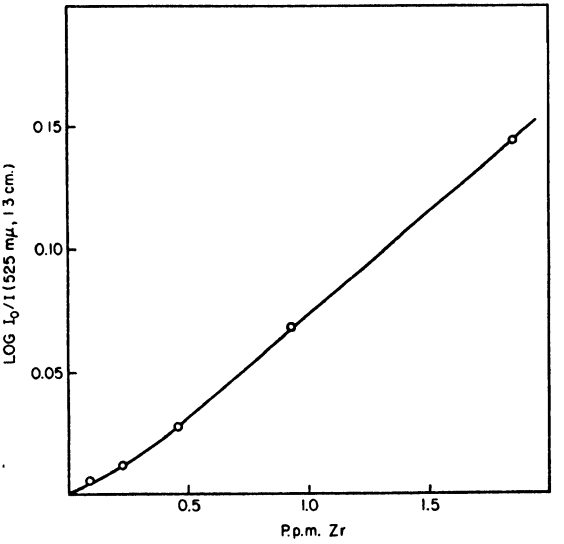


Fig. 85. Determination of zirconium with alizarin sulfonic acid. Extinction of blank has been subtracted. In the presence of 0.1 per cent mercaptoacetic acid (for reduction of ferric iron) the standard curve is almost coincident with the one shown. (From data of Brita Hök.)

Small amounts (a few mg.) of ferric iron can be tolerated, but larger amounts must be removed or reduced to the ferrous state. Up to 25 mg. of ferric iron can be made harmless by reduction with mercaptoacetic (thioglycolic) acid. Low results are obtained if too much mercaptoacetic acid is added, presumably because of complex formation with zirconyl ion. Moreover, the dithioglycolic acid formed in the reduction of iron appears to bind zirconium and low results are obtained when relatively much iron is present. Reduction of ferric iron with silver powder can also be applied (Green uses a silver reductor), although Hök found that some of the zir-

[7] D. E. Green, *Anal. Chem.*, **20**, 370 (1948).

conium appeared to be adsorbed in the process so that the standard curve must be established under the same conditions existing in the determination.

Fluoride, phosphate, and organic hydroxy acids must be absent and only very small amounts of sulfate may be present. All of these form stable complexes with zirconium in acidic medium.

The directions of Hök follow. Sulfate may be present up to 0.02 g. in this procedure.

§ Procedure

Transfer the sample solution (not less than 20 γ of Zr) to a 100 ml. volumetric flask. Adjust the concentration of hydrochloric acid in the solution so that it will be 0.20 *N* after dilution to volume. Reduce ferric iron (not more than 25 mg. may be present) by the addition of 1 ml. of 10 per cent thioglycolic acid after diluting the solution to approximately 90 ml. Allow to stand for a minute or two until the blue coloration has disappeared. Then add, while swirling, 2.00 ml. of 0.05 per cent aqueous solution of sodium alizarin sulfonate. Dilute to 100 ml. and allow to stand at room

TABLE 103

DETERMINATION OF ZIRCONIUM WITH ALIZARIN SULFONIC ACID[5]

Foreign substance[a]	Zr taken, γ	Zr found, γ
1.0 g. Na	46	45
1.0 g. Na	185	179
2.0 g. Na	46	38
5.0 g. Na	46	26
5.0 g. Na	185	129
0.1 g. Ca	46	42
0.5 g. Ca	46	17
0.1 g. Mg	46	43
0.5 g. Mg	46	35
0.1 g. Mn	46	49
0.1 g. Al	46	51
0.1 g. Al	185	190
0.01 g. Ti (IV)	46	51
0.01 g. Ti (IV)	185	178
0.02 g. Ti (IV)	46	51
0.02 g. Ti (IV)	185	179
0.025 g. Fe (III)[b]	23	20
0.025 g. Fe (III)[b]	46	45
0.025 g. Fe (III)[b]	100	99
0.050 g. Fe (III)[c]	100	87

[a] Metals present as chlorides. Volume 100 ml.

[b] 1.0 ml. 10 per cent mercaptoacetic acid added.

[c] 2.0 ml. 10 per cent mercaptoacetic acid added.

temperature (within 1 or 2 degrees of a fixed temperature) for 1 hour. Obtain the transmittancy of the solution at 525 mμ.

B. Other Methods

Phenylarsonic acid and various derivatives yield slightly soluble precipitates with zirconium in acid solution. *p*-Dimethylaminoazophenylarsonic acid[8] gives a colored precipitate which after washing can be decomposed with ammonium hydroxide and the yellow color of the resulting solution measured.[9] This method has been applied to the determination of zirconium in steel.[10] Hök was unable to obtain satisfactory results in the determination of zirconium in pure solution with this reagent.[5] At low zirconium concentrations low results were obtained because of solubility loss, and at higher concentrations the values were high (ratio of reagent to zirconium in the precipitate greater than the theoretical 1:1).

Carminic acid and morin have been used as qualitative reagents for zirconium. Morin gives a fluorescence in 0.0001 *M* zirconium solution in 10 *M* hydrochloric acid (p. 127); titanium does not react.

[8] F. Feigl, P. Krumholz, and E. Rajmann, *Mikrochemie*, **9**, 395 (1931).
[9] V. A. Nazarenko, *J. Applied Chem. U. S. S. R.*, **10**, 1696 (1937).
[10] W. G. Hayes and E. W. Jones, *Ind. Eng. Chem., Anal. Ed.*, **13**, 603 (1941).

APPENDIX

TABLE 104

FOUR-PLACE LOGARITHMS

N	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	16	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	4	5	7	9	10	12	14	16
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	12	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	5	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	7	8	9	11	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	2	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	4	5	6	7	8	9	11
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

TABLE 104—*Continued*

FOUR-PLACE LOGARITHMS

N	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	6	7	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	5	6	7	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	3	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	1	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	3	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	5	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	3	3	4	4	5	6
N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

TABLE 104—*Continued*

FOUR-PLACE LOGARITHMS

N	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	3	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	3	3	4	4	5	6
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	3	3	4	4	5	6
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	4	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	1	1	2	2	3	3	4	4	5
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	3	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

TABLE 105

TRANSMISSION-EXTINCTION TABLE

100 I/I_0	Log I_0/I	100 I/I_0	Log I_0/I	100 I/I_0	Log I_0/I
99.8	0.0009	91.4	0.039	83.0	0.081
99.6	0.0017	91.2	0.040	82.8	0.082
99.4	0.0026	91.0	0.041	82.6	0.083
99.2	0.0035	90.8	0.042	82.4	0.084
99.0	0.0044	90.6	0.043	82.2	0.085
98.8	0.0052	90.4	0.044	82.0	0.086
98.6	0.0061	90.2	0.045	81.8	0.087
98.4	0.0070	90.0	0.046	81.6	0.088
98.2	0.0079	89.8	0.047	81.4	0.089
98.0	0.0088	89.6	0.048	81.2	0.090
97.8	0.0097	89.4	0.049	81.0	0.092
97.6	0.0106	89.2	0.050	80.8	0.093
97.4	0.0114	89.0	0.051	80.6	0.094
97.2	0.0123	88.8	0.052	80.4	0.095
97.0	0.0132	88.6	0.053	80.2	0.096
96.8	0.0141	88.4	0.054	80.0	0.097
96.6	0.0150	88.2	0.054	79.8	0.098
96.4	0.0159	88.0	0.055	79.6	0.099
96.2	0.0168	87.8	0.056	79.4	0.100
96.0	0.0177	87.6	0.057	79.2	0.101
95.8	0.0186	87.4	0.058	79.0	0.102
95.6	0.0195	87.2	0.059	78.8	0.103
95.4	0.0205	87.0	0.060	78.6	0.105
95.2	0.0214	86.8	0.061	78.4	0.106
95.0	0.0223	86.6	0.062	78.2	0.107
94.8	0.0232	86.4	0.063	78.0	0.108
94.6	0.0241	86.2	0.064	77.8	0.109
94.4	0.0250	86.0	0.066	77.6	0.110
94.2	0.026	85.8	0.067	77.4	0.111
94.0	0.027	85.6	0.068	77.2	0.112
93.8	0.028	85.4	0.069	77.0	0.113
93.6	0.029	85.2	0.070	76.8	0.115
93.4	0.030	85.0	0.071	76.6	0.116
93.2	0.031	84.8	0.072	76.4	0.117
93.0	0.032	84.6	0.073	76.2	0.118
92.8	0.032	84.4	0.074	76.0	0.119
92.6	0.033	84.2	0.075	75.8	0.120
92.4	0.034	84.0	0.076	75.6	0.121
92.2	0.035	83.8	0.077	75.4	0.123
92.0	0.036	83.6	0.078	75.2	0.124
91.8	0.037	83.4	0.079	75.0	0.125
91.6	0.038	83.2	0.080		

TABLE 106

INTERNATIONAL ATOMIC WEIGHTS, 1948

Aluminum	26.97	Molybdenum	95.95
Antimony	121.76	Neodymium	144.27
Argon	39.944	Neon	20.183
Arsenic	74.91	Nickel	58.69
Barium	137.36	Nitrogen	14.008
Beryllium	9.02	Osmium	190.2
Bismuth	209.00	Oxygen	16.0000
Boron	10.82	Palladium	106.7
Bromine	79.916	Phosphorus	30.98
Cadmium	112.41	Platinum	195.23
Calcium	40.08	Potassium	39.096
Carbon	12.010	Praseodymium	140.92
Cerium	140.13	Protactinium	231
Cesium	132.91	Radium	226.05
Chlorine	35.457	Radon	222
Chromium	52.01	Rhenium	186.31
Cobalt	58.94	Rhodium	102.91
Columbium	92.91	Rubidium	85.48
Copper	63.54	Ruthenium	101.7
Dysprosium	162.46	Samarium	150.43
Erbium	167.2	Scandium	45.10
Europium	152.0	Selenium	78.96
Fluorine	19.00	Silicon	28.06
Gadolinium	156.9	Silver	107.880
Gallium	69.72	Sodium	22.997
Germanium	72.60	Strontium	87.63
Gold	197.2	Sulfur	32.066
Hafnium	178.6	Tantalum	180.88
Helium	4.003	Tellurium	127.61
Holmium	164.94	Terbium	159.2
Hydrogen	1.0080	Thallium	204.39
Indium	114.76	Thorium	232.12
Iodine	126.92	Thulium	169.4
Iridium	193.1	Tin	118.70
Iron	55.85	Titanium	47.90
Krypton	83.7	Tungsten	183.92
Lanthanum	138.92	Uranium	238.07
Lead	207.21	Vanadium	50.95
Lithium	6.940	Xenon	131.3
Lutecium	174.99	Ytterbium	173.04
Magnesium	24.32	Yttrium	88.92
Manganese	54.93	Zinc	65.38
Mercury	200.61	Zirconium	91.22

TABLE 107

SENSITIVITIES OF COLOR REACTIONS[a]

Element	Reagent	Minimum amount detectable per cm.², γ	
		Visually	Spectrophotometrically
Ag	*p*-Diethylaminobenzylidenerhodanine	—	0.01 (green filter)
	Dithionite (NH_4OH)	0.3	
	Dithizone	—	0.01 (yellow filter)
Al	Alizarin S	—	0.003 (580 mμ)
	Aurintricarboxylate (*p*H 5.5)	0.01	0.002 (green filter)
	Oxine (soln. of ppt. in $CHCl_3$)	—	0.00035 (260 mμ), *ca.* 0.0025 (395 mμ)
	Oxine (indirect, solution of ppt. in HCl)	—	0.0002 (252 mμ)
As	Molybdate-hydrazine sulfate	—	0.01 (red filter)
Au	As $AuBr_4^-$	<10	0.04 (380 mμ)
	p-Diethylaminobenzylidenerhodanine (0.1 *N* HCl)	0.05–0.1	0.01 (green filter)
	Stannous chloride	—	0.05
	o-Tolidine	0.05	0.004 (437 mμ)
Be	Aurintricarboxylate	—	0.004 (535 mμ)
	Morin (fluorescence)	*ca.* 0.002	
	p-Nitrobenzeneazoorcinol	—	0.005 (525 mμ)
	Quinalizarin	*ca.* 0.1	
Bi	Iodide	0.5	0.1 (*ca.* 460 mμ)
	Phenyldithiobiazolonethiol	—	*ca.* 0.01 (460 mμ)
Cb	Hydrogen peroxide (conc. H_2SO_4 soln.)	10	
	Quinalizarin (conc. H_2SO_4 soln.)	5	
Cd	Dithizone (CCl_4)	0.03	0.001 (520 mμ)
Ce	As Ce^{++++}	15	0.4 (blue filter); 0.025 (320 mμ)
Cl (free)	*p*-Aminodimethylaniline	—	0.004 (550 mμ)
Co	Hydrochloric acid (conc.)	—	0.2 (625 mμ)
	Nitroso-R salt	0.01	0.002 (green filter)
	o-Nitrosoresorcinol	—	0.0025 (430 mμ)
	Thiocyanate-acetone	1	
Cr	As $CrO_4^=$	1.0	0.01 (366 mμ), 0.17 (436 mμ), 0.4 (450 mμ)
	Diphenylcarbazide	0.03	0.002 (540 mμ); 0.002 (550 mμ, in cyclohexanol)
Cu	Ammonia	10	0.8 (620 mμ)
	Dithizone (CCl_4)	—	0.003 (508 mμ), 0.004 (red filter)
	Hydrochloric acid (9 *N*)	0.5	0.01 (436 mμ); 0.5 (970 mμ)
	Sodium diethyldithiocarbamate (H_2O)	0.05	0.01 (blue filter)
	Sodium diethyldithiocarbamate (CCl_4)	—	0.02 (blue filter); 0.01 (430 mμ)
Fe	*o*-Phenanthroline	0.05	0.005 (510 mμ)
	Thiocyanate (*cf.* p. 364)	0.1	0.01 (green filter)
Ga	8-Hydroxyquinoline (fluorescence in $CHCl_3$)	0.1	
Ge	As germanomolybdate	2	0.03 (400 mμ); 0.1 (440 mμ)
	Molybdate-$FeSO_4$	0.5–1	0.008 (830 mμ)

Table continued

TABLE 107—*Continued*

SENSITIVITIES OF COLOR REACTIONS

Element	Reagent	Minimum amount detectable per cm.², γ	
		Visually	Spectrophotometrically
Hg	Dithizone (CCl_4)	—	0.008 (red filter)
In	8-Hydroxyquinoline ($CHCl_3$)	—	0.02 (400 mμ)
Ir	As $IrCl_6^-$	2	
Mg	Brilliant yellow	—	0.02 (green filter)
	Quinalizarin	0.1	0.017 (600 mμ)
	Titan yellow	0.05	0.006 (green filter)
Mn	Formaldoxime	—	0.005 (470 mμ filter)
	As MnO_4^-	0.1	0.027 (522 mμ)
	4,4′-Tetramethyldiaminotriphenylmethane	—	0.0001 (475 mμ)
Mo	Hydrogen peroxide	—	0.1 (330 mμ)
	Thiocyanate-stannous chloride	—	0.03 (H_2O soln., blue filter); 0.015 (ether soln., blue filter); 0.01 (isoamyl alcohol, 475 mμ filter)
$N(NO_2^-)$	Griess	—	0.0003 (520 mμ)
$N(NH_3)$	Nessler	—	0.003 (410 mμ)
Ni	Bromine-dimethylglyoxime	0.05–0.1	0.01 (green filter); 0.004 (450 mμ)
	Dimethylglyoxime	—	0.01 (pyridine, blue-green filter)
	Sodium diethyldithiocarbamate	—	0.015 (isoamyl alcohol, 385 mμ)
Os	Thiourea	—	0.1 (blue filter)
P	Molybdate-stannous chloride	—	0.001 (700 mμ)
	As $H_3[P(Mo_3O_{10})_4]$	—	0.01 (380 mμ)
Pb	Dithizone (CCl_4)	—	0.003 (520 mμ)
Pd	*p*-Diethylaminobenzylidenerhodanine (0.02 *N* HCl)	0.01	
	Nitrosodiphenylamine	0.05	
Pt	Iodide	0.5	0.03 (blue-green filter)
	Stannous chloride	—	0.02 (blue filter)
Re	Thiocyanate-stannous chloride (ether solution)	—	0.005 (440 mμ)
Rh	Stannous chloride	0.5	<0.02 (blue filter)
	As Rh^V (persulfate oxidation)	—	0.15 (375 mμ); 0.2 (525 mμ)
Ru	Hydrobromic acid	0.4	
	5-Hydroxyquinoline-8-carboxylic acid	—	0.02 (green filter)
	Thiourea	—	0.05 (red filter)
	Phenylthiosemicarbazide	0.5	0.03 (blue filter)
Sb	Potassium iodide	1	0.04 (425 mμ)
	Rhodamine B	—	0.003 (benzene, 565 mμ)
Si	Molybdate	—	0.01 (390 mμ)
Te	Stannous chloride	—	0.05 (white light)
Ti	Disodium-1,2-dihydroxybenzene-3,5-disulfonate	—	0.003 (410 mμ)
	Hydrogen peroxide	—	0.07 (400 mμ), 0.1 (450 mμ), 1.4 (546 mμ)
U	Hydrogen peroxide (Na_2CO_3 soln.)	—	0.2 (520 mμ)
	Sulfosalicylic acid	—	0.4 (400 mμ)
	Thiocyanate	—	0.07 (365 mμ)

Table continued

TABLE 107—*Continued*

SENSITIVITIES OF COLOR REACTIONS

Element	Reagent	Minimum amount detectable per cm.^{2}, γ	
		Visually	Spectrophotometrically
V	Benzoylphenylhydroxylamine	—	0.02 (480 mμ)
	Hydrogen peroxide	2	0.17 (450 mμ)
	Phosphotungstic acid	1	0.027 (400 mμ), 0.045 (440 mμ)
W	Hydroquinone	—	0.04 (570 mμ)
	Thiocyanate-stannous chloride	0.3	0.2 (blue filter); 0.05 (390 mμ, ether)
Zn	Dithizone (CCl_4)	—	0.004 (red filter), 0.0016 (green filter)
Zr	Alizarin	—	0.02 (560 mμ)
	Alizarin sulfonic acid	—	0.013 (520 mμ)

[a] For many reactions the sensitivity will depend on the conditions. Most of the sensitivities reported in this table pertain to the methods described in the text. See p. 47 for an explanation of the method of expression of sensitivities.

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