UNIVERSAL
LIBRARY

OU_158704

UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No. 669 N155. Accession No. 34100

Author Naish, William Archibald. Sottish.

Title Select methods of metallurgical analysis. 1953

This book should be returned on or before the date last marked below.

SELECT METHODS OF
METALLURGICAL ANALYSIS

SELECT METHODS OF METALLURGICAL ANALYSIS

BY

WILLIAM ARCHIBALD NAISH

PH.D., A.R.S.M., B.SC., F.R.I.C.

Late Head of Metallurgical Department, Battersea Polytechnic, London

JOHN EDWARD CLENNELL

B.SC. (LONDON), ASSOC.INST.M.M.

Author of Chemistry of Cyanide Solutions *and of* The Cyanide Handbook

AND

VICTOR S. KINGSWOOD

M.SC., B.SC., F.I.M.

Deputy Head of Metallurgical Department, Battersea Polytechnic, London

SECOND EDITION

REVISED

LONDON

CHAPMAN & HALL LTD.

37, ESSEX STREET, W.C.2

1953

First published, 1929
Second Edition, revised, 1953

Catalogue No. 278/4

PRINTED IN GREAT BRITAIN BY J. W. ARROWSMITH LTD., BRISTOL
BOUND BY G. & J. KITCAT LTD., LONDON *Flexiback Binding*

PREFACE TO SECOND EDITION

ALTHOUGH the principles of classical methods of analysis have not changed appreciably since the original publication of " Naish and Clennell " in 1929, there has been a considerable alteration in the approach to technical methods and it became evident that if a second edition was to be prescribed, it should be on specialized lines, whilst still retaining the set-up of the first edition in that the essential chemistry of the methods given should be included preferably in a self-contained section.

My old friend and collaborator, Mr. J. E. Clennell having died, the wisest policy appeared to be to set up an Editorial Panel on which I have been fortunate to enlist the services of specialists. The composition of this Panel is given in full elsewhere and I offer grateful thanks to the members and acknowledgment for the courtesy of their respective firms.

I have personally acted as editor and chairman of the Panel, and Mr. V. S. Kingswood has been of invaluable assistance, as assistant editor, especially with regard to the alphabetical chemistry of the elements, for which he has been solely responsible.

I have also to acknowledge the help of Mr. Dauncey in the earlier stages of preparation of the edition and I wish to acknowledge, with special thanks, the extremely valuable aid given by Mr. G. B. Salkeld, F.I.M. in indexing the volume.

It has been a difficult matter to make decisions as to the deletion of certain sections of the original book and to determine the nature and extent of some additions, and the Panel can only ask that these difficulties will be appreciated by those who may not approve of the decisions made.

I sincerely trust that the new edition will be of interest, and meet the needs not only of metallurgical chemists but also of advanced students.

I dedicate the edition to the memory of my old friend Mr. Clennell.

W. A. NAISH.

PREFACE TO FIRST EDITION

THIS book aims at presenting, in a concise form, a number of recommended methods of analysis for the elements met with in metallurgical work. The methods have been selected by the authors as being, in their opinion, the most rapid, accurate, and practical for the purpose in view. In most cases they have been tested by actual trial in their laboratory, and an attempt has been made to give, where possible, modern rapid methods, without sacrificing accuracy or sound principles of analytical chemistry.

The subject-matter of the text has been compiled with the primary object of providing practical and reliable analytical methods, together with the means of easy reference to standard works and original papers, for the use of metallurgical chemists, assayers, works chemists, and professional analysts, but an attempt has also been made to meet the requirements of advanced students by the incorporation of theoretical considerations, the explanation of reactions, and brief accounts of the properties of the elements upon which many of the separations and determinations are based.

Preliminary chapters on Sampling, Solution, Qualitative Tests and Separations have been introduced in order to render the book self-contained, and an enlarged set of Tables dealing with many of the so-called rare elements has been included.

A chapter on Mineral Analysis has been contributed by C. Stansfield Hitchen, A.R.C.S., B.Sc., the proofs of which have been very kindly read by Dr. H. F. Harwood, a chapter on Electrometric Titrations by A. Hebdon, B.Sc., and also a chapter on Spectrographic Methods of Analysis by A. A. Fitch, A.R.C.S., B.Sc. These contributions are gratefully acknowledged by the authors, who consider them to be of the greatest interest and value to metallurgical chemists.

The authors also wish gratefully to acknowledge valuable information in the matter of tried works methods from friendly experts, and especially, to tender their thanks to E. J. Ilott for considerable help in connection with non-ferrous alloys, to J. A. Cashmore, A.I.C., and R. C. Chirnside for contributions on refractory materials, to J. H. Kittow for expert information on the analysis of the platinum group of metals, and to W. P. Horne for contributions on methods of ore analysis and analysis of aluminium.

Acknowledgments are also made to Messrs. J. Weir & Co., Ltd., Glasgow, and to the Metallurgical Corporation Ltd., Stratford, E., for courteously supplying special methods of analysis of Monel metal and complex zinc ores; to Messrs. Adam Hilger Ltd., London, for supplying illustrations in connection with Spectrographic Analysis; also to the Institution of Mining and Metallurgy for permission to incorporate their table of standard laboratory screens.

Finally the authors wish to acknowledge with special thanks the extremely valuable aid given by C. A. Silberrad, B.A., B.Sc., in editing the bibliographies of the individual elements.

W.A.N.
J.E.C.

METALLURGICAL DEPARTMENT,
CHELSEA POLYTECHNIC, S.W. 3.

EDITORIAL PANEL

EDITOR : W. A. Naish, Ph.D., A.R.S.M., B.Sc., F.R.I.C., Battersea Polytechnic.
ASST. EDITOR : V. S. Kingswood, M.Sc., B.Sc., F.I.M., Battersea Polytechnic.

CONTRIBUTORS

Iron, Steel and Ferro-Alloy Analysis :	J. K. Wilson, A.I.M., A.F.R.Ae.S. O. Wright, A.I.M., A.R.Ae.S. F. H. Henstock, A.Met. (Sheffield). Messrs. D. Napier & Son, Ltd., Acton.
Aluminium and Magnesium Alloy Analysis :	D. F. Phillips, A.R.I.C. late Messrs. High Duty Alloys, Ltd., Slough, Bucks.
Analysis of Copper Base Alloys :	W. T. Edwards, F.R.I.C., A.I.M. Post Office Engineering Dept., (late Messrs. Langley Alloys, Ltd., Langley, Bucks.)
Analysis of Refractory Materials :	J. A. Cashmore, F.R.I.C., F.I.M. Messrs. The Morgan Crucible Co. Ltd., Battersea.
Analysis of Coal and Coke	R. Belcher, B.Sc., Ph.D., F.R.I.C., F.Inst.F., Birmingham University. C. E. Spooner, B.Sc., M.Sc., (Tech.), F.R.I.C., M.Inst.F. Manchester College of Technology.
Analysis for Impurities in Metals :	*Aluminium.* Messrs. The British Aluminium Co. Ltd. *Copper.* W. T. Edwards, late of Messrs. Langley Alloys, Ltd. *Lead and Antimony.* Messrs. Goodlass, Wall and Lead Industries, Ltd. *Nickel.* Messrs. Telegraph Construction and Maintenance Co. Ltd. *Tin.* Messrs. Capper Pass & Son, Ltd. *Zinc.* Messrs. The Imperial Smelting Corporation, Ltd.
Analysis of Iron Ores and Iron Slags :	Messrs. Stewarts and Lloyds, Ltd., Corby.
Physical Methods of Analysis, Spectrographic Methods :	L. L. Edwards (Research Laboratories). Messrs. High Duty Alloys, Ltd., Slough, Bucks.
Micro-Analysis :	D. F. Phillips, A.R.I.C., Hon. Sec., Microchemistry Group, Society of Public Analysts and other Analytical Chemists.
Electrolytic, Electrometric, Absorptiometric, Polarographic, Colorimetric and Spectrophotometric Methods :	S. T. Payne, Esq. (Research Laboratories). Messrs. Johnson, Matthey & Co., Ltd., Wembley.

CONTENTS

PART ONE

Chapter		*Page*
I.	SAMPLING OF ORES, ALLOYS AND OTHER METALLURGICAL PRODUCTS	3
II.	STANDARD METHODS OF SOLUTION AND SEPARATION	11
III.	QUALITATIVE ANALYSIS	
	Section 1. Dry tests for the common metals .	25
	Section 2. Confirmatory tests for the detection of the metals	28
	Section 3. General classification of the metals .	41

PART TWO

IV.	SELECTED METHODS FOR THE ANALYSIS OF THE ELEMENTS, ARRANGED IN ALPHABETICAL ORDER .	45

PART THREE

V.	ANALYSIS OF COMMERCIAL METALS, INCLUDING ALUMINIUM, ANTIMONY, COPPER, LEAD, NICKEL, TIN, ZINC	275
VI.	TECHNICAL ANALYSIS OF NON-FERROUS ALLOYS	
	Section 1. Aluminium and magnesium alloys .	323
	Section 2. Commercial copper-base alloys .	356
	Section 3. White metals : tin and lead base bearing alloys	372
	Section 4. Zinc base alloys	382
	Section 5. The platinum group metals and alloys	386
VII.	TECHNICAL ANALYSIS OF IRONS, STEELS AND FERRO-ALLOYS	405

PART FOUR

VIII.	THE ANALYSIS OF ORES	497
IX.	THE ANALYSIS OF SLAGS	516

PART FIVE

X. THE ANALYSIS OF REFRACTORY MATERIALS . . 531
XI. THE ANALYSIS OF COAL AND COKE . . . 553

PART SIX

XII. MODERN PHYSICO-CHEMICAL METHODS OF ANALYSIS 577

APPENDIX

Section 1. Standard solutions for volumetric analysis 635
Section 2. International atomic weights . . 640
Section 3. Gravimetric factors 642
Section 4. The use and care of platinum apparatus 644

INDEXES 646

PART ONE

Sampling. Standard Methods of Solution and Separation. Qualitative Analysis—including Dry Tests for the Common Metals, Confirmatory Tests, and General Classification of the Metals.

CHAPTER I

SAMPLING OF ORES, ALLOYS AND OTHER METALLURGICAL PRODUCTS

Definition of Sample

The selection of a correct sample is a necessary preliminary to every assay or analysis. It is obvious that the analysis is of no value unless the portion analysed really represents the average composition of the material from which it was selected. We may thus define a sample as a small portion containing the same ingredients (or at least the ingredient which has to be estimated) in the same proportions that occur in the relatively large mass of the original material.

Heterogeneous Nature of Material to be Assayed

In the case of a chemically pure compound, there is no difficulty about this, as every portion, however large or small, contains its elements in the same proportion. In actual practice, however, such conditions are rarely found. All ordinary ores and metallurgical products contain their constituents unevenly distributed, and it is by no means always a simple matter to maintain the same proportions of these in the necessarily small portion selected for assay. The same is true, to a less extent, of alloys, bullion and other metallic material; the physical processes taking place during the cooling of these mixtures after melting frequently causes a segregation of different elements, known as liquation, resulting in a difference of composition between the inner and outer parts of the mass.

Subdivision of Samples

Ores and similar materials are generally dealt with in the first instance in the form of coarse lumps, in cars or trucks delivering ore from a mine to a mill, or in dumps, slag heaps and similar accumulations. The sampling of ore 'in place' in the mine hardly comes within the scope of this work.

Whether any further crushing should precede the selection of a first sample will depend on the relative size of the lumps and

of the entire mass, and also on the nature and distribution of the constituents.

The best way of sampling a large conical or hemispherical heap of such material is to dig one, or preferably several, channels across the heap through the centre to its full depth, the portion dug out in forming these channels being selected as a sample. In such heaps there is nearly always a difference in composition between the top and the outside edges, or between the upper and lower parts. The larger lumps in the selected portion are then broken up to a definite maximum size, thoroughly mixed (by turning over with a shovel, or otherwise), and the process repeated.

Smaller heaps are usually dealt with by the process of coning and quartering. The material is thrown into a conical heap, spread evenly on a smooth floor into a flat-topped circular heap, then divided across the centre into four equal segments. Two opposite quarters are withdrawn and rejected, the remainder being further crushed if necessary, and again coned and quartered. These operations are repeated until a sample is obtained which may conveniently be reduced to the degree of fineness required for analysis.

The crushing may be carried out by machines such as rock-breakers or gyratory crushers, or by hand, with a pestle and mortar, the finer crushing being done with a disc pulverizer or by hand with buckboard and muller. It is important to remember that every appliance used for crushing must be thoroughly cleaned after use before another sample is passed through it.

The division of the crushed sample may also be made by various sampling machines which select a definite fraction from a falling stream of material, either continuously or at regular intervals.

Size of Particles at Different Stages of Sampling

At each stage the particles of the sample should be reduced to a smaller size before mixing and subdividing. The degree of reduction necessary will depend, of course, on the nature of the material, but a safe rule, applicable to ordinary ores, is that the weight of the sample should vary as the cube of the diameter of the largest particles; in other words, if the sample has been crushed so that the size of its largest particles has been halved, it may then be divided so that one-eighth of its weight is selected for the next stage. Nearly the same result is obtained by reducing the particle size in the ratio 5 : 4 every time before halving the sample.

Harvey gives the following data for reduction of the smaller sizes :

Diameter of Largest Particles ins.	Minimum Allowable Weight of Sample lb.
$\frac{2}{3}$	256
$\frac{1}{3}$	32
$\frac{1}{6}$	4
$\frac{1}{12}$	$\frac{1}{2}$
$\frac{1}{25}$	$\frac{1}{16}$

Precautions in Preparing Samples

The necessity for careful cleaning of the appliances used has already been noted. All crushers, sieves, floors and cloths used in the process require attention in this respect, otherwise there is great probability that a sample may be 'salted' by mixture with material belonging to a previous sample. Brass-wire sieves may be cleaned by rubbing with a hard brush, and it is advisable to solder the joint between the sieve and the frame.

When the selected portion has to be passed through a sieve of given mesh, it is essential that the whole of that portion shall be reduced sufficiently fine to pass the sieve. If the harder portions which require most crushing, be rejected, the sample will be worthless.

It must also be remembered that sifting tends more or less to segregate different ingredients in the sample, according to size or specific gravity of the particles. It is therefore necessary to mix thoroughly after sifting and before further subdivision.

Aperture of Screens used in Preparing Samples

The fineness of the screens used is generally indicated by a number, which is supposed to represent the number of holes per linear inch.

There is considerable ambiguity about this, since the nature of the product passing, say, a '40 mesh' sieve will vary greatly according to the thickness of the wires and the shape of the apertures. 'Standard' screens have therefore been recommended by various authorities, the fineness of which is defined by the actual area of the apertures, in square inches or millimetres, and the wires are so arranged that the openings are exact squares. For special purposes circular apertures punched in a sheet of metal are sometimes used.

The set of screens recommended by the Institution of Mining and Metallurgy is as shown on next page.

Sampling of Sand and other Moderately Fine Material

It often happens that the assayer is called upon to sample large masses of a material which has already been crushed to a comparatively fine state of division, for example, ore leaving a gyratory crusher, rolls, stamp battery, tube mill or other pulverizer, in bulk or in separate car-loads, charges of such material in tanks, before or after some leaching process, dumps of tailings and so forth.

I.M.M. Standard Laboratory Screens

Mesh or Apertures per Linear Inch	Diameter of Wire		Aperture		Screening Area
	in.	*mm.*	in.	*mm.*	per cent
5	0·1	*2·540*	0·1	*2·540*	25·00
8	0·063	*1·600*	0·062	*1·574*	24·60
10	0·05	*1·270*	0·05	*1·270*	25·00
12	0·0417	*1·059*	0·0416	*1·056*	24·92
16	0·0313	*0·795*	0·0312	*0·792*	24·92
20	0·025	*0·635*	0·025	*0·635*	25·00
30	0·0167	*0·424*	0·0166	*0·421*	24·80
40	0·0125	*0·317*	0·0125	*0·317*	25·00
50	0·01	*0·254*	0·01	*0·254*	25·00
60	0·083	*0·211*	0·0083	*0·211*	24·80
70	0·0071	*0·180*	0·0071	*0·180*	24·70
80	0·0063	*0·160*	0·0062	*0·157*	24·60
90	0·0055	*0·139*	0·0055	*0·139*	24·50
100	0·005	*0·127*	0·005	*0·127*	25·00
120	0·0041	*0·104*	0·0042	*0·107*	25·40
150	0·0033	*0·084*	0·0033	*0·084*	24·50
200	0·0025	*0·063*	0·0025	*0·063*	25·00

The methods to be adopted vary according to circumstances, e.g. size of the mass, fineness, amount of moisture, nature of material, etc., but the general principle is the same as that given at the beginning of this chapter, viz., that the selected portion must represent the average composition of the mass.

Such samples are usually taken by means of a sampling rod. This consists of a metal tube slit for the greater part of its length and long enough to penetrate the entire mass to be sampled; the bottom end and edges of the groove are sharpened and a handle is provided at the upper end so that the rod may be twisted as it is pushed into the material. A uniform core is thus obtained representing a section of the mass in a given direction. A number of such cores taken at different points and mixed together gives a fairly representative sample.

It must be remembered that the material charged into a tank or

similar receptacle is seldom uniform. There is a tendency for the coarser and heavier particles to accumulate near the centre, and for the lighter and finer material to roll down the sides of the heap and collect at the sides or near the bottom.

Moisture Samples

When the sample is moist and especially when it contains soluble matter which it is desired to include in the assay, it is necessary to take special precautions in drying before further reduction. The temperature must be so regulated as not to alter the chemical composition of the material.

In some cases it is necessary to determine the percentage of a certain ingredient in material containing moisture. As the analysis cannot be made on the moist sample, it is necessary to take a separate 'moisture sample.' This may be done by spreading the material in a uniform layer and selecting with a scoop a sufficient amount (say 500 or 1000 g), which is weighed at once and dried in a porcelain or enamelled iron dish on a hot plate or otherwise, at the same temperature that is used in drying the assay sample. The dish and contents are then again weighed, the loss of weight indicating the moisture. The necessary correction may then be made on the assay of the dry material to give the calculated assay of the wet material.

Samples for analyses must frequently be dried in a steam oven at a definite temperature, as they may contain constituents which would be decomposed or volatilized at a higher temperature.

Final Preparation of the Assay Sample

The dry material, after each successive passage through the series of sieves, is rolled backwards and forwards and in different directions on a smooth sheet of glazed paper, rubber or oil-cloth, divided, and the selected portion further ground as already described. The fraction ultimately reserved for a sample is then reduced to the degree of fineness necessary for the analytical process to be adopted. In the case of gold and silver ores, where the assay is made on a comparatively large quantity of material, it is usually unnecessary to grind finer than 60 to 80 mesh, or in special cases, to 120 mesh. For ordinary analyses, where only a few grammes or a fraction of a gramme is taken for the actual determination, the material must generally be ground as fine as possible, this being generally done in an agate mortar, until no gritty particles can be detected. When a sample has been ground in an iron mortar it is sometimes necessary to remove with a magnet particles of iron derived from the mortar or pestle.

Treatment of Samples containing 'Metallics'

Rich ores frequently contain shots or flakes of metal (gold-silver alloys, native silver, copper, and so forth) of much higher assay-value than the remainder. As this material cannot conveniently be pulverized, it is necessary to separate it and assay it separately. The entire sample is first weighed, and as much as possible passed through a fine sieve. The whole of the material which remains on the sieve is usually treated to determine the percentage of the required constituent in it, and the same constituent is determined on an assay sample of the fines passing the sieve.

The general formula for calculating the result is as follows :

Let M = weight of metallics (remaining on sieve).
F = total weight of fines passing sieve.
a = assay of metallics (in any units).
b = assay of fines (in the same units).
x = assay of entire sample.

Then $$x = \frac{Ma + Fb}{M + F}.$$

A special case of this is given in *Cyanide Handbook*, 2nd ed. (1915), 442, for the calculation of gold or silver assays in terms of dwt. per ton of 2000 lb. A similar formula, based on oz. per ton of 2000 lb., is as follows :

Let M = weight of metallics in grammes.
F = weight of fines in grammes.
m = weight of ingredient sought, in mgr. contained in M.
f = assay value of fines, in oz. per ton of 2000 lb.

Then, since there are as many mgr. in $29\frac{1}{6}$ g. as there are oz. Troy in 2000 lb. Av., the total weight of ingredient sought is

$$m + \frac{6}{175} Ff,$$

or $$x = \frac{Ff + \frac{175m}{6}}{M + F}.$$

Sampling of Metals and Alloys

Material such as gold and silver bullion, ingots of copper, lead, zinc and other metals or alloys such as brass or bronze, cannot be

sampled by crushing and dividing in the way described above. Such products are usually sampled either in the molten condition, or by drilling, after casting into bars.

Dip Samples.—These are taken from the bath of molten metal, after thorough stirring, by means of a dipper usually made of graphite. The portion taken out is poured into a small mould, where it solidifies under a layer of slag, or if the nature of the material allows, the sample may be granulated by pouring into water. The particles may be subsequently reduced by hammering flat and cutting up with shears.

Drill Samples.—These are generally taken by means of a small machine drill, which revolves rapidly and cuts out turnings of the metal. Holes are drilled at selected points in the bar, usually to half-way through. As differences of composition exist in different parts, several holes are drilled and the drillings either mixed, or assayed separately. Any accidental impurities, such as particles of slag, are removed, and if grease is present a wash with ether or benzine may be given.

Cut samples are sometimes taken by chipping the corners or edges of bars, but this practice is not recommended, as the metal at these points is seldom of average composition.

Sampling of Metal Scrap, etc.

Heavy Scrap.—Old castings, sheet-plate, foundry 'risers,' old tube, etc.

Take representative pieces from the whole heap or consignment and then take drillings or sawings from all the selected pieces, mix together, and use these as assay sample or (preferably) remelt into a bar and take sawings.

Light Scrap.—Small light castings, thin sheet, ' spillings,' etc.

Treat as above, but it is not usually advisable to *remelt* in this case.

Gun Metal and Brass Borings.—Take several scoopfuls of material from all over heap. If in *casks* it is best to empty the same.

If uniform, take an assay sample from the amount obtained—if any doubt exists of uniformity the borings must be melted down and the resultant bar used as sample, but in this case the ' melting loss,' which may be considerable, must be noted and allowance made for same in assay result.

Mixed borings, i.e. yellow and white metal borings.

Obtain a representative sample as before, but in this case it is *essential* that the final sample should be melted, as it is impossible otherwise to obtain a true valuation. Note 'loss' as before.

Ingot or Pig Metal.—Ingot brass, bronze, lead, spelter, etc.

Drill *right through* the ingot in several places. Mix drillings and remelt for assay sample bar.

As an alternative method, sawcuts may be made right through the ingot at various places ; the sawings, which should be fine, are mixed together.

CHAPTER II

STANDARD METHODS OF SOLUTION AND SEPARATION

STANDARD METHODS OF SOLUTION

(1) *For Ores in General.*—The weighed portion of ore or mineral for analysis is placed in a suitable flask or beaker (an Erlenmayer flask of about 250 ml. capacity is usually convenient) and acids added according to the nature of the constituents present. For an ordinary siliceous ore, take 0·5 g ore and 10 ml. conc. HCl, warm gently for some time till no further action appears to be taking place, then add 5 ml. conc. HNO_3, warm gently, then more strongly till red fumes are given off. Cool somewhat, then add 5 ml. of conc. H_2SO_4 and evaporate till dense white fumes (SO_3) come off freely, filling the interior of the flask or beaker. Cool thoroughly, add about 50 ml. of water and 5 ml. conc. HCl. Boil for a few minutes, allow to settle thoroughly, filter, wash with hot water or dilute HCl.

In many cases this treatment will suffice to get the whole of such metals as copper, bismuth, iron, zinc, manganese, etc., into solution, leaving an insoluble residue consisting mainly of silica, but perhaps also containing lead or barium as sulphates and some undecomposed silicates of the alkalis or alkaline earths.

(2) *Standard Procedure for Sulphide Ores* (applicable in some cases where the sulphur is to be determined).—Treat 0·5 g with 10 ml. conc. HNO_3, heating very gently at first. Add about 0·3 g $KClO_3$ in small portions at a time avoiding if possible any separation of free sulphur by boiling gently. When all sulphides are decomposed, evaporate to complete dryness. Cool; add 5 ml. conc. HCl, gradually. Heat gently, add more HCl if necessary, and again evaporate to dryness to decompose all chlorates and nitrates. Finally, take up with 5 ml. conc. HCl and 100 ml. water, boil, settle and filter.

(3) *Procedure when Silica has to be Determined.*—(In accurate

determinations this process is preceded by fusion of the ore with alkali carbonates as described below.) 0·5 g ore is usually taken for analysis.

Add HCl to the solution of the melt in water, until the acid is in excess, or (in direct treatment of an ore) add 10 ml. conc. HCl. Evaporate on a hot plate to small bulk, then finish on water bath. (When small quantities of sulphides are present, add about 5 ml. conc. HNO_3 after digesting some time with HCl.) Bake on hot plate or sand-bath at about 150° C. for half an hour, add 20 ml. conc. HCl, warm gently (say for 10 minutes), add 100 ml. water, boil, settle, filter. For complete removal of the silica the filtrate must be evaporated again and the process repeated at least twice, washing the residue each time with hot water or hot dilute HCl.

(4) In many cases a complete removal of the silica may be obtained by treating as in Method No. 1, but boiling with conc. H_2SO_4 until no further deposition of moisture is observed on a cold watch-glass held over the mouth of the flask. This indicates that the silica has been completely dehydrated and, after cooling and diluting, may be filtered off without any of it passing into solution.

(5) *Procedure for Ores containing Lead.*—Treat 0·5 g with 10 ml. conc. HCl. When action has ceased add 5 ml. conc. HNO_3, boil off red fumes (if necessary add more HCl at this stage). When ore appears to be completely decomposed add 5 ml. conc. H_2SO_4, boil till white fumes are freely evolved. Cool, add 30 ml. water, boil, allow to stand hot till iron salts have dissolved. Cool, filter, wash with (1 : 10)H_2SO_4. (Barium is also separated by this procedure.)

(6) *Procedure for Ores containing Zinc.*—Treat 0·5 g with 5 ml. conc. HCl and 10 ml. conc. HNO_3. Boil to a small bulk; add 10 to 15 ml. conc. HNO_3 and 5 g. $KClO_3$. Evaporate just to dryness. Add about 10 g NH_4Cl and 20 to 25 ml. strong ammonia, stir and boil very gently, then add bromine water (10 to 25 ml., according to amount of Mn present). Boil, filter, wash with hot dilute NH_4Cl + NH_4OH. [This serves to separate iron, aluminium, manganese and silica from zinc and other metals.]

(7) In certain cases ores or alloys may be completely dissolved by treatment with a single acid, or a small residue may be left which is subsequently treated by fusion or with other acids. Most zinc and aluminium alloys are completely, or almost completely, soluble in HCl. Brass and other copper alloys are soluble in HNO_3 with or without a small residue. Alloys containing tin are generally evaporated with HNO_3, and the residue taken up with water or

dilute HNO_3, whereby the tin remains as insoluble metastannic acid, the other ingredients being dissolved.

STANDARD FUSION PROCESSES

It often happens that certain ingredients of an ore or alloy resist solution in acids. In such cases they may generally be taken into solution by fusing the original dry substance or the dried residue left after acid treatment with a suitable flux, extracting the mass resulting from the fusion (generally called the 'melt') with water or other solvent, and separating the required ingredient from the solution thus obtained.

(1) *Fusion with Alkali Carbonates.*—This is the commonest process used, and is applicable to all siliceous material. The crucible used must be of metal, platinum being the best, but in many cases nickel, iron or silver crucibles may be used. It must be remembered, however, that all of them are more or less attacked by the flux and that small quantities of metal from the crucible will be present in the extract of the melt.

The usual flux is a mixture of sodium and potassium carbonates, known as 'fusion mixture.' The best mixture consists of 3 parts Na_2CO_3 and 2 parts K_2CO_3 (both anhydrous). The quantity used is about 10 parts by weight of this mixture to 1 part by weight of ore. The ingredients are mixed thoroughly and the crucible and contents heated very gradually for some time till moisture and the greater part of the CO_2 have been expelled. This may be done over a Bunsen burner or at the mouth of a muffle. The crucible is then heated more strongly (at a good red heat), until all bubbling has ceased and the mass is completely fused. The crucible is then allowed to cool, and the mass disintegrated by placing in cold water and warming till dissolved. Often the greater part of the melt may be detached by suddenly cooling the outside of the crucible and allowing a drop of water to fall on the edge of the solidified cake, which is then placed in water and the crucible rinsed out.

The further treatment of the melt will depend upon circumstances. In many cases it is acidified with HCl, boiled or evaporated to dryness.

Frequently only a portion of the melt is soluble after fusion and extraction with water, as in the case of ores containing $BaSO_4$, in which case the insoluble portion (e.g. $BaCO_3$) is filtered off and washed with hot water.

(2) *Fusion with an Alkaline Oxidizing Mixture.*—This method is necessary when the material to be fused contains sulphides or

other oxidizable material which is to be removed or rendered soluble. In this case metal crucibles other than nickel or platinum are generally inadmissible, and a platinum crucible should not be used unless lead, bismuth and other readily reducible metals are absent or removed by a previous operation. Porcelain or silica vessels cannot be used, as the silica and alumina would be attacked.

The usual flux is a mixture of sodium carbonate and potassium nitrate, both dry. One part of ore may be fused with a mixture of 5 parts Na_2CO_3 and 5 parts KNO_3. For large quantities a platinum dish may be used instead of a crucible. Usually a portion of the flux is reserved and used as a cover. The crucible is heated gradually and gently till the contents are completely fused, finally at a good red heat. The melt is extracted as in Method No. 1, and further treated as required.

(3) *Fusion with Sodium Peroxide.*—This process can be carried out at a much lower temperature than the preceding, consequently nickel, silver and even iron crucibles may sometimes be used, though in all cases they are somewhat attacked. Porcelain and silica vessels are not suitable. The amount of sodium peroxide to be used is generally about five times the weight of ore taken. It is often a good plan to fuse the peroxide first by itself, allow to cool somewhat, and add the finely-ground ore in small portions at a time, allowing each portion to fuse before adding another. In general, the fusion is complete in five to ten minutes, and only a dull red heat is necessary. The melt is extracted with water and treated as in other fusion methods. It is generally necessary to boil in order to expel the H_2O_2 liberated when the excess of peroxide is dissolved in water.

The method is especially useful for tin and chromium ores, and for oxidizing small quantities of silicon to silica in the residue left after acid treatment of certain alloys.

(4) *Fusion with Caustic Alkalis.*—This method is sometimes used when the use of carbonates or oxidizing mixtures is not desirable. Nickel, silver or iron crucibles or dishes may be used, as well as platinum, but not porcelain or silica. The quantity used may be from ten to twenty times the weight of the ore to be fused. The hydroxide must be fused separately before introducing the ore, and all water driven off. In some cases, where reducing conditions have to be maintained, charcoal is sprinkled on the melt; in other cases where oxidation is desirable, a little KNO_3 or Na_2O_2 may be added. The melt after fusion is extracted with water and treated as previously described. As the extract is usually strongly alkaline, it is often necessary partly to neutralize the alkali by adding a suitable acid before filtering.

(5) *Fusion with Potassium Cyanide.*—This may be carried out in any kind of metal crucible, also in some cases in porcelain, silica or clay crucibles.

The method is chiefly used in the dry assay of easily reducible metals such as tin and bismuth. Reducing conditions must be maintained; for this reason part of the cyanide is used as a cover, and frequently charcoal or other reducer is mixed with the charge. In the case of tin ores 2 to 4 parts of potassium cyanide are required for 1 part of ore. The fusion takes place at a moderate temperature, and as the melt is very fluid, it may generally be poured out into a suitable mould.

(6) *Fusion with Potassium Bisulphate or Pyrosulphate.*—This method is employed for minerals which contain iron, aluminium, and certain other metals in forms which resist ordinary acid treatment. It is especially useful in the treatment of ores containing tungsten and titanium. Porcelain or silica crucibles are suitable, and platinum may be used, but not other metallic vessels, as they would be attacked by the sulphuric acid evolved during the fusion. The amount of bisulphate, $KHSO_4$, or pyrosulphate, $K_2S_2O_7$, to be used depends on the circumstances, and may amount to as much as thirty times the weight of the ore. Part of the flux may be used as a cover and part mixed with the ore. Prolonged fusion is sometimes necessary for complete decomposition, but a very high temperature is not necessary or desirable. The melt is extracted with water, and further treated as required.

It must be remarked that in the fusions (1) to (4), in which an alkaline flux is used, the water extract contains the silica, if any, in the form of a soluble silicate, whereas after bisulphate fusion all or most of the silica is left in an insoluble form. If it is desired to remove this, the residue is filtered off, washed with hot water or dilute acid (HCl or H_2SO_4), dried and treated as follows:

(7) *Treatment of Insoluble Residues with Hydrofluoric Acid to remove Silica.*—This operation must be performed in a platinum crucible or dish. For rough purposes a lead vessel is sometimes employed. The dried and ignited residue is mixed in the dish or crucible with 2 to 3 ml. of pure hydrofluoric acid and about the same amount of conc. H_2SO_4 (in some cases, as when formation of $PbSO_4$ or $BaSO_4$ is to be avoided, HCl is used instead of H_2SO_4). The mixture is then cautiously evaporated to dryness, the silica being expelled as volatile SiF_4. The vessel is then ignited, allowed to cool and weighed, and the treatment with HF and other acid repeated until no further loss of weight occurs. The residue, if any, may then be dissolved in HCl or H_2SO_4 or, if insoluble, fused with potassium bisulphate as in (6).

WET METHODS OF SEPARATION

In the following section it will be assumed that the substance to be analysed has been completely decomposed and brought into solution, usually in hydrochloric acid, but sometimes in sulphuric acid and in special cases in an ammoniacal or caustic alkali solution. As a general rule, nitric acid must be eliminated by evaporation with HCl or H_2SO_4 before the following processes can be carried out:

(1) *Precipitation by Hydrogen Sulphide in Acid Solutions* (HCl or H_2SO_4).—The metals usually precipitated in this way are copper, bismuth, cadmium, arsenic, antimony and tin; occasionally lead, mercury, molybdenum and other rarer elements. As a rule, lead will have been previously separated as sulphate, as already described. The precipitation is best made in a hot, moderately acid solution. Excessive acidity must be avoided or Cd, Sb and Sn may be incompletely precipitated or not precipitated at all; on the other hand, if the acidity is too slight, zinc, nickel and cobalt may be thrown down together with the metals above mentioned.

For general purposes 10 ml. of HCl or 5 ml. of H_2SO_4 per 100 ml. of liquid at about 80°C. is sufficient, but where Sn or Cd have to be precipitated a more dilute solution should be used, say not more than 5 ml. HCl or 2 ml. H_2SO_4 per 100 ml. When the solution has been saturated with the gas it is allowed to stand covered for a few moments to settle, and the precipitate immediately filtered off and washed with hot water, adding from time to time a little distilled water saturated with H_2S. The filtrate should be clear, and show no turbidity on passing a further quantity of H_2S through it.

In cases where arsenic is present in the arsenic condition, it is advisable to reduce this to an arsenious salt by previous boiling of the solution with a sulphite or by passing SO_2 through it, since the element in the arsenic condition is very slowly reduced and precipitated by H_2S.

The order of solubility of the sulphides of the commoner metals in HCl is as follows:* As, Cu, Sb, Bi, Hg, Pb, Sn, Zn, Fe, Ni, Co, Mn (As being the least soluble). [For a detailed discussion of this subject, see Ibbotson and Aitchison, *Analysis of Non-Ferrous Alloys* (1915), Chapter III. 34.]

(2) *Separation of Sulphides soluble in Alkaline Media* (Hydroxides, Alkali Sulphides and Ammonia).—The sulphides of arsenic, antimony, tin, molybdenum (gold, platinum, iridium) and of selenium and tellurium are soluble more or less freely in caustic

* Reimsch, *J. Prakt. Chem.* 13. 129.

alkalis, sulphides of the alkali metals, ammonium sulphide and ammonium hydroxide. Copper sulphide is slightly soluble in ammonium sulphide and other ammonium compounds, and sulphide of mercury is somewhat soluble in sodium sulphide. Generally speaking, however, the sulphides of Ag, Hg, Pb, Bi, Cu and Cd are insoluble in alkalis or alkaline sulphides.

The precipitate, washed free of acid, is transferred to a suitable vessel and digested at a gentle heat with the alkaline solvent best adapted to the case (e.g. ammonium compounds are avoided when Cu is present). The liquid is then diluted, filtered and the residue washed first with a dilute solution of the alkaline solvent, and finally with hot water. In some cases it may be necessary to dissolve in acid and reprecipitate with H_2S, again treating the precipitate with the alkaline solvent, to obtain complete separation.

The filtrate is then made slightly acid, generally with HCl, when As, Sb, Sn, etc., are reprecipitated as sulphides. At this stage it is generally advisable to pass H_2S to ensure complete precipitation. The mixture is filtered, to remove the excess of alkali or ammonium salts, this filtrate being rejected.

The metals in the precipitates are then separated by suitable means which will be discussed later under the headings of the different metals.

(3) *Precipitation with Ammonium Hydroxide in the Filtrate from Sulphide Precipitate.*—In general, the first step is to boil off the excess of H_2S in the solution. It is then mixed with one or two drops (or when much iron is present 1 to 2 ml.) of conc. HNO_3 or H_2O_2 to oxidize the ferrous compounds to the ferric state, boiled for a moment, and allowed to cool somewhat. Ammonia is then added in slight excess, and generally 1 to 2, or even as much as 10 g of ammonium chloride. [In special cases after evaporation with HNO_3 ammonium nitrate* is added.] The solution is then boiled, for not more than two minutes, whereby iron, aluminium, chromium (in chromous or chromic salts, not in chromates), titanium, and a number of rarer metals are precipitated as hydroxides. When insufficient ammonium chloride has been added, large amounts of zinc, manganese, nickel and cobalt and the alkaline earths may be precipitated, and in any case this method of separation is very unsatisfactory in the case of Mn, Ni, Co. Manganese may, if desired, be completely precipitated along with Fe, Al, etc., by adding sufficient bromine water to the ammoniacal solution and boiling.

In case phosphates or fluorides are present, special procedures

* Separation of Al from Ba, Sr, Ca and Mg. Deville, *J. Prakt. Chem.* **60.** 9 (1853); Fresenius, *Quant. Anal.*, Vol. I. 7th edn. 425.

are necessary which will be discussed in dealing with the respective elements.

(4) *Basic Acetate Separation for Iron and Aluminium.*—This method (though lengthy and troublesome) gives a better separation of Fe, Al and Ti from Mn, Co, Ni and Zn than the preceding. Cr is not precipitated, but passes into the filtrate along with Mn, etc. The method depends on a series of reactions of the following type (M representing Fe (ferric), Al or Ti, $\overline{Ac}$ representing $C_2H_3O_2$):

(i) $MCl_3 + 3H_2O \rightleftharpoons M(OH)_3 + 3HCl$ (hydrolysis).

(ii) $M(OH)_3 + 3Na\overline{Ac} + 3HCl = M\overline{Ac}_3 + 3NaCl + 3H_2O$.

(iii) $M\overline{Ac}_3 + 2H_2O \rightleftharpoons M\overline{Ac}(OH)_2 + 2H\overline{Ac}$.

It is evident from the last equation that free acetic acid is produced. The concentration of hydrogen ions in the solution is therefore reduced by addition of a considerable excess of sodium acetate or similar compound.

The solution is first made as nearly neutral as possible by small additions of HCl, NH_4OH or $(NH_4)_2CO_3$, as required to produce neutrality, until a precipitate forms which redissolves with difficulty in HCl, the solution (in presence of considerable Fe) being a deep red, then more $(NH_4)_2CO_3$ is added till a very slight turbidity remains. Add a little acetic acid and sufficient sodium or ammonium acetate to bring about reaction (ii) above. Boil for not more than two minutes, filter hot and wash with boiling water. It is nearly always necessary to redissolve the precipitate in HCl and repeat the precipitation as before. The united filtrates must also be concentrated, and any further precipitate collected and added to the main portion. The final filtrate should be perfectly colourless (or green in presence of Cr).

The metals may now be separated in the precipitate and filtrate respectively, by suitable means. Frequently, the precipitate is dried, ignited and weighed as $Fe_2O_3 + Al_2O_3$ [$+ TiO_2$].

A similar separation may be made by means of alkali (or ammonium) formates or succinates.

(5) *Separation by means of Zinc Oxide.*—This method is convenient, and gives a good separation of Fe‴ and Al from Mn, Ni and Co in cases where Zn is absent or when it need not be estimated in the filtrate. The solution, if acid, is neutralized by addition of NaOH or Na_2CO_3, avoiding an excess, and boiling off CO_2 if the latter has been used. To the faintly acid solution an emulsion of zinc oxide, or better, freshly-precipitated zinc hydroxide which

has been washed free of alkali, is added with agitation as long as a reaction takes place, and until a little of the zinc oxide remains undecomposed. The reaction is of the type $3ZnO + 2MCl_3 + 3H_2O = 3ZnCl_2 + 2M(OH)_3$, where M represents Fe''' or Al.

Settle, filter, wash with hot water and separate further as required, remembering that Zn will be present both in the precipitate and the filtrate. A convenient method is to make up the mixture, which need not be filtered, to a definite volume, mix thoroughly, allow to settle, and filter or decant off aliquot portions for determination of Mn, Ni or Co.

In the authors' tests this method gave a better separation of Fe from Ni and Co than either the ammonia or the basic acetate method.

(6) *Separation by means of Barium Carbonate.*—This method gives a means of separating Fe''', Al, Cr, Ti (and U) from Mn, Ni, Co, Zn and Fe''. The solution must be carefully neutralized, and agitated, cold, with an emulsion of barium carbonate. The reaction is $2MCl_3 + 3BaCO_3 + 6H_2O = 2M(OH)_3 + 3BaCl_2 + 3CO_2$ $3H_2O$. Barium will, of course, be found both in precipitate and filtrate. The process is not to be recommended except in special cases, as the reaction is slow, requiring several hours, with frequent shaking; in presence of Ni and Co the separation is not satisfactory unless NH_4Cl is also added.

(7) *Precipitation of Zinc, Manganese, Nickel and Cobalt, in the Filtrate from Group 3a, and separation of these from Alkalis and Alkaline Earths.*—The sulphides of Zn, Mn, Ni and Co are precipitated by adding ammonium sulphide, or better by passing H_2S through the hot ammonaical filtrate from Fe, Al, etc. The precipitate settles slowly and is usually somewhat troublesome to filter, showing a great tendency to pass through or redissolve from the filter. Nickel tends to form a dark-brown colloidal solution which passes through the filter, and is only completely precipitated by prolonged boiling.

Sodium sulphide is a much better precipitant for zinc than ammonium sulphide; the precipitate is dense and flocculent and more easily filtered. It may be used to precipitate the metal from its solution (as zincate) in excess of caustic alkali. Ammonium compounds may be decomposed by addition of alkali and the NH_3 expelled by boiling, before adding Na_2S.

The filtrate from the sulphides of Zn, Ni, Co and Mn eontains Ba, Ca, Sr, Mg, and the alkali metals.

(8) *Separation of Zn, Ni and Co from Manganese in Acetic Acid Solution by H_2S.*—If the filtrate from the iron group precipitate be made very faintly acid with acetic acid and a considerable quantity

of sodium or ammonium acetate added (1 to 2 g), the liquid heated to 80° C. and H_2S passed in, Zn, Ni and Co are precipitated as sulphides, leaving Mn and the alkalis and alkaline earths in solution. For complete recovery of Ni and Co it is necessary to concentrate the filtrate and repeat the precipitation. Filter and wash with hot water and a little H_2S water. The filtrate should be clear and colourless.

(9) *Precipitation of Zinc by H_2S in slightly Acid Solutions of HCl or H_2SO_4, separating from Manganese.*—By careful regulation of the acidity, and concentration, it is possible to obtain a quantitative separation of zinc by this means. A neutral ammonium salt is added, of the same radical as the acid used.

The conditions given by Vestner[1] are as follows:

For Zinc Sulphate		*For Zinc Chloride*	
Zn	6·4 grms. per litre	Zn	2·15 grms. per litre
H_2SO_4	0·49 ,, ,, ,,	HCl	0·12 ,, ,, ,,
$(NH_4)_2SO_4$	45·0 ,, ,, ,,	NH_4Cl	5·34 ,, ,, ,,

Manganese, nickel and cobalt are not precipitated under these conditions, but zinc was almost completely precipitated in one hour.

(10) *Precipitation of the Alkaline Earths by Ammonium Carbonate.*—In the filtrate from Zn, Co, Ni and Mn the elements Ba, Sr and Ca may be precipitated by means of $(NH_4)_2CO_3$, sufficient NH_4Cl being present to prevent the precipitation of Mg. In quantitative analysis, however, Ba, Ca and Sr are usually separated by other methods which will be detailed when these metals are considered. After filtering the carbonate precipitate it should be washed with hot water containing a little NH_4OH or $(NH_4)_2CO_3$.

(11) *Precipitation of Metals as Phosphates.*—Many metals, notably Al, Fe, Ni, Co, Zn, Mg and U, may be quantitatively precipitated as phosphates under suitable conditions. In most cases the precipitation is made in a hot neutral or nearly neutral solution; in the case of Mg in an ammoniacal solution. A considerable excess of the reagent over the theoretical amount is generally necessary in order to obtain precipitates of constant composition. On ignition of the precipitated phosphate or of the double phosphate of the metal and ammonium, a pyrophosphate of the general formula $M_2''P_2O_7$ is usually obtained, M'' being a divalent metal.

[1] Diss. München (1909).

DRYING AND IGNITION OF PRECIPITATES

In some cases the precipitate is of such a nature that it cannot be dried above a certain temperature without decomposition. Where this temperature is not much greater than 100° C., the material is usually collected on a filter paper which has previously been dried at the required temperature, and weighed before use. The drying of the paper with the precipitate must be continued or repeated until successive weighings agree or differ only within allowable limits.

The drying is carried out in an air, water or other suitable oven, according to circumstances. In some cases the precipitate with the paper may be dried over a hot plate, the funnel being supported on a ring stand or truncated metal cone.

Certain precipitates (e.g. AgCl, $PbSO_4$) require to be ignited apart from the filter paper. The latter is ignited separately and the ash treated with whatever reagents are required to bring the small quantity of adhering precipitate to the same form as that in which the bulk is to be weighed.

In other cases paper and precipitate are more conveniently ignited together, care being taken to burn the paper slowly under oxidizing conditions until the carbon has completely disappeared before giving the final ignition at the temperature required for conversion into the required form.

For most ignitions a porcelain crucible may be used ; a muffle is more convenient than a Bunsen burner, as the material is more uniformly heated (with less danger, on that account, of cracking the crucible) and also it is easier to avoid loss of material by draughts, as a lid may be used by which the crucible is wholly or partly covered. In certain cases the moist precipitate and paper may be safely introduced at once into the hot muffle, thus saving much time in drying.

In cases where the residue is to be subsequently treated with hydrofluoric acid, a platinum crucible should be used.

It is only necessary to weigh the empty crucible before use in cases where the precipitate adheres strongly to it, or where the ignited substance is hygroscopic, in which case the crucible must be weighed with the lid, and after ignition, allowed to cool in a desiccator before the final weighing. In most cases the ignited precipitate may be more conveniently brushed out and weighed on a counterpoised watch glass.

Procedure recommended for Ignitions in Platinum Crucibles.—It is assumed that the precipitate is of such a nature that it may be ignited without removal from the paper. The lid of the crucible is

removed and the latter is placed in an inclined position on a triangle supported over a very small flame, the tip of which barely touches the sides of the crucible. [Very good triangles are to be had, consisting of silica rods held together by stout nichrome wire; these last many times longer than the ordinary pipe-clay triangles.]

The crucible is left in this position until the paper has completely carbonized and all hydrocarbons have distilled off. It is then placed vertically on the triangle and the lid replaced in such a manner as to leave a small crescent-shaped aperture. The flame is adjusted so that the extreme bottom only of the crucible is at dull red heat. In about ten to fifteen minutes all carbon will have disappeared and the full flame of the Bunsen may be used. [The idea that the hotter the flame, the shorter will be the time required for ignition of paper and precipitate is a common one with beginners, but experience shows it to be false.]

If the filter be ignited wet, it should be given a short preliminary drying in the partly-covered crucible until it begins to carbonize. If a crucible, containing a wet paper, be placed directly in the full Bunsen flame, the carbon assumes a form which is very difficult to burn.

The same procedure may be used for ignitions in porcelain and silica crucibles, but in these the flame may be a little higher on account of their poorer conductivity.

FILTERING MEDIA

1. Filter papers

The technique of gravimetric analysis can be considerably improved by selection of filter papers specifically suitable for the various varieties of precipitates encountered. Thus pore size should be dependent on particle size of precipitate, a 'hardened' paper will be resistant to vigorous washing, and filtering speed is obviously of importance to the industrial analyst.

These points are illustrated by the following tables which are supplied through the courtesy of W. & R. Balston Ltd.

2. Pulp filters

These are prepared by tearing a 12.5 cm. No. 40 Whatman paper into small fragments and shaking vigorously in 1 litre of water until macerated. The slurry should be kept under water in a stoppered bottle.

TABLE I

Typical Applications of Whatman Papers

Application	Qualitative	Paper Washed in HCl	Paper Washed in HCl and HF	Hardened
	Grade No.	*Grade No.*	*Grade No.*	*Grade No.*
General Routine ..	1 and 2	30	70	50, 52 and 540
$BaSO_4$ (properly precipitated) ..	1 and 2	30	40	52 and 540
$BaSO_4$ (ppt cold) ..	3 and 5	32	42	50 and 542
Silica (Coarse) ..	4	31	41	54, 531 and 541
Silica (Fine) ..	1 and 2	30	40	52 and 540
Iron and Alumina	4	31	41	54, 531 and 541
Metastannic Acid	5	32	42	50 and 542
Caustic Solutions	—	—	—	All hardened Grades
'Yellow Precipitate'	1, 2 and 7	30	40	52 and 540
Buchner Funnels ..	5	32	42	All hardened Grades

TABLE II

Comparative Water Speeds of Whatman Papers

Paper Number	Type of precipitates	Water Speed
Grade		*Seconds*
1	General purposes	75
2	Finer precipitates	110
3	General nonferrous analyses	130
4	Coarse and gelatinous precipitates	23
5	Very fine precipitates and Buchner funnels	275
40	$BaSO_4$ and crystalline precipitates	95
41	SiO_2 and hydroxide precipitates	22
42	For the finest precipitates	300
44	For the finest precipitates	250

3. Asbestos

Soft scrapings from the mineral are digested with hot dilute hydrochloric acid and washed free from chlorides. It is then stored under water in a stoppered bottle.

4. Sintered glass

The use of a sintered glass porous plate in a filter crucible is extremely useful when a filtering medium which is resistant to most reagents is necessary or when a succession of fine precipitates have to be separated.

After weighing, the precipitate may be removed by reversing the direction of the washing water or by a suitable reagent.

Before use the filter should be cleaned by rinsing with hydrochloric acid and finally with water. Ignition should be carried out below 610° C., this being the softening temperature of Pyrex. In order to avoid permanent strain in the material it should be cooled down to 200° C. in the furnace before withdrawing for cooling to air temperature.

Pyrex glass is an excellent material for these filters and porous plates of this nature are available in several grades with varying average pore diameters. The following table gives these particulars.

TABLE III

Grade	Average Pore Diameter (microns)
1	100 to 120
2	40 to 50
3[1]	20 to 30
4[1]	5 to 10
5/3	1·3 to 2

The choice of porosity is an important factor and it will be seen that the grades offer a suitable medium for precipitates varying from coarse to very fine. A pressure of approximately one atmosphere is suitable.

[1] Normal requirements are usually met with these grades.

CHAPTER III

QUALITATIVE ANALYSIS

A PRELIMINARY examination of an ore or mineral often is very helpful if not essential in deciding on the exact method to be followed in any assay or analytical determination. Many excellent text-books are available for carrying out such work. The following dry tests however are given as being eminently practical and sufficiently detailed as to enable any preliminary examination to be undertaken.

Section I

DRY TESTS FOR THE COMMON METALS

A. ACTION OF HEAT

A compound of the metal is heated in a dry glass tube.

[Res. = residue; Subl. = sublimate.]

Al	Res. white, infusible.
NH_4	Subl. white, unchanged by H_2S.
Sb	Subl. white, orange on passing H_2S.
As	Subl. white, yellow on passing H_2S.
Ba	Res. white, infusible.
Bi	Res. yellow or reddish when cold, darkens on heating, very fusible.
Cd	Res. or subl. brown, lighter when cold, infusible, yellow on passing H_2S.
Ca	Res. white, infusible.
Cr	Res. green or purple, infusible.
Co	Res. black, infusible.
Cu	Res. black, infusible.
Fe	Res. dark red, infusible.
Pb	Res. red when hot, yellow cold, fusible.
Mg	Res. white, infusible.
Mn	Res. black or dark red, infusible.
Hg	Subl. of metallic Hg, silvery, blackened by H_2S.
Ni	Res. black, infusible.
K	Res. white or colourless, fusible.

Ag Res. brownish hot, metallic cold.
Na Res. white or colourless, fusible.
Sr Res. white, infusible.
Sn Res. yellow hot, paler cold, infusible.
Zn Res. yellow hot, white cold, infusible.

B. Flame Reactions

Moisten with HCl and heat on platinum wire in Bunsen flame.

Sb Pale blue, denser than As.
As Pale blue, thin.
Ba Yellow-green.
Bi Bluish.
Ca Pale red.
Cu Green.
Pb Bluish.
Li Carmine-red (very like Sr).
Mn Greenish-yellow.
K Violet.
Na Yellow.
Sr Crimson-red.
Sn Pale blue, streaky.
Zn Green, thin, streaky.

C. Borax Beads

Fuse in blow-pipe flame with borax on loop in platinum wire.

	Outer or oxidizing flame	Inner or reducing flame
Cr	Green	Green
Co	Deep blue	Deep blue
Cu	Light blue	Red
Fe	Red hot, yellow cold	Pale green
Mn	Amethyst	Colourless
Ni	Violet or Reddish	Greyish

D. Heated on Charcoal, with or without Sodium Carbonate

[Res. = residue. B. = metallic bead. Inc. = Incrustation.]

Al Res. white, luminous, blue with $Co(NO_3)_2$.
NH_4 Volatilizes, white fumes.
Sb B. white, brittle, part volatilized; Inc. bluish-white.

As	White, volatile, strong odour ; Inc. white.
Ba	Res. white, luminous.
Bi	B. white, brittle, very fusible ; Inc. yellow.
Cd	B. white, soft, very fusible ; Inc. brown.
Ca	Res. white, luminous.
Cr	Res. green or yellow. Fused with $Na_2CO_3 + KNO_3$, yellow, soluble in water to yellow liquid.
Co	Res. black, magnetic.
Cu	B. red malleable scales.
Fe	B. black, magnetic particles.
Pb	B. white, soft, marks paper ; Inc. yellow.
Mg	Res. white, luminous, pink with $Co(NO_3)_2$.
Mn	Res. black. Fused with $Na_2CO_3 + KNO_3$, blue green.
Hg	Volatilizes.
Ni	Res. black, magnetic.
K	Res. fusible, sinks into charcoal.
Ag	B. white, malleable.
Na	Res. fusible, sinks into charcoal.
Sr	Res. white, luminous.
Sn	B. white, malleable ; Inc. white. [Best fused with KCN + Na_2CO_3.] Dirty green with $Co(NO_3)_2$.
Zn	Res. white, luminous, green with $Co(NO_3)_2$; Inc. white.

E. Fused with Black Flux

(i.e. mixture of C and alkaline carbonate prepared by igniting Rochelle salt)

Sb	Black ring and mirror in glass tube.
As	Black ring and mirror in glass tube.
Cd	Brown ring and bright mirror.
Hg	Globules of metallic Hg.

General Remarks

Many of the above tests are only applicable when the compounds of the respective metals can be obtained tolerably free from impurities. Where several metals are present together the reactions of one or more of these may be masked by those of the others, for example, nickel could not be detected by the borax bead in presence of much cobalt. In general, the dry reactions only serve as a preliminary guide to the analysis.

Section 2

CONFIRMATORY TESTS FOR THE DETECTION OF THE METALS

The following confirmatory tests are included as containing, in a concise form, recommended wet tests for the purpose of preliminary examination. In the present section it is assumed that the metal has been separated in the form of some compound free from other metals, or at least from such as would interfere with the application of the test.

Aluminium. [As oxide. If present as hydrate or simple salt, ignite before applying test.]

Moisten with a few drops of dilute $Co(NO_3)_2$. Ignite at bright redness. *Blue residue.*

Or, dissolve hydroxide in HNO_3, add a few drops dilute $Co(NO_3)_2$, then slight excess NH_4OH. Filter, wash, ignite gently till carbon is burnt off, then at bright redness. *Blue residue* = Al.

Antimony. [As sulphide or simple salt.]

Dissolve (if necessary) in conc. HCl, evaporate to small bulk, cool, dilute, filter if any residue, add a piece of clean platinum, tin or aluminium, together with a rod or strip of zinc. A *black stain* on the added metal (not on the zinc) indicates Sb. The stain is insoluble in HCl, NaClO, NaBrO, or $CaOCl_2$, but soluble in HNO_3.

Arsenic. [As sulphide.]

Dissolve in NH_4OH, evaporate to small bulk, add HNO_3, heat (filter if any residue), evaporate nearly to dryness, add excess NH_4OH, then $Mg(NO_3)_2$. Shake, settle, filter. Pass $AgNO_3$ acidified with $H\bar{A}$ through the filter. *Dark red colour* = As.

Barium. [As soluble salt; if as carbonate dissolve in HCl.]

Add NH_4OH in slight excess, then slight excess of $H\bar{A}$. Add K_2CrO_4. *Yellow precipitate* = Ba.

If much Sr is suspected, dissolve the $BaCrO_4$ precipitate in hot HCl, evaporate to dryness, add $H\bar{A}$ and $NH_4\bar{A}$; dilute with water, heat nearly to boiling, add K_2CrO_4 drop by drop, heat nearly to boiling for five minutes. *Yellow precipitate* = Ba (free from Sr).

Beryllium. [As crude hydroxide, $Be(OH)_2$.]

Dissolve in $H\bar{A}$, evaporate nearly to dryness, add glacial $H\bar{A}$,

evaporate just to dryness with stirring. [Basic acetate, $BeO \cdot 3BeA_2$ is formed.] Add $CHCl_3$ free from H_2O, grind residue in a mortar, filter, wash with $CHCl_3$. Reject residue. Evaporate filtrate to complete dryness. Dissolve residue from evaporation in HNO_3, dilute, add NH_4OH in slight excess, heat nearly to boiling. *White flocculent precipitate* = Be.

Bismuth. [(*a*) As hydroxide, BiO(OH).]

Filter and wash ; pour through the filter a cold freshly prepared solution of sodium stannite, Na_2SnO_2. *Black residue* = Bi.

[Sodium stannite is prepared by adding NaOH drop by drop to a cooled solution of $SnCl_2$ till the precipitate of $Sn(OH)_2$ dissolves to a slightly turbid liquid.]

[(*b*) As sulphide or oxide.]

Dry, mix with powdered S and KI, moisten slightly, ignite on charcoal before blowpipe, in oxidizing flame. *Reddish-purple stain on charcoal, with yellow border* = Bi.

Cadmium. [As hydroxide or soluble salt.]

Add NH_4OH in excess. If Cu is also present, solution becomes blue. Add KCN till decolorized, then a little more. Pass H_2S for 30 seconds. *Immediate yellow precipitate*, insoluble in $(NH_4)_2S$ = Cd.

Note: When much Cu is present, the solution saturated with H_2S may become deep yellow and an orange-red precipitate ($CSNH_2$) may separate on standing. This is not an indication of Cd.

Calcium. [As carbonate or simple salt.]

(*a*) Dissolve in water or HCl. Boil off CO_2 if necessary. Add slight excess of NH_4OH, then $(NH_4)_2C_2O_4$. *White precipitate*, (CaC_2O_4) = Ca.

(*b*) If Sr or Mg is present, dissolve the oxalate precipitate from (*a*) in 6 × normal H_2SO_4. Filter, add a little alcohol (say 10 ml.). Let stand several minutes. *White precipitate* ($CaSO_4$) = Ca.

Note: Sr is not appreciably dissolved by 6× normal H_2SO_4 ; Mg is dissolved but not precipitated by alcohol.

Cerium. [As hydroxide, $Ce(OH)_3$.]

(*a*) Dissolve in HĀ, add HNO_3, evaporate to dryness. To residue add HNO_3 with a little $KClO_3$. Heat on steam bath for five minutes in covered dish. Add solution of KIO_3 ; cool. *Yellow precipitate*, $[Ce(IO_3)_3]$ = Ce.

(*b*) If the precipitate obtained in (*a*) is white or pale yellow, it

may contain Th. In that case, heat it with a mixture of H_2O_2 and HNO_3, add a little KIO_3. Ce is dissolved, leaving Th as a white precipitate of $Th(IO_3)_3$. Filter, to filtrate add H_2O_2 + NH_4OH. *Yellow or dark orange precipitate* = Ce (as peroxyhydroxide, $CeO_2 . H_2O_2$).

Chromium. [In solution as chromate : if as a chromic salt, precipitate with excess NH_4OH, filter, ignite with alkaline oxidizer, say Na_2CO_3 + KNO_3 or Na_2O_2; extract with water.]

(*a*) Neutralize with NaOH or HNO_3 as required, add slight excess HNO_3, then $Pb(NO_3)_2$. *Yellow precipitate*, [$PbCrO_4$] = Cr.

(*b*) Allow precipitate of $PbCrO_4$ to stand and settle. Filter, wash, redissolve in warm dil. HNO_3, cool, dilute, add a little ether and H_2O_2. Shake gently. *Blue ether layer* = Cr.

Cobalt. [As $Co(OH)_3$ or CoS.]

(*a*) Dissolve in HCl with a little $KClO_3$. Filter off any residue. Evaporate filtrate just to dryness, take up residue in dilute HĀ, add conc. KNO_2 solution; stand 15 minutes, with occasional shaking. *Yellow precipitate*, $K_3Co(NO_2)_6$ = Co.

(*b*) $Co(OH)_3$, CoS, or simple salts. Dissolve in HCl or HCl + $KClO_3$ if necessary. Cool [add H_2SO_4, evaporate to fumes, if HNO_3 or $KClO_3$ is present]. Cool, dilute, add to hot solution a warm solution of nitroso-β-naphthol in HCl or HĀ. *Deep red precipitate* = Co.

Columbium. [See Niobium.]

Copper. [Any soluble inorganic salt. If as carbonate, dissolve in HĀ; if as sulphide, dissolve in HNO_3, boil, dilute, filter.]

Add excess NH_4OH, acidify with HĀ, add $K_4Fe(CN)_6$. Let stand two to three minutes. *Reddish-brown precipitate*, ($Cu_2Fe(CN)_6$) = Cu.

Note: This test should be made even when NH_4OH gives no blue coloration, as the ferrocyanide test is more delicate. No other metal except U and Mo gives a brown precipitate, Cd gives white and Ni green with ferrocyanide.

Gallium. [In solution in NaOH.]

Add excess HĀ; precipitate is formed; filter, dissolve in 6 × normal HCl; add $K_4Fe(CN)_6$; let stand five to ten minutes. *White or bluish-white precipitate* = Ga.

Note: This is a delicate test in absence of Zn or Fe.

Germanium. [As H_2GeF_6, after precipitation of As in HF solution and separation as As_2S_3, or As_2S_5.]

(*a*) Heat to fumes with H_2SO_4, pour into 25 ml. water, saturate with H_2S; cork flask and let stand 10 minutes. *White precipitate*, GeS_2 = Ge. (Soluble in NH_4OH.)

(*b*) Confirm by filtering, extracting from filter with dilute NH_4OH. Evaporate to dryness, add 1 to 3 ml. of 27 × normal HF, boil, filter if not clear; add to residue a little 27 × normal HF, then a few drops 6 × normal K_2CO_3, and 1 ml. water. Boil, cool, let stand 15 minutes. *A greyish-white precipitate*, (K_2GeF_6) = Ge.

Gold. [As chloride $AuCl_3$, possibly with Pt metals and Hg.]

Add a drop of HCl, agitate with ethyl acetate, separate from water layer, again agitate with ethyl acetate, unite the two ethyl acetate layers [$AuCl_3$ and $HgCl_2$ free from Pt metals]. Evaporate the extract, dissolve residue in HCl + HNO_3; evaporate nearly to dryness, add 5 ml. water, 2 ml. 6 × normal NaOH and 0·5 ml. normal KI. Heat to boiling. *Purple colour or reddish precipitate* = Au. (If much precipitate, add more KI and boil again.)

Note: Pt gives a yellow colour with KI under these conditions, but no precipitate. Pd gives neither colour nor precipitate.

Indium. [Sulphide, In_2S_3, precipitated by $(NH_4)_2S$ in presence of NH_4OH and NH_4Cl.]

(*a*) Dissolve in HCl + HNO_3, boil off H_2S, filter off any precipitate; to filtrate add NH_4OH.* *White precipitate*, $In(OH)_3$ = In; confirm by (*b*).

(*b*) Filter and wash. Pour repeatedly through the filter 10 ml. of hot 6 × normal HĀ; saturate filtrate with H_2S, let stand 10 minutes. *Yellow flocculent precipitate* [In_2S_3] = In.

Iridium. [Precipitated as $(NH_4)_2IrCl_6$ by evaporation of chloride solution with NH_4Cl; may contain Pt.]

Filter, wash with cold saturated NH_4Cl. Heat the precipitate with 10 to 20 ml. of 12 × normal HCl and 0·5 to 1 ml. of 16 normal HNO_3 at 80° to 90° C., for 15 to 20 minutes. When no more Cl is present add 0·5 ml. more HNO_3. Evaporate on steam-bath till residue no longer smells of acid; add a little water and $NaHCO_3$ till alkaline to litmus; heat 5 minutes on steam bath, cool, add 1 ml. saturated Br water and 0·5 ml. normal $NaHCO_3$.

* Zn, Co and Ni, which may be present, are not precipitated under these conditions by NH_4OH.

Heat 5 to 10 minutes. *Blue colour changing to black precipitate* (IrO_2) = Ir.

Note: Filtrate from this may contain Pt.

Iron. [*A.* As ferric salt of an inorganic acid or as ferric hydroxide.]

Acidify slightly with HCl (if strongly acid make alkaline with NH_4OH, then acidify). Divide into two portions (*a*, *b*).

(*a*) Add KCNS or NH_4CNS. *Red coloration*, $Fe(CNS)_3$ = Fe'''.

(*b*) Add $K_4Fe(CN)_6$. *Blue colour or precipitate*, $Fe(Fe(CN)_6)_3$ = Fe'''.

(*B.* As a soluble ferrous salt.]

Acidify with HCl, add $K_3Fe(CN)_6$. *Blue colour or precipitate*, $Fe_3(Fe(CN)_6)_2$ = Fe''.

Lead. [As soluble salt, or as $PbCl_2$ or $PbBr_2$ dissolved in boiling water.]

(*a*) Add H_2SO_4 (say 6× normal). *White precipitate* = ($PbSO_4$) = Pb ; confirm by (*b*).

(*b*) [As sulphate or precipitate from (*a*)].

Filter (if necessary), wash with 2 × normal H_2SO_4, finally with a little water. Pour repeatedly through filter 5 to 15 ml. hot conc. $NH_4\bar{A}$. To filtrate add $H\bar{A}$ + K_2CrO_4. *Yellow precipitate* ($PbCrO_4$), soluble in cold 50 % HCl = Pb.

Magnesium. [As soluble inorganic salt, or in filtrate from calcium oxalate precipitate.]

(*a*) If not alkaline add slight excess of NH_4OH, then (say) 25 ml. of normal Na_2HPO_4 (cool if hot), shake vigorously ; settle (if no immediate precipitate) for half an hour. *White crystalline precipitate*, ($MgNH_4PO_4$) = Mg. (If not distinctly crystalline, confirm by (*b*).)

(*b*) Wash once with 95 % alcohol, digest with 5 ml. of 2 × normal H_2SO_4, add 10 ml. 95 % alcohol, shake for 2 or 3 minutes. Filter [reject precipitate = $Ca_3(PO_4)_2$ or $Sr_3(PO_4)_2$]. To filtrate add 10 ml. water, 20 ml. 6 × normal NH_4OH, 5 ml. normal Na_2HPO_4. Let stand half an hour. *White crystalline precipitate*, ($MgNH_4PO_4$) = Mg.

Manganese. [Precipitated as MnS by $(NH_4)_2S$ in alkaline solution, with metals of Group III. (*b*).]

(*a*) Dissolve in HNO_3, add NaOH + Na_2O_2 till alkaline. Filter [reject filtrate = Na_2ZnO_2]. Precipitate may contain Ni, Co or

rare earths as hydroxides. Add 5 to 20 ml. 6 × normal HCl, boil till precipitate dissolves from the filter paper ; filter to remove paper, evaporate filtrate almost to dryness ; add 2 to 3 ml. 16 × normal HNO_3, concentrate to small bulk. Place flask in a beaker of boiling water ; add gradually 0·5 g powdered $KClO_3$; heat 1 to 2 minutes. Filter, wash. *Black precipitate*, (MnO_2) = Mn. (Confirm by (*b*).)

(*b*) Pour through filter 5 ml. warm 6 × normal HNO_3 to which a little H_2O_2 has been added. Cool filtrate, add BiO_2 (sodium bismuthate) or PbO_2 about 0·1 g at a time till some brown powder remains undissolved ; agitate, settle. [If PbO_2 has been used, boil 2 to 3 minutes.] Filter if necessary. *Purple solution*, [$HMnO_4$]=Mn.

Note: Test (*b*) may be applied to any Mn compound soluble in HNO_3 and free from Cl, Br or I.

Mercury. [As soluble mercuric salt. If as $HgCl_2$ with Au, Pt or Pt metals, separate as under *Gold*, see above.]

(*a*) To solution in water (or water extract from ethyl acetate separation) add NH_4Cl, then 6 × normal NaOH, and 0·5 ml. of normal KI. Warm, let stand 5 minutes. *Orange precipitate or yellow turbidity*, ($HgINH_2HgO$) = Hg.

Molybdenum. [Oxide, sulphide or simple inorganic salt.]

(*a*) Digest with HCl + HNO_3, evaporate to dryness ; add H_2SO_4, evaporate to fumes ; cool. *Dark blue colour* = Mo.

Note: This is a very delicate and characteristic test. Only small quantities of the substance and reagents should be used.

(*b*) [As sulphide MoS_3, possibly with Te.]

Warm the precipitate with a little HNO_3 and HCl, evaporate just to dryness. Add 1 ml. of 6 × normal HCl and 5 ml. water ; heat to boiling, filter [reject residue = S]. Cool filtrate, add 5 ml. of normal KCNS. If deep red colour appears, due to Fe‴, make alkaline with NaOH, heat nearly to boiling, filter [reject precipitate $Fe(OH)_3$]. Neutralize with HCl, add slight excess, then 0·2 g finely granulated Zn. *Red colour, increasing for some minutes* = Mo as $MoO(SCN)_3$, confirm by (*c*).

(*c*) Decant solution from Zn, immerse vessel with solution in boiling water, pass H_2S slowly for 10 minutes. *Brown precipitate*, (MoS_3) = Mo.

Nickel. [Any compound free from Fe or other metal precipitated by NH_4OH. If these are present, add slight excess NH_4OH + NH_4Cl, filter.]

(*a*) If acid, make slightly ammoniacal ; if alkaline, acidify with

HCl, then make slightly alkaline with NH_4OH. Warm to about 50° C., add alcoholic solution of dimethyl glyoxime. *Red flocculent precipitate*, $(NiC_8H_{14}N_4O_4) = Ni$.

Niobium (Columbium). [As K_2NbF_5O in filtrate from Ta.]

(*a*) Evaporate to fumes with H_2SO_4, cool, dilute, add NH_4OH. A precipitate, $NbO_2(OH)$, forms which is insoluble in HCl. Dissolve by treatment with H_2SO_4 + HF. Pour through a zinc column (reductor) collecting liquid passing through in $HgCl_2$ solution. *White precipitate*, (Hg_2Cl_2), confirms Nb.

Note: Ta and Ti do not give this reaction.

(*b*) If the oxide Nb_2O_5 or a mineral containing Nb be digested with HF and KF and evaporated to small bulk, crystals of a double fluoride separate in plates. Heat to fumes with H_2SO_4, cool, dilute, boil, add HCl, which gives an opalescent solution. *Tannic acid* added to this gives *an orange-red colour or precipitate. Metallic Zn* added to the HCl solution gives a blue colour.

Note: Ta, if present, gives no colour with Zn and HCl, and a light brown or yellow precipitate with tannic acid.

(*c*) A mineral containing Nb fused with sodium metaphosphate or microcosmic salt gives a *bead* which *is blue* in the reducing flame (violet or brown with much Nb).

On moistening with $FeSO_4$ and again heating in the inner flame, bead becomes *red.*

[Ta gives no coloured bead by this test.]

Osmium. [In residue from Pt metals and Au, insoluble in HCl + HNO_3.]

(*a*) Fuse with NaOH + KNO_3. Extract with water, distil solution while passing a current of Cl ; pass evolved gas through wash bottle containing HCl [to absorb Ru], then into KOH, which absorbs Os as K_2OsO_4. Acidify distillate with HCl, add conc. solution of KCNS and ether or amyl alcohol. *Blue coloration* = Os.

(*b*) Obtain as K_2OsO_4 as in (*a*). Acidify with HCl ; add thiourea, $SC(NH_2)_2$. *Rose to dark red coloration* = Os.

Palladium. [As $(NH_4)_2PdCl_6$ in filtrate from $(NH_4)_2PtCl_6$; Rh may also be present.]

(*a*) Saturate with Cl gas ; let stand 30 minutes in stoppered bottle. Rh remains in solution. *Red precipitate*, $(H_2PdCl_6) = Pd$.

(*b*) Neutralize the filtrate from $(NH_4)_2PtCl_6$ with Na_2CO_3, add sodium formate, boil. Pd is precipitated as metal. Filter, wash, dissolve in HCl + HNO_3, evaporate with HCl, add water, then

solution of nitroso-β-naphthol in HĀ. *Bulky brown precipitate*, $Pd(C_{10}H_6NO_2) = Pd$.

Platinum. [As H_2PtCl_6, by dissolving in HCl + HNO_3 and evaporating with HCl.]

Evaporate almost to dryness. Add 1 ml. water, evaporate on steam bath till no smell of acid; add a few drops of HCl then NH_4Cl till no more dissolves, avoiding large excess. Cool thoroughly, let stand half an hour. [Redissolve any NH_4Cl which may separate, by slight warming.] *Yellow crystalline precipitate*, $(NH_4)_2PtCl_6 = Pt$.

Note: Ir, if present, gives a black precipitate; a mixture of Pt and Ir may give a red precipitate. In this case proceed as described under iridium.

Potassium. [As chloride, KCl, with other alkali chlorides, free from NH_4 salts.]

(*a*) Add 1 to 5 ml. of 9 × normal $HClO_4$, evaporate cautiously to strong fumes. Cool thoroughly, add 4 vols. of alcohol for every vol. of $HClO_4$ that was added; stopper flask, cool, stand 15 minutes with occasional shaking. Pour on to small dry filter, wash with 2 ml. 99% alcohol. *Precipitate* (*finely crystalline*), $KClO_4 = K$.

Filtrate may contain Na and Li. The precipitate may contain Rb and Cs in addition to K. If these are suspected, proceed as under *Rubidium*.

(*b*) [As chloride KCl, free from NH_4 salts.]

Dissolve in minimum of water, add H_2PtCl_6 and alcohol. Stir, allow to stand some time (if no immediate precipitate, for half an hour). *Yellow crystalline precipitate*, $(K_2PtCl_6) = K$.

Rhodium. [In solution, as ammonio-chloride after precipitation of Pd. See *Palladium*.]

(*a*) Add NH_4OH, evaporate to dryness on steam bath. To residue add 2 to 3 ml. of 6 × normal HCl, boil, transfer to small bottle, stand half an hour; add cold water to dissolve any NH_4Cl that may separate. *Light yellow residue*, $RhCl(NH_3)_5Cl_2 = Rh$.

(*b*) [As chloride.]

Add $SnCl_2$ to dilute solution. *Red coloration* = Rh.

Ruthenium. [In distillate with Cl gas. See under *Osmium*.]

(*a*) Ru is absorbed by HCl (orange or dark red colour of distillate indicates Ru). Add 2 ml. alcohol; let stand 5 minutes. *Black precipitate* = Ru.

(*b*) [In chloride solution.]

Heat with thiourea [$SC(NH_2)_2$] and HCl. *Blue coloration* = Ru.

(*c*) Heat with thiocarbanilide and HCl. Shake with ether [delicate test]. *Bluish-green ether layer* = Ru.

Selenium. [(*a*) As a selenite. If as compound insoluble in water, add HNO_3, digest till dissolved. If as selenate, evaporate repeatedly on water both with HCl to convert to selenite.]

Pass SO_2 through the solution. *Red precipitate, becoming black on boiling* = Se.

[(*b*) As chloride, $SeCl_4$ (or bromide, $SeBr_4$, as obtained by distillation with HBr + Br).]

Add sodium bisulphite drop by drop till excess Br is almost destroyed, keeping cool. [If too much bisulphite has been added, add slight excess of Br.] Add hydroxylamine hydrochloride (NH_2OH . HCl), cool. *Red precipitate, darkening on heating* = Se.

Note: The filtrate from this may contain As and Ge.

Silver. [As chloride AgCl, precipitated by HCl.]

(*a*) Filter, wash thoroughly with hot water [reject filtrate = Pb]. Pour through filter repeatedly a hot 10 ml. portion of NH_4OH solution, or if precipitate is large, digest with NH_4OH and filter. Boil filtrate to expel most of the NH_3, add a drop of HCl, acidify with $H\bar{A}$. *White precipitate*, (AgCl) = Ag.

(*b*) [As AgBr, with TlBr, precipitated by HBr.]

Through filter containing the precipitate pour repeatedly a 15 ml. portion of boiling water, then repeatedly a 15 ml. portion of saturated Br water. Wash residue with boiling water. *Pale yellow residue*, (AgBr) = Ag.

(Filtrate contains Tl.)

Strontium. [In filtrate from $BaCrO_4$, with $H\bar{A}$ and $NH_4\bar{A}$ in solution.]

(*a*) Add 6 × normal NH_4OH slowly till colour changes from orange to yellow, then 5 ml. more. Heat to 60° to 70°, add 15 ml. 95 per cent. alcohol, 5 ml. at a time, shaking 15 seconds after each addition till precipitate forms. Cool, let stand 5 minutes. *Light yellow precipitate*, ($SrCrO_4$) = Sr. Confirm by (*b*).

(*b*) Pour repeatedly through the filter 10 ml. of boiling water. Add to the solution 1 ml. of 3 × normal Na_2CO_3 and 12 ml. of 3 normal $K_2C_2O_4$. Boil in covered vessel 5 minutes. Filter at once [reject filtrate]. Wash precipitate (SrC_2O_4) thoroughly with water; pour repeatedly through filter 5 ml. of cold normal $H\bar{A}$ [CaC_2O_4

remains undissolved]. To filtrate add 2 ml. normal Na_2SO_4. Boil, let stand 10 minutes. *White precipitate*, ($SrSO_4$) = Sr. Confirm by (*c*).

(*c*) [Any compound, free from Li.]

Moisten with HCl. Heat on platinum wire in Bunsen flame. *Crimson colour in flame* = Sr.

Tantalum. [As oxide, usually with Nb.]

Fuse with Na_2CO_3, extract with water. Pass a slow current of SO_2 while heating on steam bath for 30 minutes. *White precipitate* = Ta or Nb.

Filter [filtrate may contain Mo, V, W and PO_4], wash with hot water. Dissolve precipitate by pouring repeatedly through filter on rubber funnel 2 ml. of 27 × normal HF, collecting filtrate in platinum crucible; wash out filter with 1 to 2 ml. water. To solution add 1 ml. 16 × normal HNO_3, evaporate just to dryness. To residue, add 2 ml. 27 × normal HF and 0·5 g K_2CO_3; evaporate to dryness, heat over small flame till residue becomes enamel white, without allowing bottom of crucible to become red. Dissolve residue in 2 to 3 ml. water, boil down to 0·5 ml., add 4 ml. water; boil, pour into small test tube. Let stand at least 15 minutes. *Greyish-white translucent, viscous-looking precipitate* [$2K_2TaF_7 . Ta_2O_5$] = Ta.

Note: Filtrate from this contains Nb; for other tests for tantalum see under Niobium (above).

Tellurium. [Precipitated by H_2S, together with Mo.]

(*a*) Heat precipitates with 5 to 10 ml. of normal HCl on steam bath for 5 minutes; add 1 to 2 ml. of 16 × normal HNO_3, heat at 60° to 70° C., till residue dissolves or becomes light coloured. Evaporate just to dryness. Treat residue with 6 ml. of 12 × normal HCl; cool, saturate with SO_2. Filter [reject residue = Se]. To filtrate add 20 ml. water, saturate with SO_2, boil 15 minutes. *Black precipitate* = Te. Confirm by (*b*). [Filtrate from this may contain Mo.]

(*b*) [Most compounds and native minerals.]

Heat with conc. H_2SO_4, cool somewhat, add tin foil. *Purple or carmine colour* = Te. (The colour disappears on dilution.)

Thallium. [As $Tl_2(SO_4)_3$ in filtrate from $PbSO_4$.]

(*a*) Add powdered Na_2SO_3 a little at a time till solution smells of SO_2, then 1 to 2 ml. of normal KI; let stand 5 minutes. *Yellow precipitate*, (TlI) = Tl.

Note: A yellow or orange *colour* in the solution, on addition of

KI, does not indicate Tl, as this may be due to action of SO_2 on KI; Bi, if present, forms BiI_3 which dissolves in excess KI to an orange solution.

Thorium. [Separated as fluoride, ThF_4, with Ce, possibly with In and rare earths.]

(*a*) Heat to strong fumes with H_2SO_4; cool, pour into 20 to 30 ml. water, make alkaline with 6 × normal NH_4OH. Filter [reject filtrate, NH_4F]. Wash precipitate, dissolve by pouring through it repeatedly 5 ml. of 6 × normal HĀ. Saturate at 50° to 60° C. with H_2S, place in corked vessel, stand 10 minutes. Filter off any precipitate, [In_2S_3]. Boil filtrate to expel H_2S, add 2 ml. of 16 × normal HNO_3 and 1 g $KClO_3$, heat nearly to boiling on steam bath 5 minutes in covered vessel. Add 20 ml. of 0·35 × normal KIO_3, cool at once to 20° to 25° C. *White precipitate* [$Th(IO_3)_4$] = Th.

(*b*) In case precipitate from (*a*) is yellowish, indicating presence of Ce, filter, wash with cold water and a little KIO_3. Rinse precipitate into a flask with H_2O_2. Add 5 to 10 ml. 16 × normal HNO_3; heat nearly to boiling for 5 minutes. Add 10 to 20 ml. of 0.35 × normal KIO_3, cool, stand. *White precipitate* = Th. Confirm by (*c*).

(*c*) Filter after 10 minutes, wash with cold water to which one-tenth its volume of 0·35 × normal KIO_3 has been added. Dissolve precipitate by pouring repeatedly through filter 5 to 10 ml. 6 × normal HCl. Evaporate solution just to dryness. Moisten residue with 12 × normal HCl and evaporate till no smell of acid. Add 2 ml. water, 2 drops of 6 × normal HCl and 5 ml. H_2O_2; heat 5 to 10 minutes at 60° to 70° C. *White flocculent precipitate* ($ThO_2 . H_2O_2$) = Th.

Tin. [As sulphide SnS or SnS_2, together with As and Sb sulphides, soluble in $(NH_4)_2S$.]

(*a*) Acidify strongly with HCl, filter off precipitate [As_2S_3 + S]; add metallic iron, boil for some time, settle, decant (or filter if necessary). To solution add $HgCl_2$. *White or grey precipitate,* (Hg_2Cl_2 or Hg) = Sn.

(*b*) Acidify and remove As as in (*a*). Dilute filtrate to 70 ml. Saturate with H_2S, boil off excess H_2S. Add 5 ml. H_2O_2, heat till precipitate redissolves. Add 5 to 10 g oxalic acid; pass H_2S into solution. Sb is precipitated free from Sn. Filter [reject precipitate]. Add test lead, boil, detach precipitate from lead, add conc. HCl, heat to dissolve, dilute somewhat, add $HgCl_2$. *White or grey precipitate* = Sn.

Titanium. [As oxide or hydroxide, with Fe, Al and other metals of Group III.]

(*a*) Dissolve in H_2SO_4. [If insoluble, fuse with $K_2S_2O_7$, extract melt with H_2SO_4, filter if necessary.] Neutralize with NH_4OH, acidify slightly with SO_2; add $Na_2S_2O_3 \cdot 5H_2O$, boil, settle, filter, wash with hot water. Redissolve in HCl or HNO_3, add H_2O_2. *Orange or reddish coloration* = Ti.

Note: Colour is destroyed by HF.

(*b*) [With V, in filtrate from salicylic acid precipitate of Bi, Nb, Ta and Zr.]

Cool till salicylic acid begins to separate; pour at once into separating funnel, add gradually 6 ml. of 12 × normal H_2SO_4. Keep cool. Add 40 ml. ether, shake [reject ether layer, which contains the salicylic acid]. Water layer contains Ti and V; evaporate this, without filtering, to 15 or 20 ml., make alkaline with 6 × normal NaOH; add 10 ml. in excess, boil 3 to 5 minutes, filter [V is in filtrate). Wash thoroughly with hot water. *White precipitate*, $Ti(OH)_4$ = Ti.

(*c*) The precipitate from (*b*) may contain Zr. To confirm Ti, dissolve it by pouring repeatedly through the filter 5 to 10 ml. hot 6 × normal HNO_3 with 2 to 6 ml. of H_2O_2. *Orange or reddish solution* = Ti.

(Zr gives no colour with H_2O_2.)

Tungsten. [As H_2WO_4, in residue left after ignition, and extraction with HCl to remove Sn.]

(*a*) Dissolve residue by pouring repeatedly through it 2 to 4 ml. 15 × normal NH_4OH, wash with a little water. Add 3 ml. of normal $SnCl_2$, boil, stir; add 3 ml. 12 × normal HCl, boil, cool. [If mixture shows an orange colour, due to Mo, filter and wash with dilute HCl.] *Blue precipitate* = W.

(*b*) [In presence of phosphates.]

Evaporate to dryness with HCl + HNO_3; extract with NH_4OH, neutralize with HNO_3, add (say) 20 ml. normal $Mg(NO_3)_2$, boil, add gradually 5 ml. 15 × normal NH_4OH, cool; let stand, with occasional shaking, till crystalline precipitate separates. Filter [reject precipitate, NH_4MgPO_4]. Boil filtrate to expel NH_3, acidify with HNO_3, evaporate to 10 ml., cool, add a little dilute HNO_3; heat till crystalline salts have dissolved. *White or yellow precipitate* = W. Confirm by (*a*).

Uranium. [Precipitated by NH_4OH as $(NH_4)_2U_2O_7$, or as acetate.]

(*a*) Add freshly prepared $NaHCO_3$ solution, boil filter [reject

residue]. Acidify filtrate with 6 × normal HCl, adding 2 to 5 ml. in excess, boil off CO_2, make alkaline with NH_4OH. *Yellow precipitate*, $(NH_4)_2U_2O_7$ = U. Confirm by (*b*).

(*b*) Filter, dissolve in hot 6 × normal HCl, add 10 ml. 5 × normal NaCl, cool, add 5 ml. normal $K_4Fe(CN)_6$; stand 15 minutes. *Dark red precipitate or colour*, $(Na_2UO_2Fe(CN)_6)$ = U.

(*c*) [In HNO_3 solution].

Evaporate to small bulk, cool, neutralize with NH_4OH, add 5 ml. 6 normal HĀ and 15 ml. normal Na_2HPO_4, heat to boiling; let stand 10 to 15 minutes to coagulate, filter [filtrate = V], wash with normal NH_4NO_3. *White precipitate*, $(UO_2NH_4PO_4)$ = U. Confirm by (*b*).

Vanadium. [In solution, after precipitation of U as in *Uranium* (*c*) above.]

(*a*) Neutralize with 15 × normal NH_4OH; add 5 ml. more; saturate completely with H_2S by passing gas for 10 to 15 minutes. *Pink or violet colour*, $[(NH_4)_3VS_4]$ = V.

(*b*) To solution from (*a*) add gradually about 15 ml. 6 × normal HNO_3 till distinctly acid, heat nearly to boiling. *Dark brown or black precipitate* (V_2S_4 or V_2S_5) = V.

(*c*) [As Vanadate.]

Heat with reducing agent, such as Zn, SO_2, oxalic acid or HCl + KI. *Blue coloration* = V.

(*d*) [As Sulphide.]

Dissolve in HNO_3, add water, boil, cool, add H_2O_2. *Orange-red colour* = V.

Zinc. [Any soluble salt, sulphide or carbonate.]

(*a*) Dissolve, if necessary, in HNO_3, add 1 drop of dilute (say 0·3 × normal) $Co(NO_3)_2$; evaporate just to dryness, add a little Na_2CO_3. Ignite at low temperature over a small flame. Cool, moisten with water. *Green residue*, ($CoZnO_2$?) = Zn.

Note: If residue on ignition is black, owing to too strong heating, add a few drops HNO_3, evaporate just to dryness, add Na_2CO_3 as before, ignite carefully. Excess of $Co(NO_3)_2$ must be avoided.

(*b*) [As sulphide, ZnS, in presence of Co and Ni.]

Add 10 to 30 ml. normal HCl, stir, stand 5 minutes cold, filter, wash [black residue = CoS, NiS]. To filtrate add excess NH_4OH, then a few drops of 6 × normal $(NH_4)_2S$. *White precipitate* = Zn (as ZnS).

(*c*) [Soluble salt, or solution in HCl or HĀ.]

Add $K_4Fe(CN)_6$. *White precipitate*, $[Zn_2Fe(CN)_6]$ = Zn.

Zirconium. [In insoluble residue, after fusion with Na_2CO_3.]

(*a*) Extract with water, filter, wash with water. [Filtrate may contain Nb and Ta; residue may contain Zr and Bi.] Transfer residue to a platinum crucible, incinerate filter, add 3 g. $K_2S_2O_7$, cover crucible, heat at dull redness 5 to 15 minutes. Cool by immersing lower part of crucible in water. Detach melt, add water, boil till disintegrated, cool, without filtering. Saturate with H_2S. Filter off Bi_2S_3 if any, boil off excess H_2S, filter if not clear; add 2 ml. H_2O_2 and 10 ml. normal Na_2HPO_4. Stand 1 hour. *White precipitate*, $Zr(HPO_4)_2 . H_2O = Zr$.

(*b*) [In fluoride solution, with Ti.]

Add in platinum dish 3 ml. 6 × normal H_2SO_4, evaporate to fumes, cool, add 5 ml. water and 10 ml. H_2O_2. Filter if any residue [orange-red solution indicates Ti]. Add to solution 10 ml. of normal Na_2HPO_4. Stand half an hour. *White precipitate* = Zr.

Note: This precipitate is soluble with difficulty in HCl.

Section 3

GENERAL CLASSIFICATION OF THE METALS

GROUP

I. *Ppt. with HCl* [Ag, Hg′, Pb in part].
Tl in thallous salts, as TlCl.
W as H_4WO_5.
Nb, Ta and Mo may be pptd. as acid hydrates, soluble in excess HCl.

II. *Ppt. by H_2S in HCl solution.*
(*a*) *Insol. in yellow $(NH_4)_2S$* [Pb, Hg″, Cu, Bi, Cd].
Pd, Rh, Ru, Os, Tl (as Tl_2S + S) in thallic salts.
(*b*) *Sol. in yellow $(NH_4)_2S$* [As, Sb, Sn].
Au, Pt, Ir, Mo, Ge, Se, Te.

III. *Ppt. by NH_4OH + NH_4Cl + $(NH_4)_2S$.*
(*a*) *Ppt. by NH_4OH + NH_4Cl alone.*
[Fe, Al, Cr], Be, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nb, Nd, Pr, Sm, Sc, Ta, Tb, Th, Tm, Ti, U (part), Y, Yb, Zr.
(*b*) *Ppt. by NH_4OH + NH_4Cl + $(NH_4)_2S$* (not by NH_4OH + NH_4Cl alone).
[Ni, Co, Mn, Zn], U, V, In, Ga, Tl‴.

IV. *Ppt. by $(NH_4)_2CO_3$ + NH_4OH* [Ba, Sr, Ca] Ra.

V. *Not pptd. by above reagents.*
[Mg, Na, K (NH_4)], Li, Cs, Rb.

PART TWO

Selected Methods for the Analysis of the Elements arranged in Alphabetical Order

CHAPTER IV

SELECTED METHODS FOR THE ANALYSIS OF THE ELEMENTS

ARRANGED IN ALPHABETICAL ORDER

ALUMINIUM

(Al) Atomic Weight = 26·97

Metallurgical Occurrence

Al and its alloys
Mg base alloys
Al bronzes and high tensile brasses
Zn base diecasting alloys
Certain steels
Minerals (Bauxite); Clays; Refactories.

Source of Metal as Standard

Super pure Al = 99·99 + %Al (Brit. Aluminium Co. Ltd.)
(Northern Aluminium Co. Ltd.)

Methods of Determination

GRAVIMETRIC

1. *Precipitation as hydroxide (by one of the reagents below) and ignition to* Al_2O_3.
   (*a*) by ammonia or ammonium carbonate
   (*b*) by sodium thiosulphate
   (*c*) by sodium or ammonium acetates, succinates or formates
   (*d*) by potassium iodide and iodate
   (this method is of limited use, specific applications being given at the end of the appropriate section).

2. *Precipitation as an organic complex and weighing as such or finish volumetrically*
   (*a*) as a quinolate by 8-Hydroxyquinoline from ammoniacal or acetic acid solution
   (*b*) by phenylhydrazine from neutral solution of the chloride
   (*c*) by cupferron from formic acid solution
   (again each of the above methods finds specific application and (*a*) is often favoured as an alternative to the standard phosphate precipitation (Method 3) but it is liable to interference by many base metals, (*b*) may be used for high tensile brasses or Al bronzes, and cupferron (*c*) is frequently used for Al in steels).

3. *Precipitation as phosphate by addition of a soluble phosphate*
   (this method is often considered to be the standard procedure for Al in most Al-bearing materials).

VOLUMETRIC

4. *Indirect acidimetric titration*
   (a useful approximate method for high Al contents, as in Al alloys—accuracy about 1%).

COLORIMETRIC

5. *Comparison of the red colours produced by ammonium aurine tricarboxylate ('Aluminon') with assays and standards*
   (suitable for traces of Al [up to 0·0005 g] in the absence of Fe, Cr, Be and phosphates).

6. *Comparison of the red colours produced by 'Alizarin Red S' with assays and standards*
   (suitability as in (5) but less accurate—Fe, Cr, Co, Mn and Cu interfere).

In general the phosphate precipitation is the most usually practised but the oxine method has many supporters.

METHODS

1. Precipitation as hydroxide by various reagents (as above) followed by ignition to oxide

This is based on the hydrolysis reaction:

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl.$$

The forward reaction is carried to completion provided the acid formed is immediately removed, which can be done by the presence of NH_4OH, $Na_2S_2O_3$; soluble acetates, formates and succinates and also by a mixture of potassium iodide and iodate. The use of NH_4OH and NH_4Cl as in a group separation causes the co-precipitation of Fe^{+++}, Cr^{+++}, Ti and when present Be, Ce, Th, Nb, Ta, U, Zr, V. Group II metals should be absent since these would also contaminate the precipitate.

The use of NaOH or KOH as a precipitant for $Al(OH)_3$ is unsatisfactory due to the solubility of $Al(OH)_3$ in excess reagent to give sodium or potassium aluminate solution ($Na_2Al_2O_4$ or $K_2Al_2O_4$).

(*a*) *NH_4OH Precipitation.* Best carried out in a hot or boiling solution preferably of the chloride or sulphate (HNO_3 absent) to which *just sufficient* NH_4OH is added to make the solution just alkaline to methyl orange or methyl red (pH 4·5-6·5). Any further excess of NH_4OH gives a very gelatinous precipitate which is slow to filter. The presence of the colouring matter from the above indicator (or any other) is adsorbed on the precipitate and appears to help in the filtering process as now the precipitate is somewhat granular. Washing the precipitate with hot neutral 2% NH_4NO_3 solution prevents the precipitate from passing through the filter if in the colloidal state.

Ignition of $Al(OH)_3$ to Al_2O_3 should be carried out in a porcelain crucible heated to 1100–1200° C. to ensure formation of

non-hygroscopic Al_2O_3 (further details of analytical procedure see 'Analysis of Al in Zn Base Diecasting Alloy').

(*b*) *Sodium Thiosulphate Precipitation.* Based on the reaction:

$$2Al\,Cl_3 + 3Na_2S_2O_3 + 3H_2O = 2Al(OH)_3 + 6NaCl + 3S + 3SO_2.$$

This has the advantage over NH_4OH precipitation of forming in the reaction colloidal S which helps to coagulate the precipitate of $Al(OH)_3$, and SO_2 which prevents iron contamination of the precipitate by keeping this metal in the ferrous state.

To a boiling neutral solution of Al chloride or sulphate, about 2 g $Na_2S_2O_3$ crystals are added for every 0·1 g Al. The solution is boiled until all SO_2 has been evolved (about 20 mins.). The precipitate of ($Al(OH)_3$ + S) is filtered off, washed, and ignited as above.

Unfortunately the S present often contaminates the final precipitate to give a proportion of basic Al sulphate. This may be prevented by igniting the precipitate to a lower temperature (600–800° C.) to remove the bulk of elemental S and then treating the residue by digestion with a 10% alkaline NH_4NO_3 solution which dissolves Al sulphates and on boiling precipitates as $Al(OH)_3$. The final ignition is at high temperature as previously.

Another snag encountered is the incompleteness of precipitation of $Al(OH)_3$ by $Na_2S_2O_3$ so that the filtrate from the first precipitation should be evaporated and retreated with say 0·5 g $Na_2S_2O_3$.

Furthermore, if the first precipitate is of a pinkish tinge showing iron contamination it should be redissolved in 20–50 ml. hot 50% HCl, dilute to 200–300 ml., make just alkaline with NH_4OH, pass SO_2 until all Fe is in the ferrous state, adjust acidity with methyl orange as before, heat to boiling, add 2 g $Na_2S_2O_3$ and repeat the precipitation as before.

$$Al_2O_3 \times 0{\cdot}5291 = Al.$$

(Further references see 'Al in Cast Iron and Steels'.)

(*c*) *Precipitation by sodium or ammonium acetates, succinates, formates.* These reagents neutralize the acid formed during hydrolysis of the aluminium salt (as stated previously) or in the case of the succinates, these form a basic Al succinate from a slightly ammoniacal solution.

As before Fe is preferably converted to the ferrous state by means of phenylhydrazine to prevent co-precipitation and urea is frequently added to provide ammonia during boiling and so maintain alkalinity.

The basic succinate is washed with 1% NH_4Cl solution, dried and ignited to 1200° C. for one hour as before.

(For full analytical procedure see 'Analysis of Al and Mg Alloys'.)

(*d*) *Precipitation by mixture of KI + KIO_3.* Based on the reaction:

$$2AlCl_3 + 6H_2O + 5KI + 5KIO_3 = 2Al(OH)_3 + 6KCl + 3I_2 + 3H_2O$$

in this case the liberated I_2 can be dispersed by the addition of $Na_2S_2O_3$ to give a colourless solution of sodium tetrathionate and then the $Al(OH)_3$ is filtered, washed, dried and ignited as before.

The advantage of the method is that precipitation is carried out in the cold from a neutral solution of $AlCl_3$ and the precipitate is more easily filterable, but prior to precipitation all metals which form insoluble iodides must be absent.

2. Precipitation as an organic complex, dried and weighed as such or finished volumetrically

(*a*) *By means of 8-Hydroxyquinoline or 'Oxine'.* Thought by many analysts to be the most accurate method of determining Al; unfortunately many other base metals are also precipitated by this reagent when used in acetic acid or ammoniacal solution which are the usual conditions for Al precipitation, viz.: Ag, Pb, Hg, Cu, Bi, Cd, Sb, U, Fe, Zn, Mn, Co, Ni, Zr, Cr, Cb, Ta as well as Al may be precipitated from an acetic acid solution, and Be, Mg, Ca, Sr, B, Sn and most of the previous metals as well as Al may be precipitated from an ammoniacal solution.

To remove the possibility of contamination of the Al 'oxine' or quinolate by the above metals these latter are converted into complex cyanides in an ammoniacal tartrate solution. [(Pigott) *Jnl. Soc. Chem. Ind.* 1939. **58.** 139.]

To a sulphuric acid solution of Al add 50 ml. of 20% tartaric acid solution and make just ammoniacal. Add about 5–20 g KCN (in aqueous solution) and boil. To the filtrate heated to 60° C. add either 10% solution of 'oxine' in C_2H_5OH (or acetone) (20–30 × amount of Al present) or 2% solution of 'oxine' in 50% acetic acid. In either case wash the precipitate on a sintered glass crucible with hot water and dry at 140–150° C. for one hour.

A volumetric finish may be carried out by dissolving the undried complex in 20 ml. conc. HCl, diluting to 200 ml. and titrating cold with a bromate-bromide solution.

The reactions involved in this method are :

$$3(C_9H_6N(OH)) + AlCl_3 = Al(C_9H_6NO) + 3HCl$$
(8-hydroxyquinoline) (yellow cryst. quinolate)

$[Al(C_9H_6NO) \times 0{\cdot}0587 = Al.]$

(For further details of analytical procedure see 'Analysis of Al in Aluminium Bronze' and 'Analysis of Steel and Cast-Iron'.)

As alternatives the estimation of Al by 8-hydroxyquinoline can be finished by (*a*) ignition to Al_2O_3 and weighing as such or (*b*) bromination with excess KBr + $KBrO_3$ and titration of liberated I_2 from KI with $Na_2S_2O_3$ solution (see 'Analysis of Al in Aluminium Bronze')—in this latter case the following reactions take place :

$$C_9H_6N(OH) + \underset{\substack{\text{(from KBr}\\ +\ KBrO_3\text{)}}}{2Br_2} = C_9H_5NOBr_2 + 2HBr$$

then with KI : $$2KI + \underset{\text{(excess bromine)}}{Br_2} = 2KBr + I_2$$

on titrating with $Na_2S_2O_3$:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

In certain steels the presence of Ti and/or W are likely to contaminate the quinolate precipitate. W must be removed at an early stage as WO_3 (see 'Analysis of W in Steels') and Ti is *not* co-precipitated from an acetic acid solution of Al.

It is safer perhaps to remove Ti as $Ti(C_6H_5N_2O_2)_4$ by precipitation with 6% aqueous solution of 'cupferron' ($C_6H_5N(NO)ONH_4$) from a 5% HCl or H_2SO_4 solution of the Al in the cold and Al is estimated in the filtrate EITHER by destroying the excess 'cupferron' by boiling with HNO_3 + H_2SO_4 neutralizing with NH_4OH and precipitating Al quinolate with the acetic acid solution of 'oxine' OR use the filtrate from Ti precipitation make just ammoniacal, add 20 ml. formic acid and 25 ml. of 'cupferron' solution. Al is precipitated as $Al(C_6H_5N_2O_2)_3$. Wash with 2% formic acid solution, dry and ignite to Al_2O_3.

(*b*) *Precipitation with phenylhydrazine from neutral solution of the chloride, followed by ignition to Al_2O_3 and weighing as such* (Cartwright, Collier and Charlesworth, *Analysis of Non-Ferrous Metals and Alloys*, p. 27). Dissolve the sample in nitric acid, filter off tin and antimony oxides, fume the filtrate with H_2SO_4 and filter off $PbSO_4$. Pass H_2S into the filtrate to remove Group II metals. Precipitate Fe and Al with NH_4OH. Just redissolve in HCl and nearly neutralize with NH_4OH but keep Fe in solution. Reduce to ferrous iron with 2 ml. saturated ammonium bisulphite

solution, neutralize with NH_4OH then add 5–7 drops of 50% HCl until just acid. Add 3 ml. of phenylhydrazine. Filter off the complex, wash with dilute reagent in H_2SO_3, dry and ignite to Al_2O_3.

(*c*) *Precipitation by cupferron from a cold formic acid solution* (Pigott, *Chemical Analysis of Ferrous Alloys*, 1942). Cupferron ($C_6H_5N(NO)ONH_4$) precipitates Fe, V, Ti, U, Cb, Ta, Zr from moderately strong sulphuric or HCl solution and Cu, Pb, Ag, Hg, Th, Sn are partially precipitated under these conditions.

With acids of weaker dissociation certain other metals are precipitated by the reagent, e.g. Be from oxalic acid solution, Al from formic, acetic or sulphurous acids solutions and Cr (partially) from citric or tartaric acid solutions.

The determination of Al in steel by this reagent is based on the following reaction :

$$(HCOO)_3Al + 3(C_6H_5N \cdot NO \cdot ONH_4) = Al(C_6H_5N_2O_2)_3 + 3(HCOO)NH_4.$$

Take a weight of sample containing about 0·050 g Al, dissolve in 30 ml. conc. HCl then add 5 ml. conc. HNO_3 to oxidize iron, W, Ta. Evaporate to low volume then dilute to 100 ml. with 5% HCl, bring to the boil, cool and filter off SiO_2, WO_3, Ta_2O_5, wash with hot 5% HCl and discard the precipitate. Adjust the volume of *cold* filtrate to about 100 ml. then stir in a slight excess of a 6% aqueous solution of cupferron (an excess gives a white precipitate of the reagent whereas the heavy metal complexes are coloured) adding about 10 ml. excess. (as a guide, weight of reagent used is about 10 times weight of Fe + Cu + V + Ti etc. present).

Stand for 20 minutes, filter, wash with cold 10% HCl and reject the precipitate.

If Be is present it is next removed by adding 10 g tartaric acid, making slightly ammoniacal then making quite acid with an 8% oxalic acid solution. To the cold solution about 10 ml. of cupferron solution is added and the Be complex is precipitated, filtered off and washed with cold 2% oxalic acid and rejected.

The filtrate is made just ammoniacal, neutralized with formic acid and 15 ml. of the acid added in excess. Add to the cold solution 25 ml. of the cupferron solution and after standing 10 minutes, filter, wash with 2% formic acid containing a few mls. of cupferron solution. Treat the precipitate and filter paper with 50 ml. conc. HNO_3, evaporate to 10 ml., add a further 20 ml. conc. HNO_3 and 30 ml. perchloric acid and fume strongly for 20 minutes to destroy all organic matter and convert any occluded

Cr in the precipitate to chromic acid. Cool, dilute to 150 ml. with water, neutralize with 50% NH_4OH and add 3 drops excess, boil for 1–2 minutes, filter off $Al(OH)_3$, wash with hot 2% ammonium nitrate solution and hot water. Ignite in a porcelain crucible to Al_2O_3. (Factor: $\times$ 0·5291 = Al.) Chromium is *not* precipitated as hydroxide under these conditions.

3. Precipitation as $AlPO_4$, ignited and weighed as such

Although a standard method it has been found that the precipitate of aluminium phosphate does not always conform strictly to the formula $AlPO_4$ and much depends on the conditions of the precipitation. Furthermore the precipitate is likely to be contaminated by phosphates of the metals Cr, V, Co, Mo, Ti, Zr, U, Be, Sn and Fe^{+++} and for accuracy these metals should be removed prior and subsequent to the precipitation of $AlPO_4$ and before ignition of the final precipitate.

A normal group separation is adequate except for high accuracy.

The recommended procedure is to obtain a slightly acid (HCl) solution of the Al (with probably Fe and Cr present), treat with sodium metabisulphite or H_2SO_3 to reduce Fe to the ferrous state. 2 g ammonium phosphate and 10 g $Na_2S_2O_3$ are added and the solution boiled for half an hour until all SO_2 is evolved. The precipitate is filtered from the hot solution and washed with hot water, dried, ignited at 1000° C. and weighed as $AlPO_4$. This precipitate (in steels) may be contaminated with Cr and/or V, as phosphate, which are removed by treatment with H_2SO_4 + ammonium persulphate *or* fuse in a Pt crucible with 3 g Na_2CO_3 + 1 g KNO_3, extract the melt with NaOH, filter off $Cr(OH)_3$, neutralize the filtrate with HCl, add ammonium phosphate as before and heat for about half an hour.

Filter off $AlPO_4$, wash with hot 2% ammonium nitrate solution, and ignite to 1000° C.

$$AlPO_4 \times 0{\cdot}2211 = Al.$$
$$AlPO_4 \times 0{\cdot}4178 = Al_2O_3.$$

Reactions involved are:

$$AlCl_3 + (NH_4)_2\,HPO_4 = AlPO_4 + 2NH_4Cl + HCl$$
$$4FeCl_3 + Na_2S_2O_5 + 3H_2O = 4FeCl_2 + Na_2SO_4 + H_2SO_4 + 4HCl$$
(or H_2SO_3)

(For further details see: 'Analysis of Al in Steels'.)

4. Indirect volumetric determination of Al (Snyder, *Ind. Eng. Chem.* (Anal. Ed.), Jan. 1945)

This method is said to be useful for determining Al in Al base

alloys where other constituents only total less than 10%. Based on the reaction: $Al(OH)_3 + 6KF = AlF_3 . 3KF + 3KOH$. When $AlCl_3$ is neutralized by $Ba(OH)_2$ to the phenolphthalein end point (pink) in the presence of sodium potassium tartrate, the addition of neutral KF, reacts as above and liberates KOH in direct proportion to the Al content of the test solution. Titrate the liberated KOH with standard HCl to the disappearance of the phenolphthalein pink. The HCl solution must be standardized on $AlCl_3$ solution of known strength. Ammonium salts, sulphates, and silicates interfere but Ca, Cu, Cr, Fe, Mn (< 5%), Mg, Zn do not interfere.

To the $AlCl_3$ solution (0·025 — 0·100 g Al) add a saturated $Ba(OH)_2$ solution until the pink colour of phenolphthalein is observed (also some $Al(OH)_3$ precipitate is evident). Add 30 ml. 30% NaK tartrate followed by more $Ba(OH)_2$ until the phenolphthalein pink is again observed. Then add 30 ml. 30% KF. $2H_2O$ (made neutral to phenolphthalein) and titrate the liberated KOH with N/2 HCl to the disappearance of the pink colour. Neutralization of $AlCl_3$ with NH_4OH is unsatisfactory due to the buffering action of NH_4 salts. With NaOH or KOH results are low and the end point indistinct possibly due to solution of $Al(OH)_3$ in caustic alkali.

5. **'Aluminon'** (ammonium aurine tricarboxylate) (Scherrar and Mogerman, *Jnl. Research Nat. Bureau Standards*, 1938. **21.** 105.)

The reagent gives a red solution or precipitate with solutions of Al in acetic acid in the presence of ammonium acetate and ammonium carbonate. Fe, Cr, Be and phosphates interfere. Use up to 50 ml. of test solution, add 5 ml. conc. HCl followed by 5 ml. glacial acetic acid and 5 ml. of a 0·2% aqueous solution of reagent. Neutralize with NH_4OH saturated with $(NH_4)_2CO_3$, acidify with 5 ml. glacial acetic acid, again neutralize with NH_4OH–$(NH_4)_2CO_3$ mixture adding 5 ml. excess. Dilute to 100 ml. and compare with standards similarly prepared.

6. **'Alizarin Red S'** (Atack, *Jnl. Soc. Chem. Ind.*, 1915 and others)

Al in very diluted HCl or H_2SO_4 solution is treated with 10 ml. glycerine to prevent a precipitate forming and add 5 ml. of 0·1% aqueous 'Alizarin' solution. Dilute to 35 ml., make slightly ammoniacal, stand 5 minutes, add 5 ml. 50% acetic acid, dilute to 50 ml. with water and compare the intensity of the red lake produced with known Al solutions as standards as quickly as

possible. (Fe may be prevented from interfering by the addition of citric acid at any stage prior to making ammoniacal.) Cr, Co, Mn and Cu should be absent.

ANTIMONY

(Sb) Atomic Weight = 121·76

Metallurgical Occurrence

Ores and minerals (stibnite)
Lead and tin base bearing alloys, type metal
Antimonial lead (vat linings, accumulator plates
Some Mg alloys
Impurity in bronzes and brasses

Source of Metals for Standards

Pure antimony ('Star' quality 99·85% +) (Cooksons Ltd. [Associated Lead Industries]) (St. Helens Smelting Co., Lancs.)

Methods of Determination

VOLUMETRIC

1. *$KMnO_4$ titration*
   (for most antimony-bearing materials—Fe and As interfere)
2. *$KBrO_3$ titration*
   (for most antimony-bearing materials with more than 0·5% Sb—Fe and As interfere)
3. *Iodine—$Na_2S_2O_3$ titration*
   (for ores and alloys)

METHODS

1. Potassium permanganate method

This is the most usual method for determining Sb in antifriction alloys and type metal and depends on the solution of Sb in conc. H_2SO_4 to give $Sb_2(SO_4)_3$ which is then oxidized quantitatively to $Sb_2(SO_4)_5$ with $KMnO_4$ solution. The presence of Cu, Pb and Sn do not interfere since these are present as soluble copper sulphate, insoluble $PbSO_4$ and $Sn(SO_4)_2$ but Fe^{++} may give a high result. Usually Fe is only present in very small quantities and does not materially interfere, but As may. To prevent possible hydrolysis of the antimonous and stannic salts on dilution, a little HCl is added (not more than 2% total vol.). Titration is done in the cold to the normal pink flush.

The reactions occurring are :

$$2Sb + 3H_2SO_4 = Sb_2(SO_4)_3 + 3H_2$$

$$5Sb_2(SO_4)_3 + 4KMnO_4 + 16H_2SO_4 = 5Sb_2(SO_4)_5 + 2K_2SO_4 + 4MnSO_4 + 16H_2O$$

[$KMnO_4$ solution (2·8 g/litre) 1 ml. = 0·005 g Sb.]

The removal of As in this method is best done by passing H_2S into the H_2SO_4 solution (initially used to dissolve the alloy) which has been suitably diluted and which has been further acidified with HCl to the ratio 2 volumes strong acid to 1 volume water. Under these conditions As_2S_3 is precipitated but Sb is not. Dilute the filtrate with hot water to give 20% acidity and pass H_2S again to precipitate Sb_2S_3 which is filtered, washed and dissolved in the minimum NaOH solution. This is then boiled with conc. H_2SO_4 to ensure reduction and treated as before with $KMnO_4$ (after Low).

2. Potassium bromate method

This is based on the reaction: $KBrO_3 + 3SbCl_3 + 6HCl = 3SbCl_5 + KBr + 3H_2O$. Any Fe^{++} and As interferes as before giving high results. Most suitable for ores and alloys containing more than 0·5% Sb.

Dissolve about 1 g ore or 0·5 g alloy (10% Sb) in 30 ml. conc. HCl + 5 ml. HCl saturated with bromine. Reduce the Sb solution to $SbCl_3$ with 3–5 g Na_2SO_3 crystals, and evaporate to 10–15 ml. to expel SO_2 and to volatilize arsenious chloride. Dilute with 20 ml. conc. HCl and 40 ml. hot water, and boil for 1 minute to expel last traces of SO_2. To the boiling solution add 2–5 drops methyl orange solution as indicator and titrate hot with $KBrO_3$ solution (1·41 g/litre : 1 ml. = 0·003 g Sb approx.) until the colour of the indicator is destroyed.

Standardize on pure Sb treated in a similar manner or on $AsCl_3$ solution made from A.R. As_2O_3 (0·8123 g) dissolved in warm 10% NaOH solution (5 ml.) and 5 ml. conc. HCl added. Make up to 500 ml. with water, then 50 ml. of this solution = 0·10 g Sb.

3. Iodine—$Na_2S_2O_3$ titration

0·5–2 g of the ore or alloy is dissolved in 20–40 ml. of conc. HCl + bromine or 15 ml. conc. HCl + 15 ml. conc. HNO_3. Dilute to about 100 ml. with water, boil out excess bromine or Cl_2, make strongly alkaline with NaOH and saturate with H_2S. This keeps Sb in solution as sodium sulphantimonite whilst Pb, Cu, Bi, Fe, Ni, Co, Zn, Mn are precipitated as sulphides. Filter and wash well with H_2S water. Acidify the filtrate with HCl, warm, repass H_2S if necessary and filter off Sb_2S_3. Dissolve the precipitate in 10–20 ml. conc. HCl with addition of 0·5 g $KClO_3$. Dilute to 100–150 ml. with water, boil out excess chlorine by evaporating to low bulk—this also volatilizes As as chloride. Cool, dilute with 20 ml. conc. HCl and 200 ml. cold

water ; add 5 g KI and titrate liberated I_2 with standard $Na_2S_2O_3$ solution using starch as indicator preferably near the end point. The main reaction is :

$$SbCl_5 + 2KI = SbCl_3 + 2KCl + I_2$$

which shows that :

$$126{\cdot}92 \text{ g I} = 60{\cdot}9 \text{ g Sb}$$

or

1 ml. N/10 iodine = 0.00609 g Sb
= 1 ml. N/10 thiosulphate solution
(N/10 $Na_2S_2O_3 . 5H_2O$ = 24·82 g/litre).

Standards of pure Sb should be treated in an identical manner.

Notes :

(1) Tin does not interfere as it is in the stannic condition.

(2) Do not evaporate excessively at any stage for fear of volatilizing $SbCl_5$.

ARSENIC

(As) Atomic Weight = 74·91

Metallurgical Occurrence

Arsenides of Cu, Ni, Co and Fe in Cu/Ni ores
Minerals (arsenopyrite etc.), speisses
Arsenical Cu and Pb
Impurity in steel, cast iron, copper and its alloys.

Source of Metal for Standards

Metallic arsenic 99·9% (Imperial Smelting Corporation) (Blackwell Ltd., Liverpool) but usually more convenient to use A.R. arsenious oxide (As_2O_3).

Methods of Determination

GRAVIMETRIC

1. *Precipitation of Mg ammonium arsenate and ignition to Mg pyroarsenate* ($Mg_2As_2O_7$)
(this is probably the least accurate method and 2 (*a* or *b*) are preferable. May be used for ores).

VOLUMETRIC

2. (*a*) *Reduction to As by hypophosphites followed by I_2 titration*
(suitable for steels and irons).
(*b*) *Distillation as $AsCl_3$, conversion to sodium arsenite and titrate with iodine*
(suitable for Pb, Sn and Cu alloys).

COLORIMETRIC

3. *Gutzeit test* : *yellow coloration when AsH_3 is absorbed in $HgCl_2$ solution.*
Marsh test : *formation of As 'mirror' by thermal decomposition of arsine* (AsH_3)
(the film of metallic As can be compared with that from known quantities and is used to detect as little as 0·00001 g As.

METHODS

1. Precipitation of magnesium ammonium arsenate and ignition to pyroarsenate

When 'magnesia mixture' is added to the solution of a soluble arsenate, the mixed solutions then made ammoniacal, ammonium magnesium arsenate is precipitated ($MgNH_4AsO_4$) which on ignition becomes Mg.pyroarsenate ($Mg_2As_2O_7$).

The ore or alloy is dissolved in HNO_3 to give a concentrated solution of arsenic acid (H_3AsO_4), to this is added about 50 ml. of 'magnesia mixture' followed by approximately one third the total volume of 10% NH_4OH. On standing overnight a white crystalline precipitate of ammonium magnesium arsenate can be collected, filtered, washed free from chlorides with 2% NH_4OH solution, dried and ignited *gradually* to about 800° C. Weigh as magnesium pyroarsenate ($Mg_2As_2O_7 \times 0{\cdot}4828 = As$). (Phosphates and uranium salts interfere since they are co-precipitated.)

$$(NH_4)_3\,AsO_4 + MgCl_2 = Mg(NH_4)\,AsO_4 + 2NH_4Cl$$
$$2Mg(NH_4)\,AsO_4 = Mg_2As_2O_7 + 2NH_3 + H_2O$$

Magnesia Mixture.—68 g $MgCl_2 \cdot 6H_2O$ and 165 g NH_4Cl are dissolved in 300 ml. water, 200 ml. NH_4OH (conc.) added, and make up to 1 litre with water.

2. (*a*) Reduction to metallic As by hypophosphites followed by I_2 titration

Solution of 5 g of the ferrous material is effected by treatment with 30 ml. 25% H_2SO_4 and 15 ml. conc. HNO_3 in the presence of 0·5 g pure Cu. This gives arsenic acid:

$$As + 5HNO_3 = H_3AsO_4 + 5NO_2 + H_2O.$$

Treatment with $KMnO_4$ oxidizes C and the addition of 5 ml. H_2SO_3 removes HNO_3. Elemental As is precipitated by boiling with conc. HCl in the presence of sodium hypophosphite.

$$2H_3AsO_4 + 5H_3PO_2 = 2As + 5H_3PO_3 + 3H_2O.$$

After filtering, As is dissolved in a known excess of standardized I_2 solution which gives arsenious acid due to hydrolysis of the As iodide.

$As + 3I \rightarrow AsI_3 + 3H_2O \rightarrow H_3AsO_3 + 3HI$ and with excess I_2 arsenic acid is produced.

$H_3AsO_3 + I_2 + H_2O \rightarrow H_3AsO_4 + 2HI$. The excess I_2 is titrated with standard sodium arsenite solution in the presence of $NaHCO_3$ with starch as indicator. The end point is the disappearance of blue 'starch-iodide' $I_2 + Na_3AsO_3 + H_2O \rightleftharpoons Na_3AsO_4 + 2HI$. The reversible reaction is prevented by the

presence of sodium bicarbonate which removes HI thus: $HI + NaHCO_3 = NaI + H_2O + CO_2$.

Notes: Only W interferes under these conditions of determination and would be co-precipitated with As by the sodium hypophosphite. To remove W, fix as phospho-tungstic acid by addition of H_3PO_4 after solution of the steel in mixed acids.

Cu acts as a catalyst during solution of steel and reduction of ferric salts by H_2SO_3. (For full details see under 'Arsenic in Steels'.)

2. (*b*) Distillation as arsenious trichloride, conversion to sodium arsenite and titration with I_2

Here the alloy is attacked with a mixture of 25% HCl, 30% $FeCl_3$ solution and *either* 60% $CaCl_2$ solution *or* 5% KBr solution (the last three solids being dissolved in the diluted HCl) and the products distilled in a simple round-bottomed flask with condenser attached to the side arm. The distillate is collected in cold water as arsenious acid thus:

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O$$

then

$$2AsCl_3 + 6H_2O = 2H_3AsO_3 + 6HCl.$$

The distillate is then neutralized with NaOH solution, *just* reacidified with HCl and the arsenious acid is oxidized quantitatively to arsenic acid by a standard I_2 solution using starch solution as indicator. The end point is the permanent formation of blue 'starch iodide'.

As above, an excess of $NaHCO_3$ must be present to destroy liberated HI which would reverse the reaction $H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2HI$.

Note: The presence of KBr in the initial distillation is useful to overcome the possible loss of As as AsH_3 during solution of the alloy. Bromine converts AsH_3 into arsenic acid thus:

$$AsH_3 + 4Br_2 + 4H_2O = H_3AsO_4 + 8HBr.$$

(For further details on method of procedure see 'As in Cu Alloys' and 'As in White Metals'.)

BARIUM

(Ba) Atomic Weight = 137·36

Metallurgical Occurrence

As Ba minerals, the sulphate, carbonate, oxide and hydroxide (e.g. Barytes $BaSO_4$) often found associated with calcite and galena (PbS)
Pb-Ba-Ca bearing alloys.

Source of metal for Standards

Metallic Ba is obtainable (99·95%) but more usual to use A.R. salts such as $BaCl_2$.

Methods of Determination

GRAVIMETRIC

1. *Precipitation of $BaSO_4$, conversion to chromate, igniting and weighing same* (suitable for ores and alloys).
2. *Precipitation of $BaSO_4$ which is then ignited and weighed as such* (as 1).

VOLUMETRIC

3. *Titration of a soluble Ba salt with standard N/10 or N/2 N_2SO_4 using a* 0·1% *aqueous solution of Rhodizonic Acid as external indicator.*

METHODS

1. Chromate Method

This is applicable in the presence of Pb and Sr and is fairly accurate.

Digest 0·5 to 1 g with HCl and HNO_3 until decomposed. Add 3 ml. H_2SO_4, evaporate to strong fumes, cool, add 100 ml. water, boil, settle, cool, filter, wash with cold 10% H_2SO_4; reject filtrate. Wash residue from filter paper with a minimum of hot water. Add about 5 g ammonium acetate. Boil, refilter on the same paper. Wash with hot dilute ammonium acetate until all lead is extracted.

Dry the residue and ignite, (weigh, if required, as $BaSO_4 + SrSO_4 + SiO_2$). Fuse with 5 to 6 g $Na_2CO_3 + K_2CO_3$ in a nickel crucible, extract with hot very dilute NH_4OH, filter, wash with hot water and dilute NH_4OH until free of sulphates. (Test filtrate with $BaCl_2$ + HCl.) Reject filtrate.

Wash the precipitate off the filter paper with the minimum amount of hot water, dissolve in HCl, refilter through the same paper, wash with hot water, reject residue.

Make the filtrate alkaline with NH_4OH, then just acid with acetic acid, and add excess K_2CrO_4. Boil, settle, filter, wash with hot dilute ammonium acetate until free of soluble chromate. Dry, and ignite at moderate temperature. Weight as $BaCrO_4$ ($BaCrO_4 \times 0{\cdot}542 = Ba$). The principles involved in this method are acid attack of the material followed by 'fuming' with H_2SO_4 to precipitate $BaSO_4$, $PbSO_4$, $SrSO_4$ and SiO_2. $PbSO_4$ is dissolved from the precipitate by hot ammonium acetate solution and the residue fused with $Na_2CO_3 + K_2CO_3$ to give $BaCO_3$ and $SrCO_3$ (mixed alkali carbonates give lower melting point than either carbonate alone).

$$\left.\begin{matrix}BaSO_4\\SrSO_4\end{matrix}\right\} + Na_2CO_3 = \left.\begin{matrix}BaCO_3\\SrCO_3\end{matrix}\right\} + Na_2SO_4$$

(Leaching the melt with very dilute NH_4OH instead of water is preferable, since $BaCO_3$ is less soluble in this reagent.) The carbonates are converted to chlorides with HCl and insol. SiO_2 is filtered off. The neutralization and acetic acid addition converts the Ba and Sr to acetates and from this solution Ba chromate only is precipitated by addition of K_2CrO_4 solution.

$$K_2CrO_4 + Ba(CH_3COO)_2 = BaCrO_4 + 2KCH_3COO$$

2. Sulphate method (after Low)

Quite an accurate method. Proceed as in Method (1) until Ba, Pb, Sr, Ca, etc., are precipitated as sulphates by H_2SO_4 'fuming'. If Pb is present in the material add 5 g NH_4Cl to the diluted H_2SO_4 solution after 'fuming' and before boiling. This will dissolve $PbSO_4$ and form a soluble ammonium lead sulphate ($[NH_4]_2SO_4 . PbSO_4$). The precipitate containing Ba, etc., as sulphates is filtered and washed with hot dilute (2%) $(NH_4)_2SO_4$, dried and ignited and the residue fused with 5 g of 1 : 1 $Na_2CO_3 + K_2CO_3$ mixture in a Pt. or Ni. crucible. Leach out the melt as before with 1% NH_4OH, filter and wash with 1% NH_4OH until all sulphates are absent. The residue of impure $BaCO_3$ is warmed with 5 ml. conc. HCl to dissolve, diluted to about 300 ml. with water, heated nearly to boiling and 20 ml. of 10% H_2SO_4 added. This will precipitate $BaSO_4$ but not $SrSO_4$. Allow to stand 4 hours or preferably overnight, filter by decantation of most of the liquid, wash with cold water, dry and ignite at low temperature with excess air until all carbon from the filter paper has been oxidized. Raise the temperature to about 800° C. for 15 minutes, cool and weigh.

$$(BaSO_4 \times 0{\cdot}5885 = Ba.)$$

Ca if present is likely to contaminate the final precipitate of $BaSO_4$ thus for greater accuracy, instead of igniting, re-fuse with alkali carbonates exactly as before and reprecipitate $BaSO_4$.

3. Titration with standard H_2SO_4 solution using an external indicator

Based on the fact that as soon as all the barium has been converted into insoluble sulphate, the red colour produced by Ba salts with Rhodizonic acid (Ba rhodizonate) is discharged. A moderately accurate method.

(For full details see Gibin, *Analyst*, 1933. **58**. 752.)

BERYLLIUM (Be) or GLUCINUM (Gl)

Atomic Weight = 9·02

Metallurgical Occurrence

The mineral Beryl ($3BeO \cdot Al_2O_3 \cdot 6SiO_2$)
Beryllia refractories (BeO)
Beryllium—copper alloys; Be-Ni and Be-Ni-Fe alloys
Occasionally in some special steels.

Source of metal for standards

Metallic beryllium 99·8% (Beryllium Smelting Co.)
or A.R. grade (BeO) or ($BeSO_4\ 4H_2O$)

Methods of Determination

GRAVIMETRIC

1. *Fusion with potassium-sodium carbonate mixture, precipitation of basic Be carbonate, ignition to BeO*
   (suitable for ores).
2. *Fusion with Na_2CO_3 followed by potassium bisulphate fusion, then precipitation of Be as hydroxide and ignition to BeO*
   (more accurate for ores).
3. *Precipitation of Be-tannin complex from NH_4OH solution and ignition to BeO*
   (suitable for small quantities in ores and other materials).
4. *Precipitation of Be as a complex by cupferron from oxalic acid solution*
   (suitable for steels).

COLORIMETRIC

Detection of beryllium (in say the presence of Al) by quinalizarin.

6. *Determination of Be using p-nitrobenzene—azo-orcinol employing standards and the use of a photometer or Spekker absorptiometer.*

METHODS

1. Alkali carbonate fusion, precipitation as hydroxide and ignition to oxide

0·5 g ore or mineral is fused with 5 g $Na_2CO_3 + K_2CO_3$ (1 : 1) in a Pt or Ni crucible, the melt is extracted with water, then evaporated with 5 ml. conc. H_2SO_4, diluted with water, SiO_2 filtered off. The filtrate contains $BeSO_4$ and $Al_2(SO_4)_3$ etc. On evaporation, potash alum [$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$], containing nearly all the Al crystallizes out leaving $BeSO_4$ in solution. The crystals are removed and washed and the filtrate is poured into a hot saturated solution of $(NH_4)_2CO_3$. This precipitates $Al(OH)_3$ and $Fe(OH)_3$ whereas beryllium hydroxide and carbonate stay in solution. The precipitate should be redissolved in dilute HCl and reprecipitated with $(NH_4)_2CO_3$. The combined filtrates can either be boiled to precipitate basic beryllium carbonate ($BeCO_3 \cdot 3BeO \cdot 2H_2O$) which is washed with water, dried and ignited to BeO at 800–1000°C., *or* acidify the filtrates with HCl adding 5 ml. excess boil out CO_2

and precipitate $Be(OH)_3$ with excess NH_4OH (in which reagent $Be(OH)_3$ is quite insoluble in an excess). The hydroxide is filtered, washed with 2% ammonium acetate in 2% NH_4OH and ignited to BeO as before.

(BeO × 0·3605 = Be.)

Note: The alkali carbonate fusion gives sod. or pot. beryllate (K_2BeO_2) also aluminate and $Fe(OH)_3$ which on treatment with H_2SO_4 gives the respective metal sulphates.

$$BeO + Na_2CO_3 = Na_2BeO_2 + CO_2$$
$$Na_2BeO_2 + 2H_2SO_4 = Na_2SO_4 + BeSO_4 + 2H_2O$$
(on boiling) $$2\,(BeCO_3)(NH_4)_2\,CO_3 + H_2O$$
$$= \underbrace{BeCO_3 \,.\, BeO \,.\, 2H_2O}_{\text{basic carbonate}} + 2CO_2 + 2NH_3$$

The final precipitate may be contaminated with traces of Fe_2O_3 and Al_2O_3 on ignition.

2. **Alkali carbonate fusion followed by potassium bisulphate fusion, precipitation as Be hydroxide and ignition to BeO** (Low, Weinig and Schoder, *Technical Methods of Ore Analysis.* 63, etc.)

This is an improvement on the previous method and gives a fairly high degree of accuracy.

Attack 0·5 g of the material either with mixed acids or fusion with 5 g of Na_2CO_3 in a Pt crucible. Assume the latter, the resulting colour of the melt gives an indication of other elements present (e.g. green—Mn, Ni; brown—Fe; yellow—Cr; blue—Co, Cu, Mo, Mn).

Leach the melt with 5% HCl then add sufficient HCl to acidify the solution, evaporate and bake to dehydrate SiO_2. (N.B. If original acid attack was used, evaporate down for the same reason.) The oxides of Al, Be, Fe, Si, etc., are then taken up in 10% HCl, SiO_2 filtered off, washed with hot 5% HCl and water. To the filtrate add NH_4OH until just alkaline to methyl red and boil. Filter off hydroxides of Fe, Al, Be, etc., wash with dilute NH_4OH, dry and ignite in a porcelain crucible at about 700–800° C.

Fuse the mixed oxides with 5 g Na_2CO_3 in a Pt or Ni crucible leach the melt with water and filter off $Fe(OH)_3$ and basic Be carbonate leaving Al in solution as sodium aluminate ($Na_2CO_3 + Al_2O_3 = Na_2Al_2O_4 + CO_2$). The precipitate is dried and ignited to mixed oxides of Fe and Be then fused with 3 g of potassium bisulphate in a silica crucible, leach the melt in hot 10% HCl

and little Br water, nearly neutralize with NaOH and pour into 100 ml. of a warm 10% NaOH solution—(this precipitates $Fe(OH)_3$ and takes Be into solution as sod. beryllate)—for accuracy, redissolve and reprecipitate twice. Acidify the filtrate with HCl, add 5 g NH_4Cl and make *just* ammoniacal with NH_4OH—this treatment converts the beryllate solution first to $BeCl_2$ then to $Be(OH)_2$. Filter, wash with hot 2% amm. nitrate solution (redissolve in HCl and reprecipitate with NH_4OH for greater accuracy) dry and ignite to BeO.

3. Precipitation of Be as a complex with tannin in NH_4OH solution and ignition to oxide (Schoeller and Webb, *Analyst*, 1936. **61.** 235)

To a sulphate solution of Be containing not more than 0·1 g Be add 25 ml. saturated ammonium acetate solution, dilute to 500 ml. and adjust acidity to pH 4·6 (just acid to methyl red) by adding dil. H_2SO_4 or NH_4OH as required. To this boiling solution, add slowly with stirring 50 ml. of 3% aqueous solution of tannin ($C_{14}H_{10}O_9 \cdot 2H_2O$) to precipitate the Al-tannin complex which is washed with 5% amm. acetate solution containing a little tannin and adjusted to pH 4·6. This precipitate may be dried and ignited to Al_2O_3 if required. To the filtrate add fresh 3% tannin solution equal in weight to 12 × wt. of Be present then add NH_4OH to the nearly boiling solution until it is *just* alkaline to litmus. Collect the pale yellow Be-tannin complex and treat exactly as described previously for the Al complex. Ignite to BeO and weigh.

Note: Fe can be removed by an initial Na_2CO_3 fusion.

4. Precipitation of Be as a complex with cupferron from oxalic acid solution and ignition to BeO. (Pigott, *Chemical Analysis of Ferrous Alloys*, 1942)

Dissolve 0·5 g steel in 20 ml. conc. HCl and 5 ml. conc. HNO_3, evaporate nearly to dryness, take up in 100 ml. 5% HCl, bring to the boil and filter off SiO_2 (and WO_3)—(wash with hot 2% HCl). Evaporate the filtrate to 100 ml. and to the *cold* solution add sufficient of a 6% aqueous solution of cupferron ($C_6H_5N(NO)ONH_4$) to produce a white precipitate, which will *just* dissolve, and then add 10 ml. excess of the reagent (under these conditions Fe, Cu, V, Ti, Cb, U, Zr, Ca, Ta are precipitated—see below). Stand for 20 minutes and filter cold, washing with cold 10% HCl solution containing a little cupferron.

To the filtrate add 10 g tartaric acid, make slightly ammoniacal then make acid with an 8% oxalic acid solution. To the cold

solution add 10–20 ml. of 6% cupferron solution as before and after 15 minutes filter the complex washing with 2% oxalic acid solution. Then either ignite to BeO or treat precipitate and filter paper with 50 ml. conc. HNO_3, evaporate to 10 ml., add 30 ml. perchloric acid and 20 ml. conc. HNO_3 and evaporate to fumes of perchloric acid for 10–20 minutes.

Cool, dilute to 150 ml. and make ammoniacal and allow $Be(OH)_2$ to settle. Filter, wash with 2% ammonium nitrate and then with water. Dry and ignite to BeO.

$$FeCl_3 + 3(C_6H_5N \cdot NO \cdot ONH_4) = \underset{\text{(red precipitate)}}{Fe(C_6H_5N_2O_2)_3} + 3NH_4Cl$$

(similarly other metals as stated above)
Then with oxalic acid,

$$BeC_2O_4 + 2(C_6H_5N \cdot NO \cdot ONH_4) = Be(C_6H_5N_2O_2) + (NH_4)_2C_2O_4$$

Treatment with HNO_3 and perchloric acid is to completely oxidize the organic complex and any Cr (if co-precipitated) to chromate so that it will not be precipitated when the solution is next made alkaline to precipitate $Be(OH)_2$.

Note: SiO_2 and WO_3 would contaminate so remove at very early stage in the process.

5. Detection of Be using quinalizarin (H. Fischer, *Z. Anal. Chem.*, 1928. **73**. 54)

To about 10 ml. of a chloride or sulphate solution of Be add 10 drops of an 0·05% solution of quinalizarin in N/4 NaOH solution and make the mixture alkaline with NaOH. The initial violet colour of the reagent with Be present will assume a cornflower blue colour which is only similar to the colour produced by Mg salts. To overcome this trouble the Mg colour is destroyed by first neutralizing the test solution (HCl or NH_4OH), adding 5 ml. of 10% NH_4Cl solution then make alkaline with NH_4OH and add the quinalizarin solution. The addition of a few drops of Br water will remove any blue colour due to Mg but leave the blue 'lake' of Be unaltered.

Fe does not interfere if tartaric acid is added prior to neutralizing.

Al must be kept in solution with excess NaOH.

Cu, Ni and Co giving coloured solutions would interfere unless rendered colourless by conversion to a complex cyanide by addition of KCN to ammoniacal solution.

6. Colorimetric determination of Be using p-nitrobenzene —azo—orcinol (Stross and Osborn, *Metallurgia*, 1944. **30.** 3)

Be in alkaline solution changes the yellow colour of this dyestuff to golden-brown, but difference in tone not being very well marked, it is necessary to use a photometer or Spekker absorptiometer.

The method is suitable for Be contents up to 5%. Thus 0·1–0·5 g of material is suitably treated in order to obtain the Be in solution as sodium beryllate (see methods 1 and 2). Adjust alkalinity to be equal to 3 ml. of 2N NaOH then add 5 ml. of 0·64M boric acid solution, dilute to 20 ml. with water and add 6 ml. of reagent (0·025% in N/10 NaOH solution). Compare in a photometer or Spekker, with standard cells containing varying amounts of Beryllium sulphate solution (1 ml. = 0·00002 g Be) similarly treated.

Notes:

Al does not interfere and Zn although affecting slightly, can usually be ignored.

Si is best removed. (H_2SO_4 + HF on initial sample after acid solution.)

Cu MUST be removed—electrolysis best. The method is then suitable for Be in Be/Cu alloys.

BISMUTH

(Bi) Atomic Weight = 209·0

Metallurgical Occurrence

Detrimental impurity in Cu and Cu alloys, also Al alloys
Impurity in Pb and Sn and their alloys
Necessary constituent in low melting point alloys
Oxide and sulphide bismuth minerals

Source of Metals for Standards

Metallic bismuth 99.9% + (Johnson Matthey & Co.)
(T. W. Senier & Co., London)
(Blackwell's Ltd., Liverpool)

Methods of Determination

GRAVIMETRIC

1. *Precipitation as basic carbonate and ignition to oxide* (suitable in absence of Pb).
2. *Precipitation as oxychloride, drying and weighing as such* (suitable for ores and minerals also Pb and Sn alloys).
3. *Precipitation of Bi as a complex using Pyrogallol, drying and weighing as such* (suitable for high Bi contents in presence of Pb).

4. *Precipitation of Bi as a complex using salicylaldoxime and ignition to Bi_2O_3*
(moderately accurate for high Bi contents. Ag and Zn do not interfere).

VOLUMETRIC

5. *Treatment of oxychloride (as in 2) with excess $AgNO_3$ and back titrate with NH_4CNS*
(for high Bi content in alloys).

COLORIMETRIC

6. *Comparing the intensity of yellow colour of potassium bismuth iodide with standards*
(for Cu alloys up to 0·1% Bi).

7. *Comparison of the colour produced with KI following a diphenyl-thiocarbazone separation for Bi*
(for up to 0·005% Bi in Cu).

METHODS

1. Precipitation as basic carbonate and ignition to oxide

From 0·5 to 5 g of the finely-ground ore is taken, the quantity depending on amount of Bi present. Add 6 to 15 ml. conc. HNO_3, boil nearly to dryness, then add 5 ml. conc. HCl, heat gently till action appears to be complete, then add 5 to 10 ml. conc. H_2SO_4 and boil down to strong white fumes, cool, add 75 to 100 ml. of water and boil gently for a few minutes. Cool, filter, wash with H_2SO_4 (1 : 10). Residue will contain $PbSO_4$. This filtration should be done as soon as possible, otherwise there may be a separation of basic bismuth sulphate.

Dilute further, if necessary, heat nearly to boiling and precipitate with H_2S. Settle, filter, wash with hot water and H_2S water and reject filtrate. The residue may contain As, Sb, Cu, Sn, Cd, etc., as well as Bi. Rinse as completely as possible off the filter and digest with 3 to 10 g pure KCN, warming gently. (With ordinary amounts of Cu, As, Sb and Sn the sulphides of these metals are dissolved, but Cd will remain with the Bi together with any Pb that may still be present.) Filter through the filter paper previously used, and wash thoroughly with hot water.

Rinse the precipitate off the filter paper into a beaker, by means of hot water. Extract the paper with hot HNO_3(1 : 2) and add the extract to the beaker; add more conc. HNO_3 if necessary and warm till everything dissolves except sulphur. Dilute, filter, wash thoroughly with HNO_3(1 : 2). Dilute filtrate to 100 to 300 ml. and heat to boiling.

Nearly neutralize the hot solution with ammonia, boil and add a very slight excess of ammonium carbonate. Bismuth is precipitated as a basic carbonate, $Bi_2(CO_3)_3 . 2Bi_2O_3$. (This precipitation can only be used in the absence of Pb and Cd. When these are present the method is modified as below).

Heat for some time until the carbonate has settled, filter, wash

with hot water. Dry the precipitate, remove as much as possible from the paper to a weighed porcelain crucible. Burn the paper carefully in a separate vessel and add the ash to the bulk of precipitate in the weighed crucible. Ignite slowly at first, finally at a dull red heat, cool in desiccator and weigh as Bi_2O_3.

($Bi_2O_3 \times 0{\cdot}897 = Bi$)

It is best to moisten the ash with HNO_3 and evaporate cautiously to dryness, before adding to the crucible.

Procedure in presence of much arsenic or antimony.—Before treating with cyanide, extract the sulphide precipitate with ammonium sulphide, finally washing with hot water, then continue treatment with cyanide as above.

Separation from cadmium.—When this metal is present, add, before precipitating with $(NH_4)_2CO_3$, an excess of NH_4OH, free from carbonates ; filter off the $Bi(OH)_3$ and wash with warm dilute NH_4OH. Cadmium passes into the filtrate. Dissolve the precipitate of $Bi(OH)_3$ from the filter with dilute HNO_3 and precipitate with ammonium carbonate as above.

Notes :

1. Any Ag is precipitated as AgCl and can be filtered at the solution stage.
2. Pb, Cd, Hg may be co-precipitated as basic carbonates and must be dealt with as above or use Method (2).

2. Precipitation as oxychloride, drying and weighing as such. (Low, Weinig and Schoder, *Technical Methods of Ore Analysis*, 1947)

In the case of ores, proceed as in Method 1 until a solution nearly neutralized with ammonia is obtained. Add dilute ammonia (1 : 2) very cautiously until a faint opalescence is obtained, and then add 1 ml. of HCl (1 : 3). The solution clears at first, then a precipitate of BiOCl begins to form. Heat without boiling for one hour. The settled precipitate may contain a little Pb and Sb. Filter and wash once or twice with boiling water. Reject filtrate.

Redissolve in a little hot HCl (1 : 3), wash with hot water, but do not dilute sufficiently to precipitate BiOCl. Pass H_2S to saturation, filter, wash with water, then once or twice with warm ammonium sulphide, finally again with water. Reject filtrate which contains the Sb.

Dissolve residue by placing filter and contents in a beaker and digesting with HNO_3 (1 : 4). Dilute with hot water and filter. Wash well with warm HNO_3 (1 : 4), then with hot water. Nearly neutralize with NH_4OH, dilute largely with warm water, finish

the neutralization with NH_4OH (1 : 2) as before, add 1 ml. HCl (1 : 3) and proceed as above until the BiOCl (which is now free from Sb and Pb) has completely settled.

Filter on a weighed Gooch crucible, wash with hot water, dry at 100° C. and weigh as BiOCl.

(BiOCl × 0·8024 = Bi.)

Note: Pb, Sb and Sn may co-precipitate unless dealt with as prescribed for Pb and Sb. Any Sn should be removed as metastannic acid at the first stage of dissolution of the material with HNO_3.

3. Precipitation of Bi as a complex using pyrogallol ($C_6H_3[OH]_3$)—drying and weighing as such (Ostroumow, *Z. Anal. Chem.*, 1936. **106.** 36)

To a hot sulphate or nitrate solution of bismuth containing up to 0·25 g Bi, add a slight excess of 10% aqueous pyrogallol solution. Make just alkaline to litmus with NH_4OH and then just acid with dilute HNO_3. The yellow precipitate of $C_6H_3O_3$ Bi is collected on a Gooch crucible, washed with 1% HNO_3 and then water, dried at 110° C. and weighed as such.

($C_6H_3O_3$ Bi × 0·6295 = Bi.)

(Sb interferes and should be removed as in previous methods.)

4. Precipitation of Bi as a complex using salicylaldoxime and ignition to Bi_2O_3

To a sulphate or nitrate solution of bismuth containing not more than 0·1 g Bi per 100 ml., add 1 g NH_4NO_3 followed by 15 ml. of the reagent for each 0·1 g Bi present. Stir and warm the solution to 50° C. then make alkaline (pH9) by adding NH_4OH stirring constantly. Collect the yellow precipitate on a Gooch crucible, wash with 1% NH_4OH, dry at 110° C. but do not weigh due to inconsistency of composition of the complex. Instead add 0·3 g NH_4NO_3 to the dry precipitate and heat strongly to about 800° C. Weigh as Bi_2O_3.

(Bi_2O_3 × 0·897 = Bi.)

(Salicylaldoxime reagent : 1 g dissolved in 5 ml. alcohol and poured into 95 ml. hot water.)

(Most common base metals do not interfere under these conditions.)

5. Volumetric finish to oxychloride precipitation (Method 2)—suitable for high Bi concentration

Proceed exactly as in Method (2) for oxychloride precipitation but instead of drying the precipitate dissolve in hot 50% HNO_3, cool, run in an excess of standard $AgNO_3$ solution, shake to

coagulate AgCl and titrate the excess silver nitrate with standard NH_4CNS solution using 5 drops ferric alum as internal indicator. End point is blood red colour of $Fe(CNS)_3$.

Standard $AgNO_3$ solution : 1·626 g/litre
„ NH_4CNS „ : 0·7281 „
or KCNS „ : 0·9295 „
} 1 ml. = 0·002 g Bi

Ferric Alum Indicator.—Saturated solution with sufficient HNO_3 to decolorize.

Reactions involved:

$$Bi\,OCl + 3HNO_3 = Bi(NO_3)_3 + H_2O + HCl$$
$$AgNO_3 + HCl = AgCl + HNO_3$$
$$AgNO_3\ (\text{excess}) + NH_4CNS = \underset{\substack{\downarrow \\ (\text{white precipitate})}}{AgCNS} + NH_4NO_3$$
$$6\,NH_4CNS + Fe_2(SO_4)_3 = 2Fe\,(CNS)_3 + 3(NH_4)_2SO_4$$

6. Colorimetric iodide method

It is essential that Cu be absent. Separation is effected from a solution of copper or its alloys in nitric or sulphuric acid by one of the following methods :

(*a*) Electrolysis.

(*b*) Treatment with excess NH_4OH gives a precipitate of $Bi(OH)_3$.

(*c*) Precipitate copper with KI from an acetic acid solution and removal of displaced I_2 with $Na_2S_2O_3$ as in iodometric Cu estimation.

(*d*) Separation of basic Bi nitrate from very dilute HNO_3.

(*e*) Precipitate of bismuth sulphide (black) from a KCN solution of the Cu alloy by passing H_2S.

In any case Bi in acetic acid solution has added 5 ml. 5% aqueous KI solution, a few drops of weak H_2SO_3 and the yellow colour of the pot.-bismuth iodide solution is matched against standards prepared from standard bismuth sulphate solution all contained in Nessler glasses.

Notes:

(1) If separation (*c*) is used, the filtrate contains the yellow bismuth iodide and is matched directly but there is usually some occlusion in the Cu_2I_2 precipitate.

(2) H_2SO_3 is added to discharge the colour of any free iodine produced by decomposition of KI.

The reactions concerned are:

Separation (*b*)

$$Bi_2(SO_4)_3 + CuSO_4 + 10NH_4OH =$$
$$2Bi(OH)_3 + Cu(NH_3)_4SO_4 + 3(NH_4)_2SO_4 + 4H_2O$$
(white precipitate) (blue solution)

(Fe is kept in solution with citric acid.)

Separation (*c*)

$$2Cu(CH_3COO)_2 + 4KI = Cu_2I_2 + 4K(CH_3OO) + I_2$$
(cream ppt.)

$$\text{then } I_2 + 2Na_2S_2O_3 + H_2O = 2NaI + H_2O + Na_2S_4O_6$$
(colourless solution)

$$Bi(CH_3COO)_3 + 4KI = KIBiI_3 + 3K(CH_3COO)$$
(yellow solution)

Separation (*d*)

$$Bi(NO_3)_3 + 2H_2O = Bi(OH)_2NO_3 + 2HNO_3$$
(excess) (white ppt. of basic nitrate)

Separation (*e*)

Copper sulphide is *not* precipitated by H_2S from a solution of potassium cuprocyanide whereas bismuth sulphide is since Bi does not form a complex cyanide.

$$2Cu\,SO_4 + 10KCN = 2K_3Cu(CN)_4 + 2K_2SO_4 + (CN)_2$$
(colourless solution)

$$Bi_2(SO_4)_3 + 3H_2S = Bi_2S_3 + 3H_2SO_4$$
(black precipitate)

(For details of procedure see 'Bi in Cu and Cu Alloys'.)

7. Colorimetric method using diphenyl-thiocarbazone separation (Haddock, *Analyst*, 1934. **59**. 163 and *B.D.H. Book of Organic Reagents*, 1948)

A 0·1% chloroform solution of the reagent forms co-ordination compounds with most heavy metals when shaken with an alkaline aqueous solution of the metals. The presence of KCN inhibits this reaction for all metals except lead, bismuth and thallium which form reddish compounds.

Thus 2 g of Cu drillings are dissolved in 20 ml. 50% HNO_3, fumed with H_2SO_4 to remove Pb, 1 g citric acid added (to keep Fe in solution) and the solution made just ammoniacal. 50 ml. of 20% KCN solution is added, dilute to 200 ml. and shake with three successive portions of 10 ml. of the reagent in a separating funnel. The chloroform extracts are distilled to remove chloroform and the residue fumed with 1 ml. conc. H_2SO_4 to destroy

organic matter (a little H_2O_2 helps). Cool, dilute with 15 ml. water, filter any further $PbSO_4$ and treat the filtrate with KI solution and H_2SO_3 exactly as in previous method. Compare in Nessler glasses or absorptiometrically with standard bismuth solutions similarly treated with KI and H_2SO_3.

Note: The yellow coloration of $KI.BiI_3$ is accentuated by the presence of quinine sulphate solution ; thus instead of adding KI solution only, Aubrey's reagent may be used (5 ml.) : 1 g quinine sulphate dissolved in 15 ml. water containing 0·2 ml. conc. H_2SO_4. Add 2 g KI and dilute to 100 ml. with water. Shake, stand, filter any residue and use the clear solution.

BORON

(B) Atomic Weight = 10·82

Metallurgical Occurrence

Mineral borates
Borax and boric acid—fluxes in brazing etc.
Ferro-boron
In certain steels (about 0·05%) as a scavenger and deoxidizer
Calcium boride—non-ferrous deoxidizer
Boron carbide—abrasives, cutting wheels and tools.

Source of Metal as Standards

The metal is not usually produced of sufficient purity for standards, instead A.R. boric acid or borax is used.

Methods of Determination

GRAVIMETRIC

1. *Distillation of methyl borate in the presence of mineral acid and lime and ignition of resulting calcium borate*
   (for boron minerals and salts, less accurate than Method 2).

VOLUMETRIC

2. *Alternative finish to* (1). *Convert methyl borate to boric acid and titrate with standard alkali*
   (applicable to most boron compounds including salts, ferro-alloys, steels etc.).

COLORIMETRIC

3. *Comparison of the blue colour produced with quinalizarin with standards of boric acid similarly treated*
   (suitable for small quantities (0·001 g) of B or boric acid etc.).

METHODS

1. Methyl borate distillation, conversion to calcium borate and ignition of same

During the distillation process below, methyl borate is first produced thus : $Na_2B_4O_7 + 12CH_3OH + 2HCl = 4B(OCH_3)_3$

+ 2NaCl + $7H_2O$ and is soon converted to calcium borate by the lime present as shown by reactions below.

(Applicable to borax, boracic acid, borates of the alkalis and alkaline earths and minerals containing boron.)

The quantity taken for distillation should contain not more than 0·2 g of boron trioxide (B_2O_3). Substances soluble in water are slightly acidified with HCl or acetic acid and placed at once in the distillation pipette (*A*, Fig. 1). Substances soluble in HCl are

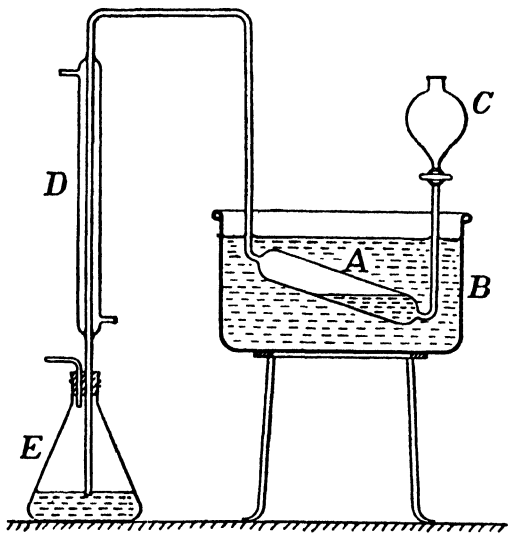


FIGURE 1

dissolved in normal HCl, digested in a flask under a reflux condenser for half an hour, filtered if necessary, neutralized with NaOH to methyl orange or paranitrophenol, then slightly acidified with acetic acid. Silicates and substances insoluble in HCl are fused with five times their weight of Na_2CO_3, the melt extracted with water, evaporated to small volume, the excess of Na_2CO_3 neutralized with HCl, and slightly acidified with acetic acid.

The slightly acid solution (in all cases) is transferred by means of the separating funnel (*C*) to the 200-ml. pipette (*A*) (Fig. 1), and rinsed in to the same by means of a little water. The stop-cock of (*C*) is then closed and the pipette (*A*) heated in the paraffin

bath (*B*), not above 140° C. The distillate is collected in flask (*E*), which contains about 1 g pure CaO previously ignited to constant weight and exactly weighed.

When all liquid has been distilled from (*A*) the bath is lowered and the pipette allowed to cool; then 10 ml. methyl alcohol free from acetone is added and distillation continued. The boron is carried over into (*E*) as a volatile methyl borate, which decomposes in contact with lime according to the reaction $2B(OCH_3)_3 + CaO + 3H_2O = 6CH_3OH + Ca(BO_2)_2$.

This process is repeated three times with fresh additions of 10 ml. methyl alcohol. The contents of the pipette (*A*), which will now have become alkaline, are reacidified with acetic acid, and three more distillations made with 10 ml. portions of methyl alcohol.

The flask (*E*) is then disconnected, stoppered and allowed to stand for half an hour for completion of the reaction given above; the contents are transferred to a dish, evaporated at a temperature below the boiling point of methyl alcohol (66° C.) to avoid loss of boric acid, until all alcohol has been removed. The flask (*E*) is rinsed out with a little dilute HNO_3, into the same dish, and the whole evaporated to dryness. The residue is gently heated to destroy any calcium acetate that may have been formed and the contents transferred to the crucible used for the original ignition of the CaO. This is then heated, first on a water bath, then, with cover on, over a small flame, and finally ignited.

It is allowed to cool in a desiccator for 10 minutes, weighed and again ignited and cooled as before, until constant weight is obtained. The increase in weight of the crucible and contents represents the B_2O_3 derived from the substance assayed. Results by this method are usually about 0·001–0·002 g too high.

$$(Ca(BO_2)_2 \times 0{\cdot}086 = B.)$$

2. Conversion of methyl borate to boric acid and titration with standard alkali (Pigott, *Chemical Analysis of Ferrous Alloys*)

A 5 g sample of ferrous material in a round-bottomed distillation flask (later becomes flask *B*) is dissolved in 25 ml. of conc. HCl, 10 ml. of 100 vols. H_2O_2 are added, the solution heated gently until all O_2 evolved, cool, add 20 g $CaCl_2$ and connect up flask (*B*) to a double distillation train as shown in Fig. 2. Heat flask (*A*) containing methyl alcohol until about 25 ml. have condensed in flask (*B*) then warm the water bath under (*B*) and distil over into connecting flask (*D*) in two fractions, plus solution in U tube. The total distillate is made alkaline to phenolphthalein with

0·25–0·5 g NaOH, evaporated to dryness in a Pt. dish to remove alcohol and convert methyl borate to sodium borate thus:

$$B(OCH_3)_3 + 3NaOH = Na_3BO_3 + 3CH_3OH.$$

Five drops methyl red are added and solution just acidified with HCl to convert to boric acid thus:

$$Na_3BO_3 + 3HCl = 3NaCl + H_3BO_3.$$

Just boil, cool rapidly, just neutralize with $\frac{N}{10}$ NaOH until no red colour exists with 5 drops phenolphthalein as indicator, add 1 g mannite and titrate with N/10 NaOH to a pink end point.

$$H_3BO_3 + NaOH = NaH_2BO_3 + H_2O.$$

Standardize N/10 NaOH against N/10 boric acid by similar titration. N/10 boric acid : 3·22 g/litre : (1 ml. = 0·001 g B.)

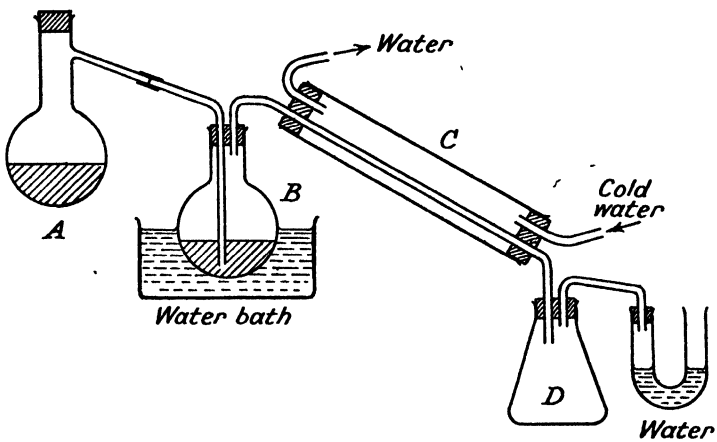


FIGURE 2

In substances such as borax, if alkalis are absent, the titration of boric acid may be very simply carried out by adding one or two drops of 0·1% methyl orange to the cold solution and running in normal H_2SO_4 (Beringer), or preferably HCl or HNO_3 (Treadwell and Hall) until a pink tint remains permanent. About 3 g of borax is a convenient quantity for the titration. The reaction is as follows:

$$Na_2B_4O_7 + H_2SO_4 = H_2B_4O_7 + Na_2SO_4$$

or $$Na_2B_4O_7 + H_2SO_4 + 5H_2O = 4H_3BO_3 + Na_2SO_4,$$

from which 1 ml. normal acid = 0·0216 g B, = 0·0696 g B_2O_3, = 0·1006 g $Na_2B_4O_7$, = 0·1907 g $Na_2B_4O_7 . 10H_2O$.

An Alternative Procedure

Dissolve a convenient quantity, say 5 to 10 g of borax or similar compound in about 250 ml. of water, neutralize exactly with acid and methyl orange as above. To the whole, or an aliquot part, add 50 g of glycerine or (better) 1 g of mannitol, with a few drops of 0·5% alcoholic solution of phenolphthalein, and titrate in the cold with standard alkali, until, on further addition of glycerol or mannitol, the pink colour no longer disappears.

If carbonates are present, excess of acid is added and the CO_2 expelled by boiling in a flask connected with a reflux condenser to avoid loss of any volatilized boric acid. The liquid is then cooled, any deposit from the condenser rinsed in, the solution then neutralized exactly to methyl orange, glycerol or mannitol added, with phenolphthalein and titration with alkali made as above.

The reactions are as follows:

(i) $Na_2B_4O_7 + H_2SO_4 + 5H_2O = 4H_3BO_3 + Na_2SO_4$

(ii) $H_3BO_3 + NaOH = NaBO_2 + 2H_2O$.

3. Colorimetric method using quinalizarin (Kar, *Metals and Alloys*, 1938. **9.** 175)

Boric acid produces a blue coloration from the original reddish-violet colour of the reagent (0·01% in 90% H_2SO_4 solution).

Boron in the material under test must first be converted to boric acid by similar methods to those discussed above, then about 2 ml. of the test solution containing up to 0·001 g B as H_3BO_3 is taken, 8 ml. conc. H_2SO_4 added, followed by 0·5 ml. of reagent.

The blue colour produced is matched against samples of standard boric acid solution similarly treated. (Suitable standard H_3BO_3 solution is: 0·025 g H_3BO_3/litre in 90% H_2SO_4.) No common base metals have been found to interfere.

CADMIUM

(Cd) Atomic Weight = 112·41

Metallurgical Occurrence

Die-casting alloys
White metals and Cd/Ag bearings
Silver solders
Fusible alloys
Cadmium-copper alloys
Roaster and smelter flue dust, ores and minerals (particularly associated with zinc minerals)
Some Al alloys
Cd Plating

Source of Metal as Standards

Pure Cadmium 99·95% (Imperial Smelting Corpn.)
(Johnson Matthey & Co.)

Methods of Determination

GRAVIMETRIC

1. *Weighing as CdS or $CdSO_4$*
   (for ores, flue dust etc.).
2. *Electrolysis of an alkaline cyanide or diluted H_2SO_4 solution*
   (for Cd in zinc and copper and zinc alloys).
3. *Vacuum Distillation*
   (for Cd in white metals, tin, copper and lead alloys).

VOLUMETRIC

4. *Precipitation of a complex by means of β-naphthoquinoline and titration with standard potassium iodate solution*
   (for Cd in the presence of zinc)
5. *Precipitation of a complex by means of phenyl-trimethyl-ammonium iodide and titration with standard potassium iodate solution*
   (for Cd in spelter and light alloys)
6. *Conversion to sulphide and titration with iodine*

METHODS

1. Weighing as CdS or Cd SO_4

0·5–2 g of material are dissolved in 15–25 ml. aqua regia, the solution is fumed with 5 ml. conc. H_2SO_4, cool, dilute with 25 ml. water, boil to dissolve anhydrous salts, cool, filter off Pb SO_4 and SiO_2, washing with cold 1% H_2SO_4. Copper if present will be observed by the colour of the filtrate which is next neutralized with NH_4OH, EXACTLY 15 ml. conc. H_2SO_4 added, dilute to 125 ml. with water, add 5 g $(NH_4)_2SO_4$ and pass H_2S for 10 minutes (under these conditions of acidity Group II sulphides and CdS in particular are completely precipitated). Filter, wash precipitate with 2% H_2SO_4 saturated with H_2S, rinse precipitate into a beaker and treat filter and precipitate with the minimum 10% KCN solution to dissolve copper sulphide leaving orange-yellow CdS undissolved.

If Bi is suspected or the colour of CdS is dark due to Bi or Pb, dissolve in 20 ml. 50% HCl, boil out H_2S, dilute with 25 ml. water and filter if necessary. To the filtrate diluted to 100 ml. neutralize with and add a slight excess of Na_2CO_3 followed by 2 g KCN. Bi and Pb will be precipitated as carbonates but Cd will be in the solution as a cyanide. Filter, wash with water and pass H_2S into the filtrate, pure CdS is precipitated.

Wash the CdS with 2% NH_4NO_3 solution saturated with H_2S, then with water, and either dry at 105–110° C. and weigh as CdS (CdS × 0·778 = Cd) or better, dissolve the final precipitate of CdS in the minimum hot 50% HCl in a porcelain dish. Evaporate to small volume, add 10 ml. 50% H_2SO_4 and evaporate gently to

'fuming' and until all H_2SO_4 has been removed. Finally heat to 550° C., cool and weigh as $CdSO_4$.

($CdSO_4 \times 0{\cdot}5392 = Cd$.)

Note: To ensure clean precipitation of CdS, free from Bi, Cu, and Zn, it is essential to redissolve each sulphide precipitate in 50% HCl and neutralize with NH_4OH make 10% HCl and pass H_2S to reprecipitate CdS, the operation to be done twice or thrice in each instance.

2. Electrolysis from an alkaline cyanide or dilute H_2SO_4 solution

Proceed as in Method 1 to obtain pure CdS, dissolve in 50% HCl, evaporate with 5 ml. H_2SO_4 to 'fuming', cool, dilute to about 50 ml. with water, boil, cool, make just alkaline to phenolphthalein with 10% NaOH solution, just dissolve precipitate of $Cd(OH)_2$ with minimum 10% KCN solution and electrolyse with previously dried and weighed Pt electrodes at approximately 3 volts, 1–2 amps (average) for 1–4 hours. Wash with water and alcohol, dry and weigh the cathode. Increase in weight = metallic Cd. Some analysts prefer a coppered Pt cathode (details, see 'Cd in Copper-Cadmium alloys').

For Electrolysis from H_2SO_4 Solution.—Dissolve CdS in HCl and fume with H_2SO_4 as before, dilute, boil and cool. Just neutralize to methyl orange with NH_4OH then reacidify with 10% H_2SO_4 and add 3 ml. excess and dilute to 150 ml. with water, i.e. about 2% H_2SO_4 concentration. Electrolyse for 3 hours at 3 volts and 1 amp (approx.) using Pt electrodes. Wash, dry and weigh cathode as before. (Full details—see Cd in Zn base die-casting alloys.)

3. Vacuum distillation of Cd (International Tin Research Technical Publication Series A55)

4. Precipitation of a complex with β naphthoquinoline and titration with standard KIO_3 (Pass and Ward, *Analyst*, 1933. **58**. 667)

Suitable for Cd in zinc since the latter gives no precipitate with the reagent. When other heavy metals are present, Cd must first be removed—see Method 1.

To each 100 ml. of a sulphate or nitrate solution of Cd containing up to 0·1% Cd, add 5 g sodium tartrate in 5% H_2SO_4 followed by 10–50 ml. of 5% solution of the reagent dissolved in 2·5% H_2SO_4 so that a slight excess of reagent exists. Afterwards add 20–50 ml. of 5% KI solution, stand 15 minutes, collect the precipitate of $(C_{13}H_9N)_2H_2(CdI_4)$, wash with a mixture of (100 ml. reagent

+10 ml. 5% KI solution + 90 ml. water). Dissolve precipitate in 20 ml. 2N (i.e. 14%) NH_4OH, add 60 ml. 2N (i.e. 18%) HCl followed by 5 ml. of 10% aqueous KCN and titrate with 0·025 M KIO_3 using starch as indicator (1 ml. KIO_3 solution = 0·0014 g Cd).

$$CdI_4 = CdI_2 + I_2$$

(from complex)

then $2I_2 + KIO_3 + 6HCl = KCl + 5ICl + 3H_2O$.

5. Precipitation of a complex with phenyl-trimethyl-ammonium iodide and titration with standard KIO_3 solution (Pass and Ward, *Analyst*, 1933. **58.** 667)

Ag, Pb, Cu, Hg, Bi interfere and should be removed prior to determination. Zn, Co, Ni, Mn, Mg, stannous, ferrous, chromic and arsenious salts do NOT interfere.

Dissolve 2–5 g spelter in 50 ml. 2N H_2SO_4 in the presence of 2 ml. H_2SO_3 and a piece of bright Fe wire, bring to the boil and simmer for an hour—this treatment precipitates Pb, as $PbSO_4$, and Sn, Cu, As, Sb and Bi as metals.

For Al alloys (British Aluminium Company's method) dissolve 1–2 g alloy in 50 ml. mixed acids (70 ml. water + 15 ml. conc. H_2SO_4 + 7·5 ml. conc. HCl + 7·5 ml. conc. HNO_3) and evaporate to 'fuming', cool, dilute to 200 ml. and boil until clear. Filter off SiO_2, wash with hot water, neutralize with NaOH solution and then make 2% acid with H_2SO_4, heat to 60° C and pass H_2S. Filter off CdS (Cu absent), dissolve in hot 50% HNO_3, add 5 ml. conc. H_2SO_4 and 'fume', cool, dilute to 150 ml., boil, cool. In the presence of copper treat the sulphide precipitate as before with HNO_3 and H_2SO_4 but to the diluted sulphate solution add NH_4OH to neutralize and follow with 25 ml. sulphurous acid. Heat to boiling and stir in a slight excess (10 ml.) of a 10% solution of NH_4CNS. Filter off cuprous thiocyanate and wash with cold water, evaporate the filtrate to 100 ml. and treat as below.

To the Cd SO_4 solution in either case add 3 g KI with constant stirring, followed by 30 ml. of a 2·5% aqueous solution of reagent. Allow precipitate $(C_6H_5(CH_3)_3N_2)\,CdI_4$ to settle 6 hours or overnight, filter, wash with water containing 1 g KI and 40 ml. reagent per 200 ml. solution. Dissolve precipitate in 20 ml. 2N NH_4OH, add 60 ml. 2N HCl and 5 ml. of 10% KCN solution and titrate with M/40 KIO_3 solution using starch as indicator. (The presence of 5 ml. of chloroform is helpful in judging the disappearance of iodine, i.e. when chloroform layer is colourless. This method may be used instead of starch.)

(1 ml. M/40 KIO_3 = 0·0014 g Cd.)

Standardize KIO_3 solution with a standard Cd SO_4 solution by similar method. Reactions involved are :

$$(C_6H_5(CH_3)_3N)_2CdI_4 \rightarrow 4HI$$

then $2HI + HIO_3 + 3HCN = 3HCl + 3ICN + 3H_2O$.

6. Precipitation as CdS and titration with standard iodine solution

Prepare CdS as in Method 1 or as described in section on 'White Metals' and *either* dissolve in 50% HCl and titrate with standard iodine solution using starch indicator *or* dissolve CdS in a known excess volume of standard iodine solution and titrate excess iodine with standard $Na_2S_2O_3$ solution using starch as indicator.

$$CdS + I_2 = CdI_2 + S$$

or $$CdCl_2 + 2I_2 + HCl = CdI_2 + ICl + HI$$

(See also under 'Cd in White Metals'.)

CALCIUM

(Ca) Atomic Weight = 40·08

Metallurgical Occurrence

Al and Al alloys
Alkaline earth hardened bearing alloys
As Ca compounds in slags, limestone, fluxes, fluorspar, phosphate rock, ironstone, clays

Source of Metal for Standards

Metallic Ca is obtainable but is too unstable to be used as a standard. For the volumetric estimations, $KMnO_4$ is standardized with AR sodium oxalate.

Methods of Determination

GRAVIMETRIC

1. *Precipitation as a complex using picrolonic acid and weighing as such*

VOLUMETRIC

2. *Precipitation as calcium oxalate and ignition to CaO or more usual to titrate the oxalate with standard $KMnO_4$ solution*
(standard method for most calcium-bearing materials).

METHODS

1. Precipitate with Picrolonic Acid (*BDH Book of Organic Reagents*, 1948. 134)

Pb, Cu, Ba, Sr interfere since these are co-precipitated but Mg may be present up to 10 × wt. of Ca.

To a warm neutral solution of Ca salts containing not more then 0·1 g Ca add 2 g reagent dissolved in 750 ml. warm water.

Allow to stand 6–8 hours and collect precipitate on a sintered glass crucible. Wash with water and dry by aspirating air for 2 hours.

The precipitate has the composition: $Ca(C_{10}H_7N_4O_5)_2 8H_2O$ and contains 5·642% Ca.

2. Precipitate as oxalate and ignition to oxide or titrate oxalate with $KMnO_4$

This method is essentially one of first obtaining effective solution of the calcium-bearing material which may require variations of procedure depending on the type of material to be analysed. Thus with calciferous ores (e.g. hydrated oxide and carbonate iron ores), attack with HCl alone or mixed acids HCl, HNO_3, H_2SO_4 may be required, on the other hand a sodium carbonate fusion may be required depending on the constituents of the gangue. The first treatment should be suitable for obtaining solution of slags of the iron blast furnace variety. More complex silicates may require combinations of acid attack followed by sodium carbonate fusion of the residue.

Fluorspar is usually attacked in a Pt dish with 3 g $KHSO_4$ + 10 ml. conc. H_2SO_4 per 0·5 g sample.

Phosphate rock often completely dissolves in HNO_3 but should some residue persist it is usually effectively dealt with by a sodium carbonate fusion.

For fireclays and other refractories CaO estimation necessitates initial treatment of the finely ground refractory by sodium carbonate fusion (as for complex silicates).

With Al and Al alloys, solution in 12% NaOH followed by 50% HCl treatment of any residue is usually effective, whereas alkali hardened lead base bearing alloys are easily attacked with 40% HNO_3.

Once solution has been obtained the general procedure in all cases is virtually a normal group separation down to the removal of Group IV (Zn Group) metals with reactions omitted if certain metals are known to be absent. Finally to the alkaline filtrate from this group, Ca is precipitated as oxalate by addition of ammonium oxalate solution. The precipitated oxalate is then ignited to oxide ($CaO \times 0{\cdot}715 = Ca$) or more usually dissolved in dilute H_2SO_4 and titrated hot with standard $KMnO_4$ solution previously *standardized by similar titration* against a standard sodium oxalate solution. (For specific details see 'Ca in White Metals'; 'CaO in Ironstone and Blast Furnace Slags'; 'CaO in Fireclay'.)

In many ores the calcium may be completely dissolved by digestion with HCl alone. Where sulphates or silicates are present it is

generally necessary to carry out the regular attack by acids. (See chapter on 'Solution and Separation'.)

For 1 g ore take 15 ml. HCl, 5 ml. HNO_3 and 7 ml. conc. H_2SO_4. Boil off most of the H_2SO_4, cool, dilute, filter off insoluble residue.

In many cases it is unnecessary to precipitate the filtrate with H_2S, thus copper in moderate amount does not interfere with subsequent treatment. Iron and manganese, however, must be removed. If H_2S is used boil off excess and oxidize the solution with 1–2 ml. conc. HNO_3. Boil, add ammonia in slight excess, then if Mn is present 15–20 ml. of saturated bromine water; boil settle, filter.

If the precipitate is large redissolve in HCl, again add a slight excess of NH_4OH and Br, filter and unite the filtrates. Wash with hot water.

Dilute considerably, heat to boiling; add gradually a boiling solution of ammonium oxalate as long as a precipitate forms. Settle, filter, wash with hot water. If much Mg or Zn is present, redissolve the oxalate precipitate in a minimum of HCl, add NH_4OH in excess, and again precipitate from dilute boiling solution with ammonium oxalate. Wash the final precipitate thoroughly with hot water until the liquid passes through free from soluble oxalates.

Dissolve the calcium oxalate precipitate by placing filter and precipitate in a flask or beaker containing 100–125 ml. of dilute H_2SO_4 (1 : 20 by volume). Heat to 70° C. with gentle agitation, until the precipitate is entirely dissolved, without disintegrating the paper. Titrate with standard permanganate. A N/20 solution, containing 1·58 g $KMnO_4$ per litre is suitable.

The reactions are as follows:

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl.$$

$$Ca(C_2O_4) + H_2SO_4 = CaSO_4 + H_2C_2O_4.$$

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

1 ml. N/20 $KMnO_4$ = 0·0010 g Ca.
= 0·0014 g CaO.

Estimation of Calcium Oxide and Hydroxide in Commercial Lime. (Titration with standard acid and phenolphthalein, in the presence of sugar.)—This method utilizes the fact that CaO and $Ca(OH)_2$ are somewhat more soluble in a solution of sugar than in pure water, whereas $CaCO_3$ and the aluminates and silicates of Ca are insoluble.

A 2 g sample, previously crushed to 60 mesh, is agitated with 1 litre of 2% cane sugar solution, free from CO_2 (or other quantities

in proportion) for about two hours, or with intermittent agitation for six hours, preferably settling overnight. An aliquot part, say 50 ml. is then taken out with a pipette and titrated, with addition of phenolphthalein or rosolic acid as indicator, by N/10 or N/5 HCl or H_2SO_4 until colourless—

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$

1 ml. N/10 acid = 0·00285 g CaO.
= 0·00370 g $Ca(OH)_2$

The operations must be conducted as much as possible without exposure to the atmosphere.

CARBON

(C) Atomic Weight = 12·01

Metallurgical Occurrence

In steels, irons, nickel alloys, ferro-alloys, flue dusts, sinter, coal, coke, ores, fluxes, foundry washes, etc. etc.

Source of Analytical Standard

For ferrous materials it is usual to use analysed steel and cast-iron samples (Messrs. Bureau of Analysed Samples Ltd., Middlesbrough).
For non-ferrous alloys, ores, sinter, flue dust, foundry washes etc. it is not usual to use a standard.

Methods of Determination

GRAVIMETRIC

1. *Combustion in oxygen followed by absorption of CO_2*
   (standard method for all types of steels, irons and ferro-alloys, also most carbonaceous materials).

VOLUMETRIC

2. *Combustion in oxygen followed by titration*
   (less usual, alternative to Method 1).
3. *Direct acidimetry or alkalimetry*
   (for alkali and alkaline earth carbonates and bicarbonates).
4. *Gasometric using the Strohlein apparatus*
   (more recent routine method for steels and irons).

COLORIMETRIC

5. *Eggertz method—nitric acid solution and matching with standards*
   (for plain carbon steels and cast irons or low alloy steels Ni < 0.5% Cr < 0·2%).
6. *For 'fixed carbon' in coal: distillation of volatiles and moisture, weighing, and deduct separate ash weight*

METHODS

1. Combustion followed by absorption in caustic alkali (for 'total' and 'graphitic' carbon)

The principle of the process is to combust the carbon (both free and combined) in the ferrous material by heating in a stream of oxygen and when mixed with oxidizing catalysers, such as red

lead, lead chromate, tin or lead foil, all carbon free. The CO_2 produced is absorbed in a weighed bulb containing alkali absorbents.

Combustion is carried out at 1050–1150° C. usually in single or multi-tube (up to 4) electric resistance furnaces since gas furnaces give trouble with products of combustion of fuel gases.

The oxygen used must have any CO_2 removed from it and must be dried before entering the furnace (use soda-asbestos and $CaCl_2$ respectively). Following combustion the gases leaving the combustion tube must be freed from moisture and SO_2 before CO_2 is absorbed in the tared absorption bulb. Usually a train of bottles of various purifying agents are used thus: A plug of platinized asbestos at the exit end of the combustion tube to catalyse most of the SO_2 to SO_3 which is retained by the plug (As_2O_3 would also be held back). The P in the steel or iron becomes oxidized during combustion and stays behind as ferric phosphate whereas H_2 becomes steam and N_2 passes through the train unaltered. Moisture is usually removed from the exit gases by one or more of the following desiccants $CaCl_2$; conc. H_2SO_4, silica gel, anhydrone or barium perchlorate.

SO_2 is absorbed in chromic acid, acidified $KMnO_4$ or neutral precipitated MnO_2. Finally the dried and purified CO_2 is absorbed in the NaOH contained in soda-asbestos or soda-lime (caustic potash is also occasionally used) and the gain in weight of the bulb noted.

Fireclay combustion boats and tubes are usual and must be pre-ignited in oxygen to working temperature (to remove any organic carbon) before use. Tube life can be extended by protecting from corrosive flux splashings by using a sheet nickel lining for the tube in the heating zone.

Combustion time depends largely on the rate of oxygen flow. At 300–400 ml./mn., time is 5–20 minutes depending on type of steel and O_2 rate. Since $CO_2 \times 0{\cdot}2727 = C$, it is time saving to take a 2·727 g sample (special weight can be purchased) for medium C steels, but often greater and less weight is used for low carbon steels and pig iron respectively. With the factor weight, gain in weight of bulb $\times$ 10 = %C. Truly representative sampling is essential, for steels, small millings or turnings are best. If coarse or fine particles are present, screen on 30 mesh, determine proportions present and arrange sample similarly—this is most important for cast irons where 'fines' usually include a high proportion of graphite torn out during preparation of the millings, turnings or sawings.

A 'blank' determination on all reagents used (other than the

sample) or the use of an analysed sample is essential for checking periodically the accuracy of the apparatus.

With high Cr steels it is often difficult to completely decompose carbides during combustion and is often advisable to dilute the sample with a low C iron (e.g. Armco Iron) of known C content and of similar state of subdivision.

For 'free or graphitic' carbon in pig irons and cast irons it is usual to treat a 1 g sample with 50 ml. HNO_3 sp. gr. 1·2 (i.e. about 30% by vol.), this dissolves combined carbon (carbides) leaving graphitic carbon (and SiO_2). This is filtered on ignited asbestos in a Gooch crucible washed with water, 5% NaOH (to remove SiO_2), 5% HCl and finally water and combusted in oxygen as before. (For example of typical procedure and description of apparatus see 'C in Steel and Cast Iron'.)

(For estimation of C as coke in BF flue dust and sinter, see section on 'Iron Ores'.)

2. Combustion to CO_2, absorption in NaOH solution and titration with standard acid (for total C in Al alloys see British Aluminium Company Publication No. 405 (1947))

In this instance, the Na_2CO_3 produced by absorption of CO_2 from combustion in a known volume of standard NaOH solution is titrated with standard HCl solution using first phenolphthalein and then methyl orange as indicators. The difference in the two titration readings gives CO_2 absorbed.

A convenient strength of acid and alkali to use is N/10 (1 ml. = 0·0012 g C).

3. Estimation of CO_2 or CO_3 in alkali or alkaline earth carbonates by direct titration with standard acid or alkali

If the carbonate is soluble in water, this is very simply done by titration with standard acid, using methyl orange as indicator, thus:

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O,$$

this indicator being practically unaffected by carbonic acid. 1 ml. N/10 acid = 0·0022 g CO_2. Bicarbonates are decomposed according to the equation

$$NaHCO_3 + HCl = NaCl + CO_2 + H_2O,$$

so that in this case 1 ml. N/10 acid = 0·0044 g CO_2.

Since phenolphthalein is alkaline to carbonates, but not to bicarbonates, the quantity of both substances in a mixture may be determined as follows:

The solution is first titrated, using phenolphthalein as indicator,

the pink tint disappearing at the completion of the reaction $Na_2CO_3 + HCl = NaHCO_3 + NaCl$, in which 1 ml. N/10 acid = 0·0044 g CO_2 as carbonate. Methyl orange is then added and the titration continued until the pink tint appears, showing that the whole of the bicarbonate has been decomposed. Deducting an amount equal to that found in the titration with phenolphthalein, the remainder represents the bicarbonate originally present in the solution, and as before 1 ml. N/10 acid = 0·0044 g CO_2 as bicarbonate.

In the case of carbonates such as those of Ca, Sr and Ba which are insoluble in water, the sample is dissolved in a measured excess of standard HCl, and the excess titrated with standard alkali. In this case 1 ml. N/10 NaOH or HCl = 0·0022 g CO_2.

In cases where alkali hydroxides are present together with carbonates, the whole of these is recorded by titration with standard acid, whether methyl orange or phenolphthalein be used as indicator, according to the reaction

$$NaOH + HCl = NaCl + H_2O.$$

In such cases the amount of CO_2 may be found by titrating hydroxide and carbonate together, using phenolphthalein, then adding methyl orange and completing the titration, the amount of acid used in this final stage of the titration representing the CO_2 originally present as carbonate, on the basis 1 ml. N/10 acid = 0·0044 g CO_2.

4. Gasometric—using the Strohlein apparatus

CO_2 is produced by combustion of the C as in Method (1) but instead of allowing absorption in the alkali bulb in the usual train, the whole volume of CO_2 plus excess oxygen from the combustion tube is treated with soda-lime or KOH solution to absorb CO_2. The decrease in volume of the gas sample after absorption is read off directly as %C after correcting decrease in volume for temperature and pressure. (For full details and sketch see 'C in Steel and Cast Irons'.)

5. Colorimetric—Eggertz Method

This method is based on matching the intensity of the soluble brown nitrated compound of iron and Mn carbides when treated with dilute HNO_3 with that produced in a standard steel of similar carbon content.

It has been found that for most accurate results, the test and standard steels should both be in similar conditions of heat treatment to ensure similar proportions of carbon present in a similar combined condition.

This method is still widely used as a routine check on plain carbon steels and irons and may be used for low alloy steels provided similar standards are used. With steel of high alloying contents the colour produced by Ni and Cr vitiates the result.

With steels of %C less than 0·3% use 0·2 g sample
,, ,, ,, ,, between 0·3 and 0·9% use 0·1 g sample
,, ,, ,, ,, greater than 0·9% use 0·05 g sample

dissolve sample and similar weight of standard (of very similar %C) contained in graduated Eggertz tubes in *exactly* 3 ml. (for 0·05 and 0·1 g samples) or 4 ml. (for 0·2 gm sample) of HNO_3 (sp. gr. 1·2) without heating. Decompose brown flocculent matter by warming the tubes suspended vertically in a water bath. Shake tubes occasionally to release entrapped gas bubbles. Warm until a clear solution results (15–30 minutes). Cool tubes quickly, dilute the standard until say 2 ml. = 0·1% C, then dilute the test solution until colours match (against a common background of damp filter paper held against good daylight). The carbon content of the test is then in proportion to the volume of solution and relative to the standard volume.

This method is applicable for determining combined carbon in cast irons, by dissolving a 1 g representative sample (alongside a similar standard) in 20 ml. HNO_3 (sp. gr. 1·2), heat in a water bath as before for 30 minutes (this time graphite flakes persist), dilute exactly to 50 ml., filter off a suitable fraction (5 ml.) into Eggertz tubes, dilute and compare colours as before (for further details see also 'C in Steels and Cast Irons').

6. Fixed Carbon in Coal (B.S.I. Method)

1 g of coal is heated in a porcelain or silica crucible closed with a well-fitting lid. The covered crucible and contents are then heated for 7 minutes in a muffle at 970–1000° C. then allowed to cool in a desiccator. The contents of the crucible are weighed and loss in weight represents 'moisture and volatiles'. The actual weight of the residue (assuming no oxidation has occurred) represents the coke produced and is made up of 'fixed carbon' and 'ash'. If this residue be next heated at 800° C. for 1 hour, spread out in a thin layer on a porcelain dish to oxidize all the carbon, the final residue when cooled in a desiccator and weighed gives the ash content from which the 'fixed carbon' can be readily calculated from the difference in the last two weighings. (See also 'Estimation of Carbon' in Fuels Section.)

CERIUM

(Ce) Atomic Weight = 140·13

Metallurgical Occurrence

Some light alloys (e.g. ceralumin)
Mischmetal (Ce + La + Th + rare earths)
Lighter flints
CeO_2 in incandescent mantles

Source of Metal as Standards

Metallic cerium is obtainable (New Metals & Chemicals Ltd., London) but preferable to use AR ceric sulphate or nitrate.

Methods of Determination

GRAVIMETRIC

1. *Precipitation as oxalate and ignition to oxide* (for Al and Mg alloys).
2. *Precipitation as hydroxide and ignition to oxide* (minerals, mischmetal, flints).
3. *Precipitation as fluoride and ignition to oxide* (for ferrous materials).

COLORIMETRIC

4. *Detection in presence of Al, Cr, Fe and rare earth metals*

METHODS

1. Precipitation as Ce oxalate and ignition to oxide (British Aluminium Company's Method)

About 1 g of alloy is attacked with 20–40 ml. 20% NaOH solution. When dissolved, dilute to 250 ml. with hot water, boil and filter off heavy metals, Ce, etc., wash with hot 1% NaOH solution. Dissolve precipitate in 25 ml. hot 50% HCl adding 2–5 ml. conc. HNO_3 if necessary. Evaporate to about 5 ml., dilute to 250 ml., add 20 ml. 25% NH_4Cl solution and make alkaline with NH_4OH. Boil until most of the NH_3 is removed and filter off hydroxides of iron, aluminium and cerium, wash precipitate with hot 2% NH_4OH containing a little ammonium nitrate.

Dissolve the precipitate in 25 ml. hot 50% HCl and evaporate just to dryness, take up in 25 ml. N/2 HCl, heat to boiling and add 40 ml. of boiling 15% oxalic acid solution. Stand overnight, filter through a weighed Gooch crucible washing with cold 0·25% oxalic acid solution and ignite at 1000° C. for half an hour, cool and weigh as CeO_2 ($CeO_2 \times 0{\cdot}8142 = Ce$).

2. Precipitation as hydrated oxide and ignition to CeO_2 (separation from thorium, lanthanum and didymium)

Minerals are best brought into solution by fusion in a silica crucible with $KHSO_4$ and extraction with water. The extract is acidified with HCl or H_2SO_4 and Cu, Bi etc., removed by precipitation with H_2S, filtered, excess H_2S boiled off, HNO_3 added,

and the hydroxides precipitated by NH_4OH in the ordinary way. The precipitate is filtered off (best on a Buchner funnel), washed, and redissolved in HCl (reprecipitated if large). The solution in HCl is then diluted considerably, made nearly neutral with NH_4OH, Br water added, boiled and 3 g oxalic acid added for every 100 ml. of liquid. It is then stirred thoroughly, settled and allowed to stand in a warm place overnight.

Filter and wash with cold 1% oxalic acid until free from Fe. (At this stage the residue may be ignited if desired, and weighed as $CeO_2 + ThO_2 + La_2O_3 + Di_2O_3$.)

Redissolve in HNO_3. (If it has been ignited, fuse again with $KHSO_4$, extract melt with water and add HCl.) Nearly neutralize with NaOH. Add 2–3 g sodium acetate and 10 ml. Br water or sodium hypochlorite. Boil, settle, filter, wash with hot water the precipitated Ce and Th dioxides, dry, ignite and weigh as $CeO_2 + ThO_2$. The filtrate contains the La and Di.

The separation may also be made as follows : Obtain the metals in H_2SO_4 solution. Heat to expel excess of H_2SO_4, extract with cold water, filter. (Remove Cu, Bi, etc., if necessary by H_2S.) Add oxalic acid as previously. Ignite the oxalate precipitate or dissolve in HNO_3. To the solution add excess of KOH, make up to 200 ml., pass Cl_2 gas through the liquid until no longer alkaline. $Ce(OH)_3$ is precipitated, and later becomes converted to deep yellow $Ce(OH)_4$. La and Di remain in solution. Filter, wash and ignite to CeO_2.

If Th is also present, proceed by following method.

The hydroxide precipitate finally obtained (after separation of La and Di) as in above paragraphs is dissolved in HCl, or the ignited oxides are fused with $KHSO_4$, extracted with water and acidified with HCl. The solution is nearly neutralized with NH_4OH, 2 g sodium thiosulphate added and the mixture boiled for 15 minutes. It is then filtered, and the precipitate, which contains the Th, washed with hot water until free of sulphates. The filtrate is made alkaline with ammonia, boiled two minutes, settled, filtered, washed with hot very dilute NH_4OH, dried, ignited and weighed as CeO_2.

3. Precipitation as fluoride and ignition to oxide (Pigott, *Chemical Analysis of Ferrous Alloys*, 1942)

A 2 g sample of the alloy steel or cast iron is dissolved in 60 ml. hot 50% HCl followed by oxidation of ferrous solution and decomposition of carbides with 5 ml. conc. HNO_3. Add 60 ml. 25% tartaric acid solution followed by 30 ml. of 10% Sn Cl_2 solution (in 75% HCl) and 10% NaOH solution to slight excess.

Under these conditions, ferric salts are reduced to ferrous (by $SnCl_2$) and then precipitated as hydroxide by NaOH in the presence of tartaric acid whereas cerium stays in solution. Make up to 500 ml. and filter off 250 ml. Acidify filtrate with HCl, boil, add 2 g ammonium fluoride, neutralize using NH_4OH then re-acidify with HCl. Cerium fluoride is precipitated and allowed to settle for an hour, is filtered, washed with 3% NH_4F solution and finally ignited to CeO_2 in a Pt crucible.

$$3NH_4F + CeCl_3 = CeF_3 + 3NH_4Cl$$
$$2CeF_3 + 2O_2 = 2CeO_2 + 3F_2$$
$$(CeO_2 \times 0{\cdot}8142 = Ce.)$$

4. Colorimetric detection of Ce using arsanilic acid
(Miller, *Ind. Eng. Chem.*, Anal. Edn., 1937. 9–181)

This is based on the formation of a pink coloration with the reagent in the presence of Ce when the hydroxides of Fe, Al, Cr and Ce are dissolved in the minimum dilute H_2SO_4 and 2–3 drops of the reagent dissolved in N/10 NaOH are added.

(H_2S group metals must be previously removed.)

CHROMIUM

(Cr) Atomic Weight = 52·01

Metallurgical Occurrence

Constructional, stainless and heat-resisting steels, armour plate
Ni/Cr electrical resistance alloys, stellite
Al alloys
Plating baths
Cu-Cr alloys
Chromite-iron ores
Ferro-chromium
Chromite and chrome-magnesite refractories

Source of Metal for Standards

Metallic Cr (99%+ pure) (Murex Ltd., Rainham, Essex), but more desirable to use A.R. potassium dichromate solutions.

Methods of Determination

GRAVIMETRIC

1. *Precipitation as hydroxide and ignition to Cr_2O_3—rarely used*
(applicable to low Cr content in ores, minerals, clays etc.).

VOLUMETRIC

2. *Fusion with oxidizing flux and titration of dichromate with ferrous ammonium sulphate and $KMnO_4$ or $K_2Cr_2O_7$ solutions*
(standard method for high chromium contents in ores, minerals, high C ferro-chromium).
3. *As (2) but titration of dichromate with KI and $Na_2S_2O_3$*
4. *Solution in acids, oxidation to dichromate by one of the following reagents: $KMnO_4$ (Vignal's method), ammonium persulphate, sodium bismuthate or*

perchloric acid and titration with ferrous ammonium sulphate and $KMnO_4$
(for all steels, cast irons and chrome iron ore, plating baths etc., where Cr exceeds 0·2%).

COLORIMETRIC

5. *Comparison of the yellow sodium chromate colour from fusion with oxidizing flux with that produced with caustic alkali and standard* $K_2Cr_2O_7$ *solution*
(for less than 0·25% Cr in rocks, clays, steels).
6. *Comparison of the reddish-violet colour produced by dichromate with Diphenyl-Carbazide* ($CO(NH \cdot NH \cdot C_6H_5)_2$) *in dilute* H_2SO_4 *solution with that of standard* $K_2Cr_2O_7$
(applicable to less than 0·2% Cr in ferrous materials) (more accurate than Method 5).

METHODS

1. Precipitation as hydroxide and ignition to Cr_2O_3 (Low, Weinig and Schoder, *Technical Methods of Ore Analysis*, 1947)

None of the common metals substantially interfere with the method.

1 g of ore is fused with 5 g Na_2CO_3 + 0·5 g KNO_3 in a Pt crucible. Leach melt with hot water. If colour of solution is pink or brown due to Mn add 5 ml. alcohol and warm to precipitate Mn as MnO_2. After filtering off any MnO_2 a yellow filtrate indicates the presence of Cr as Na_2CrO_4 (Note: any insoluble residue from first fusion should be re-fused as before.) Acidify filtrate with HCl, evaporate to dryness and bake—this dehydrates any SiO_2 and converts Na_2CrO_4 to sodium dichromate and finally to Cr_2O_3 ($2Na_2CrO_4 + 2HCl = Na_2Cr_2O_7 + 2NaCl + H_2O$), then $Na_2Cr_2O_7 \rightarrow Cr_2O_3$. Dissolve up in minimum HCl (10%), filter off SiO_2. To the filtrate add a very slight excess of NH_4OH to precipitate Cr (and any Al) as hydroxides $Cr(OH)_3$. The dried precipitate is fused with $Na_2CO_3 + KNO_3$ as initially, leach with water and add NH_4NO_3 until all CO_2 is evolved. When this point has been reached a few ml. of NH_4OH will precipitate $Al(OH)_3$ leaving Cr in solution as sodium chromate. Reduce the chromium solution to chromic sulphate with SO_2 ($H_2SO_3 + O = H_2SO_4$ then

$$H_2SO_4 + 2Na_2CrO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O)$$

$$(Na_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 = Cr_2(SO_4)_3 + Na_2SO_4 + 4H_2O)$$

Boil out excess SO_2, add slight excess NH_4OH, filter off $Cr(OH)_3$, wash with hot water, dry, ignite at high temperature and weigh as Cr_2O_3 ($Cr_2O_3 \times 0{\cdot}6842 = Cr$).

2. Fusion with oxidizing flux and titration of dichromate with ferrous ammonium sulphate (Low, Weinig and Schoder, loc. cit.)

Place 3–4 g of sodium peroxide in a nickel crucible; add 0·5 g

of the very finely ground ore, mix thoroughly and heat gently till completely fused, which requires about ten minutes. Keep fused for a further ten minutes, then cool; add more sodium peroxide (say 1 g) as a cover and fuse again for about five minutes.

Cool, extract with water, remove and rinse crucible, and dilute solution to about 100 ml. If permanganates are present, indicated by a purple colour, add sodium peroxide to the solution. Boil for ten minutes to decompose excess of sodium peroxide, then add about 5 g $(NH_4)_2CO_3$ to neutralize part of the NaOH present. Filter and wash with hot water.

The insoluble residue is treated with HCl and the extract added to the filtrate. If any portion still remains undissolved, it should be dried, ignited and again fused with Na_2O_2, the melt being treated as above.

Acidify the filtrate with H_2SO_4 (1 : 4), adding at least 25 ml. in excess. Dilute to about 300 ml. Add a weighed amount of ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4 . 6H_2O$, in excess of the chromate present, adding the salt gradually, with stirring, until the yellow colour has disappeared and a drop of the liquid gives a blue colour with potassium ferricyanide.

The excess of ferrous ammonium sulphate may now be determined by titration either with standard permanganate or dichromate solution. (For details see under 'Iron'.)

With $KMnO_4$ titrate to the usual pink flush, but with $K_2Cr_2O_7$, potassium ferricyanide external indicator solution must be used and titrate to a disappearance of the blue ferrous ferricyanide

$$Na_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + Na_2SO_4 + 7H_2O.$$

The iron equivalent of either the $KMnO_4$ or $K_2Cr_2O_7$ must be known by previous standardization.

The difference between the weight of Fe salt added (or volume of a standard Fe solution) and the Fe value of the oxidizing agent used for back titration gives the iron equivalent of the Cr present. From the above equation: 335 parts Fe = 152 parts Cr_2O_3 (or 104 parts Cr)

$\therefore$ Fe $\times$ 0·3107 = Cr, or Fe $\times$ 0·4537 = Cr_2O_3

or 1 part $FeSO_4(NH_4)_2SO_4 . 6H_2O$ = 0·04427 parts Cr.

(See also 'Cr in High C Fe/Cr'.)

Fusion with Alkali Carbonates.—The fusion may be made with a mixture of sodium or potassium carbonates (or both) with potassium nitrate, but for high-grade ores sodium peroxide is preferable, as it fuses at a much lower temperature. For the above fluxes a platinum crucible should be used. The subsequent procedure

is as above, except that the boiling to decompose Na_2O_2 is not necessary.

3. As method (2) but titration of dichromate with KI and $Na_2S_2O_3$

Fuse with sodium peroxide, as above, add ammonium carbonate to the extract till most of the NaOH is neutralized, then acidify with H_2SO_4 or $KHSO_4$, and boil until any oxidizer (such as Na_2O_2, $KClO_3$ or KNO_3) is reduced, and all nitrous or chlorous fumes expelled. Cool, add HCl until not more than 5% HCl in the solution, followed by 1–2 g KI and titrate the iodine liberated by the dichromate, with standard $Na_2S_2O_3$ solution using starch solution as indicator:

$$2K_2CrO_4 + 2HCl = K_2Cr_2O_7 + 2KCl + H_2O$$
$$K_2Cr_2O_7 + 14HCl + 6KI = 2CrCl_3 + 8KCl + 7H_2O + 3I_2$$
$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6$$

1 ml. N/10 sodium thiosulphate solution = 0·001733 g Cr.

4. Solution in acids, oxidation to dichromate and titration with ferrous ammonium sulphate and $KMnO_4$ as before

There are many standard oxidizing agents used by analysts for converting to dichromate the chromic salt produced from the acid solution of the alloy steel or cast iron. Brief mention of the respective reagents are listed below with references to the full analytical details of each particular scheme of analysis.

(*a*) *Vignal's Method.*—The alloy steel sample (0·5–2 g) is dissolved in 50–70 ml. of 14% H_2SO_4 (by volume), all carbides are oxidized with 5 ml. conc. HNO_3 and the chromic sulphate solution is oxidized to $K_2Cr_2O_7$ with 1·2% $KMnO_4$ solution. Any Mn present and excess $KMnO_4$ is precipitated as MnO_2 by means of $MnSO_4$ solution on boiling. The resulting cold filtered dichromate solution is titrated with ferrous ammonium sulphate and $KMnO_4$ as before.

$$Cr_2(SO_4)_3 + 2KMnO_4 + 3H_2O = K_2Cr_2O_7 + 2MnO_2 + 3H_2SO_4$$

and

$$Cr_2(SO_4)_3 + 3MnO_2 + H_2O = H_2Cr_2O_7 + 3MnSO_4.$$

1 ml. N/10 $KMnO_4$ = 0·001733 g Cr.

(Reference 'Cr in Steels'.)

(*b*) *Ammonium Persulphate Method.*—As before the steel is attacked either with a H_2SO_4 — HNO_3 mixture or advantageously with a H_2SO_4 — H_3PO_4 mixture (150 ml. conc. H_2SO_4 + 100 ml. conc. H_3PO_4/litre) since at a later stage H_3PO_4 decolorizes the iron solution and makes for an easily observed titration.

Oxidize ferrous solution and decompose carbides as before with 5 ml. conc. HNO_3, dilute to about 0·5–1% H_2SO_4 concentration, add 10 ml. of 0·3% $AgNO_3$ solution, bring to the boil and add 2 g ammonium persulphate. The presence of the silver nitrate catalyses the oxidation of Cr (and any Mn) by the persulphate to the dichromate and permanganate conditions respectively. The presence of Mn is useful by serving as an indicator of the progress of oxidation, i.e. when the permanganate colour appears, both Mn and Cr have been oxidized to the higher valency, but the permanganate present must obviously be removed before the addition of excess ferrous ammonium sulphate and titration of the excess with $KMnO_4$ solution.

This is most effectively done by dropwise addition of weak oxalic acid solution (0·7% solution) until only a faint pink colour exists in the solution, then add 5 ml. of 25% HCl and boil 5 minutes. Under these conditions, excess $KMnO_4$ and ammonium persulphate are decomposed and the silver (from $AgNO_3$) reacts with excess HCl, and is precipitated as AgCl which will not interfere subsequently. Cool and titrate with ferrous ammonium sulphate and $KMnO_4$ as before

(with Cr) $3(NH_4)_2S_2O_8 + Cr_2(SO_4)_3 + 7H_2O = H_2Cr_2O_7 + 3(NH_4)_2SO_4 + 6H_2SO_4$

(with Mn) $(NH_4)_2S_2O_8 + MnSO_4 + 3H_2O = (NH_4)_2SO_4 + MnO_2 \cdot H_2O + 2H_2SO_4$

(then with oxalic acid) $2KMnO_4 + 5C_2H_2O_4 + 6HCl = 2KCl + 2MnCl_2 + 10CO_2 + 8H_2O$

and

$2MnO_2 + C_2H_2O_4 + 6HCl = 2MnCl_2 + Cl_2 + 2CO_2 + 4H_2O.$

Using the above principles both Mn and Cr can be estimated in the sample.

(References 'Cr and Mn in Steel' and 'Cr in Al Alloys'.)

(*c*) *Sodium Bismuthate Method.*—Most usual oxidant for Mn to permanganate, but occasionally used for Cr (expensive reagent however). Solution of the alloy should be effected preferably with HNO_3 (often difficult) or H_2SO_4 with HNO_3 added subsequently.

The addition of sodium bismuthate in large excess (25 × weight of Cr) to a warm 20% HNO_3 solution of chromic nitrate or sulphate gives dichromic acid $H_2Cr_2O_7$ thus :

$$3NaBiO_3 + 2Cr(NO_3)_3 + 6HNO_3 = H_2Cr_2O_7 + 3Bi(NO_3)_3 + 3NaNO_3 + 2H_2O$$

the dichromic acid being titrated with ferrous ammonium sulphate and $KMnO_4$ as before.

(Mn seriously interferes and must be separated (as in 'b') also excess sodium bismuthate must be removed by filtration.)

(Reference: 'Cr in Al Alloys', British Aluminium Company's Publication No. 405, 1947.)

(*d*) *Perchloric Acid Method.*—Very suitable for alloy steels containing a large proportion of complex carbides since these are readily decomposed by this reagent. After digestion in this reagent, Cr is oxidized to chromic acid but to ensure complete oxidation to dichromic acid further treatment with ammonium persulphate and $AgNO_3$ is recommended (as in (*b*) above). Conclude with the normal volumetric finish using ferrous ammonium sulphate and $KMnO_4$ solutions.

Iron may be removed from the solution (for colorimetric estimation) by treatment with 10% NaOH solution, the sodium chromate produced being compared with standard chromate solutions.

(References: 'Cr in Al Alloys' also 'Perchloric Acid Treatment for Chromite'—(Smith and Getz), *Ind. Eng. Chem. Anal. Edn.*, 1937. **9**. 518.)

Notes:

1. In the volumetric methods using a final titration of ferrous ammonium sulphate and $KMnO_4$ the titration reactions are:

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

$$10FeSO_4(NH_4)_2SO_4 + 2KMnO_4 + 8H_2SO_4 \text{ (excess)} = 5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

2. The factor weight of 1·7336 g (or multiples or fractions depending on Cr content of material) is frequently used with steel samples to simplify calculation since as each 1 ml. of N/10 titration solutions = 0·0017336 g Cr, on a factor weight sample 1 ml. = 0·1% Cr.

3. If the concentration of Cr is high in the assay solution the green colour of chromic salts, after addition of excess ferrous ammonium sulphate, may be so intense that the determination of the end point with $KMnO_4$ may be uncertain. To sharpen this end point an internal indicator is strongly recommended—diphenylamine, diphenylbenzidine or sodium or barium diphenylamine sulphonate. (Diphenylamine or diphenylbenzidine 1% in N_2 free conc. H_2SO_4; Na or Ba diphenylamine sulphonate 0·2% in water.) The end point is a change from green to violet on completion of the oxidation of excess ferrous salts in the presence of

HCl, H_2SO_4 and H_3PO_4. These oxidation-reduction indicators can be used with either $KMnO_4$ or $K_2Cr_2O_7$ (not advisable to have HCl present with $KMnO_4$ titration even in presence of phosphoric acid). The most usual acid concentrations of mineral acids in the solution prior to titration with these internal indicators (5 drops) are between 3 and 10% and the mineral acid mixture used consists of 50 ml. of (100 ml. conc. H_3PO_4 + 150 ml. conc. H_2SO_4/litre) + 10 ml. conc. HCl where applicable, all to be added to the assay solution diluted to about 250 ml. These indicators are dyestuffs and their change in colour at the end of the titration is due to their oxidation or reduction. Thus for very accurate work, deduct 0·05 ml. from the volume of N/10 titrating solution to bring about this change.

4. As an alternative to the use of the above internal indicators, some analysts prefer to use 2 drops of ortho-phenanthroline (internal) indicator solution when titrating with $KMnO_4$. This titration does not require the presence of H_3PO_4 but only the normal H_2SO_4 concentrations as described in Vignal's Method.

The indicator solution is made up as follows: 0·695 g ferrous sulphate crystals dissolved in 100 ml. water, stir in 1·485 g ortho-phenanthroline until dissolved giving a dark red solution. This indicator turns from red to pale green in the presence of excess $KMnO_4$ at the end point of the back titration. (See 'Cr in Al Alloys'.)

5. It is essential to filter off graphite from the initial solution stage of cast irons prior to oxidation of Cr otherwise graphite will disturb the reaction because of its reducing properties.

6. Tungsten when present usually precipitates as WO_3 during initial solution of the steel after oxidation with nitric acid or perchloric acid. With the methods described above this precipitate does not normally interfere with the procedure but removal by filtration (with any SiO_2) is preferable in order to minimize absorption losses.

7. Se and Te react similar to Cr during treatment with excess ferrous ammonium sulphate and back titration with $KMnO_4$, thus if present their removal is essential. This is done by passing SO_2 into a dilute HCl solution (not more than 15% HCl) of the material, when elemental Se and Te are precipitated.

8. Vanadium also behaves as Cr during reduction by excess ferrous solution and titration with $KMnO_4$ and gives a fading end point until all tetravalent V has been oxidized to the pentavalent state. However, quite accurate results are obtained if on adding the last drop of $KMnO_4$ solution, shaking and standing for 30 seconds the pink tinge still persists then that is the end point

for the Cr titration. The reducing action of the vanadyl salts is fairly sluggish in cold solutions.

One method of estimating Cr and V in the same solution is to proceed exactly as described under Vignal's Method—here the *nett* amount of N/10 ferrous ammonium sulphate used to give a pink flush during back titration with N/10 $KMnO_4$ which persists for 30–60 seconds is proportional to the Cr content of the sample (1 ml. = 0·00173 g Cr). Now back titrate the solution with N/10 ferrous ammonium sulphate until the last drop gives a blue colour with a drop of 0·1% $K_3Fe(CN)_6$ external indicator. Then titrate with N/10 $KMnO_4$ slowly with constant shaking until a pink flush persists for at least 60 seconds. This final titration with N/10 $KMnO_4$ gives the V content (1 ml. = 0·00509 g V).

Reaction of dichromate with ferrous ammonium sulphate and $KMnO_4$—see Note 1.

Reaction of metavanadic acid with ferrous ammonium sulphate and $KMnO_4$ is as follows :

$$2FeSO_4 + 2HVO_3 + 3H_2SO_4 = \underset{|}{(V_2O_5)}$$

$$Fe_2(SO_4)_3 + 2(VO)SO_4 + 4H_2O \underset{|}{(V_2O_4)}$$

then

$$10(VO)SO_4 + 2KMnO_4 + 12H_2O = 10HVO_3 + 7H_2SO_4 + K_2SO_4 + 2MnSO_4.$$

5. Colorimetric comparison of yellow colours of sodium chromate solutions

This is not as accurate as the next method but is frequently used for routine checking of small amounts of Cr (less than 0·2%) in ores, slags, clays and even steels.

The solutions from alkaline oxidizing fusion (for ores, slags, etc.) after removal of $Fe(OH)_3$ by filtration, is diluted to a known volume (say 200 ml.) and an aliquot portion taken for comparison in Nessler glasses with the colour produced by adding a dilute standard $K_2Cr_2O_7$ solution (say N/50) to 50 ml. distilled water containing 5 ml. of a 10% NaOH solution. Then 1 ml. N/50 $K_2Cr_2O_7$ solution = 0·00035 g Cr (approximately).

For ferrous materials a 1 g sample is brought into solution EITHER by treatment with 10 ml. 25% H_2SO_4 followed later by 5 ml. conc. HNO_3 for oxidation of ferrous salts and decomposition of carbides OR solution and fuming with 60 ml. 20% perchloric

acid. Mn is removed by $KMnO_4$ as in Vignal's Method. The chromic acid produced in both cases is then converted to sodium chromate by boiling with 25 ml. 25% NaOH and 1 g Na_2O_2 (or an excess of 7 g NaOH + 7 g Na_2HPO_4 in 100 ml. water). Fe, Mn, Ti, Ni, Cu, Co, Be, Zr, Ce and U are precipitated and filtered off and the filtrate (sodium chromate (yellow) and Al, V, Se, Te, P, As and Mo salts (colourless)) is matched against standard chromate solutions as described above.

6. Colorimetric comparison of the violet colours produced by diphenylcarbazide ($CO(NH . NH . C_6H_5)_2$)

Used widely for low Cr steels and Cr in Al alloys.

Proceed exactly as in previous method to obtain the Cr in solution as sodium chromate. Just acidify with a few ml. of 25% H_2SO_4 followed by 2 ml. of reagent and 20 ml. of 25% H_2SO_4 and dilute to 100 ml. with water.

For the standard take 50 ml. water, add 20 ml. 25% H_2SO_4 and then 2 ml. of reagent. Mix, and run in from a burette standard $K_2Cr_2O_7$ solution until the violet colour intensities of assay solution and standards match, using Nessler glasses as the solution containers. A convenient $K_2Cr_2O_7$ solution is: 0·0566 g $K_2Cr_2O_7$ per litre (1 ml. = 0·00002 g Cr). Diphenylcarbazide solution: 0·5 g dissolved in 50 ml. ethyl alcohol and acidified with 3 drops of conc. H_2SO_4.

The violet coloration is an oxidation product of diphenylcarbazide (V produces a similar colour and may interfere if in large quantities).

COBALT

(Co) Atomic Weight = 58·94)

Metallurgical Occurrence

Ores, speisses
Impurity in refined nickel (up to 0·4%)
Cemented carbides (3–20% Co)
Stellite (Co 45–65; W 5–20; Cr 25–30; C 1·5–2; Fe balance)
Magnet alloys (e.g. Co 30–40; W 5–9; Cr 1·5–3; C 0·4–0·8; Fe balance)
(Alnico—Co 10; Ni 20; Al 10; Fe balance)
Cu-Be-Co alloys (0·25% Co)
Kanthal electrical resistance alloy (Co 3; Cr 20; Al 5; Fe 72)
Turbine Blade Alloys (Vitallium—64 Co (+ Cr, Mo, Ni, Si, Mn, C)
(Hastalloy—29 Co (+ Ni, Fe, Si, Mn, C) etc.

Source of Metal as Standard

Pure cobalt 99% + (electrolytic or from carbonyl decomposition)
(Mond Nickel Co. Ltd., London)
(Murex Co. Ltd., Rainham)

Methods of Determination

GRAVIMETRIC

1. *Separation of iron (by basic acetate or zinc oxide methods), precipitation of Co as a complex by α-nitroso-β-naphthol and ignition to Co_3O_4*
   (applicable to all materials containing Co. Standard method for steels, Co alloys and Co ores etc.) (Not affected by presence of Ni.)

VOLUMETRIC

2. *Titration with standard KCN and $AgNO_3$ (in the presence of Fe but absence of Ni and Cu)*

COLORIMETRIC

3. *Using α-nitroso-β-naphthol*
   (suitable in all cases for up to 0·001 g Co).
4. *Using potassium ferricyanide solution*
   (suitable in all cases for up to 0·01% Co).

ELECTROLYTIC

5. *Electrolysis of a solution of Co and Ni freed from Group II and III metals*
   (suitable for ores and other products with high Co content).

METHODS

1. Precipitation with α-nitroso-β-naphthol and ignition to oxide

Since this reagent will also precipitate ferric iron, copper, palladium and to some extent Cr, Mo, W, U, Ti, Zr, Pb, Sn, Ag and Bi, it is essential that interfering elements be removed prior to precipitation of Co. This is best done by dissolving the material in HCl if possible, followed by HNO_3, filtering off $WO_3 + SiO_2$ if present. The filtrate has H_2S passed through it to precipitate Group II metals. Boil out H_2S from the Group II filtrate, oxidize iron with bromine water, boil, cool, nearly neutralize with NH_4OH and add a slight excess of zinc oxide suspension (50 g ZnO shaken with 250 ml. water). Filter off precipitate of base metal hydroxides and excess ZnO—dissolve in 50% HCl, neutralize with NH_4OH and reprecipitate with ZnO as before. The filtrates are acidified to 2–3% HCl, warmed to 70 ° C. and treated with an excess of α-nitroso-β-naphthol (2% solution in 50% acetic acid)—20 × weight of Co present. This produces a brownish red precipitate of the cobalt complex ($Co(C_{10}H_6 . NO.O)_3$). This is washed with hot 5% HCl followed by water, then dried and ignited in a porcelain crucible at 800–850° C. Weigh as Co_3O_4 (factor : × 0·7342 = Co). The reaction of ZnO suspension with ferric salts can be taken as typical of those other metals precipitated by the reagent :

$$3ZnO + 2FeCl_3 + 3H_2O = 2Fe(OH)_3 + 3ZnCl_2.$$

With α-nitroso-β-naphthol :

$$CoCl_2 + 3C_{10}H_6(NO)OH + HCl = Co(C_{10}H_6O(NO))_3 + 3HCl + C_{10}H_6(NO) + H_2O.$$

Since the Co complex is always contaminated with some

co-precipitated $C_{10}H_6(NO)$, ignition to Co_3O_4 is essential. (References: 'Cobalt in Steels'.)

Notes:

1. The final oxide precipitate may contain traces of Fe and/or Ni. To allow for this dissolve the ignited oxide in conc. HCl, make just ammoniacal to precipitate Fe as $Fe(OH)_3$ on boiling whilst Ni and Co stay in solution as ammines. The precipitate is filtered, washed, dried and ignited to Fe_2O_3—deduct this from weight of Co_3O_4 obtained.

The filtrate (containing Ni) is just acidified with acetic acid and 10–20 ml. of 1% alcoholic dimethyl-glyoxime added to precipitate Ni glyoxime which is filtered, washed with water, dried and ignited to NiO—deduct this weight from original Co_3O_4.

2. The zinc oxide separation has been found more reliable than the basic acetate method since the latter only removes Fe, Al, Ti, Zr and Be, leaving Cu, Cr, Mo, U and V in solution. (Cu and Mo can be previously removed by H_2S in Group II) and Cr may be co-precipitated by the reagent at a later stage. Zinc oxide however precipitates Fe, Cr, Al, Ti, Zr, Mo, V, Cu, U, Be, W.

3. A group separation to Group IV followed by precipitation of Co, Ni and Zn as sulphides, ignited to oxides, dissolved in aquaregia and subsequently Co determined with α-nitroso-β-naphthol is unreliable due to absorption loss on the Group III precipitate if Fe is predominant in the material.

4. Ignition of the complex to temperatures much above 850° C. is liable to cause conversion of Co_3O_4 to CoO.

2. Titration with KCN and $AgNO_3$ (in the absence of Cu and Ni) (Pigott, *Chemical Analysis of Ferrous Alloys*, 1942)

0·5–1 g of material is dissolved in 30–50 ml. conc. HCl, then oxidized with 5 ml. conc. HNO_3. Filter off WO_3 and SiO_2 if necessary. Wash with hot 5% HCl. To the filtrate add 30 ml. 20% H_2SO_4 and 20 ml. 40% citric acid solution then neutralize with NH_4OH and add 10 ml. excess. Add 2 g $NaClO_3$ and boil 5 minutes. Cool, dilute to 300 ml., neutralize with dilute HNO_3 then make slightly alkaline with 3 ml. conc. NH_4OH. Add 5 ml. of 2% KI solution, run in a few ml. of standard $AgNO_3$ solution (noting the volume used) until a distinct turbidity of AgI is produced. Now add a known volume of standard KCN solution until the precipitate of AgI just dissolves to a clear solution of potassium argentocyanide. Run in carefully the $AgNO_3$ solution until a faint permanent precipitate of AgI persists on shaking—note the volume used.

Deduct from the volume of KCN used the equivalent (in terms

of KCN) of the *total* $AgNO_3$ solution added—the difference represents the equivalent of Co.

KCN Solution: 5·6 g KCN + 1 g KOH per litre, to be standardized against the $AgNO_3$ solution.

Standard $AgNO_3$ solution: 7·206 g $AgNO_3$ per litre — 1 ml. = 0·001 g Co.

Here Fe is held in solution by citric acid, Co is oxidized to the trivalent state by sodium chlorate in ammoniacal solution to give cobaltic ammine thus:

$$6Co(NH_3)_6Cl_2 + NaClO_3 + 6NH_4Cl + 3H_2O = 6Co(NH_3)_6Cl_3 + NaCl + 6NH_4OH.$$

With KCN, potassium cobalticyanide is formed thus:

$$6KCN + CoCl_3 = K_3Co(CN)_6 + 3KCl.$$

Silver nitrate solution is used to deal with the excess KCN using KI solution as an indicator.

$$AgNO_3 + 2KCN = KAg(CN)_2 + KNO_3$$

$$AgNO_3 + KI = AgI + KNO_3$$

$$AgI + 2KCN = KAg(CN)_2 + KI$$

AgI is soluble in KCN only when the formation of potassium cobalticyanide is complete ∴ acts as an indicator.

3. Colorimetric estimation using α-nitroso-β-naphthol

For very small amounts of Co the complex normally obtained with α-nitroso-β-naphthol is converted into a red solution by the presence of citric acid. The red tint being matched in Nessler glasses with a standard cobalt solution similarly treated.

Small quantities of cobalt may be determined colorimetrically (in such material as the ash of varnish) by means of α-nitroso-β-naphthol, the effect of other metals being eliminated by the addition of ammonia and ammonium citrate. The material is treated successively with HCl, *aqua regia*, again with HCl, then evaporated to dryness to remove HNO_3, taken up with water, slightly acidified with HCl, and ammonium citrate and ammonia added. α-nitroso-β-naphthol is then added and the tint compared with equal volumes of standards containing the same reagents, to which standard cobalt solution is added. The citric acid prevents precipitation of iron, and dissolves the cobalt compound of α-nitroso-β-naphthol to a reddish solution. (Quantities of 0·01–0·5 mg. Co may be estimated in presence of twenty times the amount of Fe by adding 10 ml. of 10% ammonium citrate, 5 ml. conc. NH_4OH, 5 ml. 0·1% α-nitroso-β-naphthol in acetic acid, and making up to 50 ml.)

4. Colorimetric estimation using potassium ferricyanide solution

This is more reliable and more accurate than Method 3. Co_3O_4 from ignition of CoS or the α-nitroso-β-naphthol complex is dissolved in 3 ml. of 30% HNO_3 and then made just ammoniacal. If the solution is now blue (due to Cu or Ni) clear with the minimum of a 1% KCN solution. Now add 3 ml. of 1% $K_3Fe(CN)_6$ solution and match the pink colour against a standard cobalt solution similarly treated.

The pink coloration is due to the formation of cobalt ammine ferricyanide ($3Co(NH_3)_6\ 2Fe(CN)_6$).

A convenient standard Co solution is : 0·6 g cobalt ammonium sulphate/litre : 1 ml. = 0·0001 g Co.

(Reference : 'Colorimetric Estimation of Co in Steels'.)

5. Electrolytic Method (Low, Weinig and Schoder, *Technical Methods of Ore Analysis*, 1947)

1 g ore is taken into solution with 10 ml. conc. HNO_3 + 5 ml. conc. HCl. When dissolved, fume with 10 ml. conc. H_2SO_4, cool, dilute to 50 ml. with water, add 5 ml. conc. HCl and boil to take salts into solution. Into the warm solution pass H_2S until Group II metals are precipitated (particularly As). Filter, boil H_2S out of the filtrate and add 20 ml. 20 volumes H_2O_2 to oxidize Fe, etc. Remove Fe, Al and Ti from Co, Ni, Zn and Mn by the basic acetate separation (for details see 'Co in Steels')—the zinc oxide method is unsuitable here since Zn interferes subsequently. Boil down the filtrate (from Fe, etc., removal) to 100 ml., add NH_4OH to neutralize and 20 ml. excess. Electrolyse at 70° C. at 3V and 0·5–1 amp. for 2–4 hours using Pt electrodes (gauze cathode).

(*Note:* If Zn is present, remove as ZnS by passing H_2S into 0·5% H_2SO_4 solution of the material *prior* to electrolysis.) The cathode deposit gives combined Co and Ni. This is washed with water and then with alcohol, dried at 100° C. and weighed.

Dissolve the cathode deposit in 10 ml. conc. HNO_3, evaporate to a syrup, add 20 ml. water and 20 ml. of 10% KOH (an excess) until blue cobaltous hydroxide (and Ni) are precipitated. Now acidify with acetic acid and add a slight excess followed by 25 g of KNO_2, boil 20 minutes, dilute to 300 ml. and stand overnight. This effects the separation of Co from Ni since potassium cobaltinitrite is precipitated:

$$CoCl_2 + 7KNO_2 + 2CH_3COOH = K_3Co(NO_2)_6 + 2KCl + 2CH_3COOK + NO + H_2O$$

(potassium cobaltinitrite)

whereas Ni stays in solution as the nitrate or acetate. Filter,

wash the precipitate with cold 5% KNO_2 solution acidified with acetic acid, then dissolve it in 15–20 ml. hot 50% H_2SO_4 and evaporate to 'fumes'. Cool, dilute to 100 ml. with water, heat to boiling to dissolve all salts, cool, neutralize with NH_4OH, add 20 ml. excess and electrolyse the solution exactly as before. Treat the cathode deposit as before but this time the gain in cathode weight gives the Co present (Ni can be obtained by difference in the two cathode weights).

This method is not widely used due to the lengthy separations necessary and due also to the fact that Co may not be entirely freed of Ni when precipitated as potassium cobaltinitrite and thus the final cathode deposit may contain traces of nickel.

COLUMBIUM (Cb) (or Niobium) (Nb)

Atomic Weight = 92·91

Metallurgical Occurrence

Up to 1% in certain alloy steels as grain refiner and preventive of 'weld decay'. Increases creep and impact values and depth of nitrided case. In certain light alloys (ceralumin) used as a grain refiner. In the radio valve industry as a 'getter' for gases. Ferro-niobium.

Source of Metal as Standard

99·9% Cb (New Metals & Chemicals Ltd., London) but not usual to have a standard.

Methods of Determination

GRAVIMETRIC

1. *Dehydration of columbic acid to oxide followed by removal of silicon as a volatile fluoride*
   (for alloy steels [W, Ta, Ti, Zr absent]).
2. *As previous but removal of W by carbonate fusion followed by Ta removal by treatment with oxalic acid and tannin*
   (for alloy steels [W and Ta present but Ti absent])
3. *Precipitation as a complex by cupferron from 10% H_2SO_4 solution and ignition to oxide*
   ([not accurate in the presence of ferric Fe, Cu, Ta, Ti, W, Zr] for certain steels and Al alloys).
4. *Precipitation as oxyfluoride and conversion to oxide*
   ([Ti may interfere] suitable for ores).

METHODS

1. Dehydration of columbic acid to oxide followed by removal of silicon as a volatile fluoride (Pigott, *Chemical Analysis of Ferrous Alloys*, 1942, and others)

This method depends on the solution of the steel and dehydration of silicic, tungstic, tantalic and columbic acids to the appropriate oxides by means of a mixture of HCl, HNO_3 and

perchloric acids. The precipitated oxides are then treated with conc. H_2SO_4 and HF in a Pt crucible to volatilize Si as silicon tetrafluoride $SiO_2 + 4HF = SiF_4 + 2H_2O$. This gives a residue of Cb_2O_5 which will be contaminated with WO_3, ZrO_2, Ta_2O_5, TiO_2 if these are present. Assuming only Ti and Zr present with W and Ta absent.

Fuse the impure precipitate with about 5 g potassium pyrosulphate in a porcelain crucible and extract with hot 10% H_2SO_4 solution, this takes Ti and Zr into solution as sulphates but Cb (and Ta if present) is precipitated as hydrated pentoxide which can be filtered, washed with water, dried and ignited to about 800–900° C.

Weigh as Cb_2O_5 (factor × 0·699 = Cb).

Alternatively estimate Ti colorimetrically in the filtrate by addition of H_2O_2 (see under Ti) and Zr by treating the same filtrate heated to 60° C. with 10 ml. 10% sodium phosphate solution, filter off zirconium phosphate, wash with 5% ammonium nitrate solution and ignite at 900° C. to zirconium pyrophosphate ZrP_2O_7 (factor × 0·518 = ZrO_2). Deduct equivalent weights of TiO_2 and ZrO_2 from weight of contaminated oxides precipitate and report balance as Cb_2O_5 (still contaminated with Ta_2O_5 if this metal is present).

(See also 'Determination of Cb and Ta in Steel'.)

2. As Method (1) but complete separation of Cb from Ta and W (Ti absent) (Schoeller and others, *Analyst.* **60.** 1935)

Here, the impure mixed oxides from initial acid attack is fused with potassium carbonate and leached with a weak solution of ammonium salts. W goes into solution as potassium tungstate ($WO_3 + K_2CO_3 = K_2WO_4 + CO_2$) but Cb and Ta are precipitated as potassium columbate and tantalate [$4K_2O \cdot 3Ta_2O_5 \cdot 16H_2O$ and $7K_2O \cdot 6Cb_2O_5 \cdot 32H_2O$] (any Ti forms K_2TiO_3 as a precipitate).

Filter off the precipitate of Cb, Ta (and Ti if present) compounds, wash with saturated NH_4Cl solution and treat with dilute HCl which dissolves the precipitate to give columbic, tantalic (and titanic) acids. (With Ti some titanic chloride may also be produced.) On treating this solution with NH_4Cl and NH_4OH until just faintly acid and adding ammonium acetate and a 2% (or 5%) aqueous tannin solution the precipitated hydrated oxides of Cb and Ta adsorb tannin to form orange-red and yellow coloured complexes respectively (Ti if present gives a similar coloured complex to that produced by Cb). If the precipitated

complexes are washed with NH_4Cl solution and ignited, the respective pentoxides are produced of Cb and Ta.

To effectively separate Ta from the mixed oxides, use is made of the differential hydrolysis of the oxalo-tartrates of the two metals in the presence of tannin. In weak acid solutions, oxalotantalic acid forms a yellow complex with tannin, but in weak alkaline solution, a red precipitate of oxalo-columbic acid is produced having a formula approximately $Cb_2O_3 \cdot 3(NH_4)_2O \cdot 6C_2O_3 \cdot 3H_2O$.

Using this principle, first Ta and then Cb are precipitated almost entirely free from each other.

(For details see 'Estimation of Cb and Ta in Steel'.)

3. Precipitation as a complex by cupferron and ignition to Cb_2O_5 (*Standard Methods of Analysis*, United Steel Co., 1945, and Cunningham, *Ind. Eng. Chem.* (Anal. Edn.), 1938. **10.** 233)

Cupferron ($C_6H_5N(NO)ONH_4$) precipitates Cb as a reddish brown complex from cold 10% H_2SO_4 solution, but ferric iron, tantalum, titanium and zirconium are also co-precipitated under these conditions and therefore these metals should be absent or previously removed.

(For details of method for alloy steels see 'Estimation of Cb and Ta in Steels'.)

For Cb in Al alloys (British Aluminium Co. Ltd.'s Method).—2 g of alloy are attacked with 20 ml. 20% NaOH solution, then acidified with 75 ml. conc. HCl and diluted to 350 ml. On boiling, the bulk of Cb_2O_5 is precipitated together with undissolved Fe, Cu, Mn, etc. Filter, wash with cold 25% HCl and reserve filtrate (A). Ignite the precipitate and then fuse with 5 g potassium bisulphate. Leach out melt with 35 ml. 10% tartaric acid solution and boil to dissolve all sulphates. Saturate with H_2S and filter off CuS, then make this filtrate ammoniacal and repass H_2S. Filter off FeS washing with NH_4OH saturated with H_2S. Reserve this filtrate (B).

To filtrate (A) add 3 ml. 3% H_2O_2 and boil to oxidize Fe and to decompose excess peroxide, dilute to 300 ml. with cold water and to the *cold* solution add with stirring 50 ml. 6% aqueous cupferron solution to precipitate Fe, Ti and Cb complexes. Stand 10 minutes and filter off, washing precipitate with cold 33% HCl containing 5 ml. cupferron solution. Ignite precipitate and fuse with 5 g potassium bisulphate in a silica crucible. Treat melt exactly as before, with tartaric acid, then H_2S in both acid and ammoniacal solutions to remove Cu and Fe.

Combine the final filtrate with filtrate (B) and boil to decompose any $(NH_4)_2S$ and filter off any S produced. Dilute to 400 ml.,

add 5 g oxalic acid, nearly neutralize with NH_4OH, add 5 g NH_4Cl and heat to boiling. To the boiling solution add with stirring 50 ml. 2% aqueous tannin solution. Cb (and Ti) is precipitated as a complex. Filter off, wash with hot 5% NH_4Cl solution and ignite at 900° C. to Cb_2O_5 (and TiO_2). Ti if present must be determined separately and deducted.

($Cb_2O_5 \times 0{\cdot}699 = Cb.$)

4. Separation as oxyfluoride and conversion to oxide

Cb is separated as follows: The ore is digested with HCl, whereby Cb, Ta and W are separated as insoluble oxides. The material is filtered and washed (removing Fe and Mn) and the residue extracted with ammonia to remove W. The Cb, Ta (and Sn) remain undissolved and are filtered off. The dried residue is then fused with three times its weight of acid potassium fluoride (KHF_2), extracted with hot water, and HF added. On evaporating the solution, potassium fluo-tantalate, K_2TaF_7, crystallizes out first (soluble in 200 parts water). This is separated and the evaporation continued, when potassium columbium oxyfluoride ($2KF \cdot CbOF_3 \cdot H_2O$) crystallizes in plates (soluble in 12 parts water).

This is purified by recrystallization and finally heated with conc. H_2SO_4 till all HF is expelled. Cool, dilute and boil, whereupon Cb is precipitated as columbic acid. Filter, wash with water, dry, add ammonium carbonate and ignite to Cb_2O_5.

($Cb_2O_5 \times 0{\cdot}6995 = Cb.$)

The fraction containing the tantalum is treated in the same way and resulting residue weighed as Ta_2O_5.

The fusion may be made with $KHSO_4$ instead of KHF_2; in this case the latter salt is added to the boiling extract of the melt.

Note: For methods giving complete separation from Ti and Zr see Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Metals.*

COPPER

(Cu) Atomic Weight = 63·54

Metallurgical Occurrence

Aluminium and aluminium alloys
Magnesium alloys
Certain steels
Copper ores, minerals, mattes, drosses
Copper and copper based alloys (brasses, bronzes, Al bronzes, Cu/Ni, Cu/Ni/Zn)
White metals
Zinc base die-casting alloys

Source of Metal for Standards

Electrolytic Cu sheet 99·99% (Thos. Bolton & Sons, Widnes, Lancs.)
(Johnson Matthey, London)

Methods of Determination

GRAVIMETRIC

1. *Precipitation as CuS with H_2S and ignition to CuO*
   (for small percentages but seldom used).
2. *Precipitation as copper quinaldinate from acetic acid solution in the presence of tartaric acid*
   (Sn and Ag interfere. Mn, Ni, Co, Ca, P, As, Sb, Pb, Hg, Bi do not)—for Cu in Al hardeners.
3. *Precipitation, as a co-ordination compound, with α-benzoin-oxime from ammoniacal tartrate solution*
   for small quantities in the presence of Fe, Al, Pb, Ni).

VOLUMETRIC

4. *Titration of cupric salt with sodium thiosulphate after addition of potassium iodide*
   (standard method for Cu in copper-based alloys, Al alloys, Mg alloys, copper ores, mattes, white metals, zinc die-casting alloys and ferrous alloys etc.) (Ferric iron, As, Sb removed or inhibited, Bi, Ag, Pb preferably absent).
5. *Titration with KCN of an ammoniacal copper solution*
   (sometimes used for Cu ores as a routine method but requires careful manipulation for consistant results—Fe, Co, Ni, Zn must be absent).
6. *Precipitation as thiocyanate and titration with potassium iodate using carbon tetrachloride as internal indicator*
   (accurate method for ores and alloys of fairly high copper contents. Compares favourably with the iodide-thiosulphate method. [Pb, Ag, Hg should be absent and Bi, Sb, Sn, Cb and Ta should be inhibited by use of tartaric acid.]).

COLORIMETRIC

7. *Comparison, on the addition of NH_4OH, of the blue colours of copper ammine solutions*
   (for low-grade ores, steels etc.)
8. *Comparison of the brown colours produced with potassium ferrocyanide solution*
   (for low-grade ores, steels etc.).
9. *Comparison of the brown colours produced by sodium diethyldithiocarbamate*
   (iron should be inhibited by citric acid. Bi, Cd, Pb, Hg, Sn and Zn give white turbidities)—used for traces of Cu in Al, Mg and their alloys.

PHOTOMETRIC

10. *As* (9) *but intensity of brown colours matched in a Spekker absorptiometer*

ELECTROLYTIC

11. *Electrolysis from dilute HNO_3 or H_2SO_4 solution or mixtures of both*
    (for pure copper and routine copper and Al alloy analysis).

METHODS

1. Precipitation of CuS and Ignition to CuO

A convenient acid solution of the material is obtained, any Si or W is first removed as oxides by concentrating the acid solution, diluting and filtering and the Cu in the filtrate is precipitated as CuS by passing in H_2S or by boiling with 10 g $Na_2S_2O_3$ crystals (in dilute H_2SO_4 solution approximately 5–10%). The filtered and washed sulphides (some contamination from Group II metals, and

V, Mo, W possible) are treated by boiling with 10% NaOH solution and then leaching with ammonium sulphide if necessary.

(*Note*: Any Bi present in the precipitate may be removed by the normal cyanide group separation.)

The purified CuS is then washed with 2% ammonium nitrate solution and ignited at 650–800° C. in a porcelain crucible. Cool and weigh as CuO (slightly hygroscopic).

(CuO × 0·799 = Cu.)

Note: Many analysts dissolve the ignited oxide residue in dilute HNO_3 and finish volumetrically by the iodide titration, colorimetrically or electrolytically (see (4), (7), (8), (9), and (11) below).

2. Precipitation as quinaldinate and drying and weighing the complex (British Aluminium Company's method—Publication No. 405, 1947)

0·1 g Al alloy is dissolved in 5 ml. HCl + 20 drops 30% H_2O_2, evaporate to low bulk, then dilute to 100 ml., add 5 ml., 20% tartaric acid solution. Neutralize with NH_4OH, just acidify with acetic acid and add 5 drops excess. Dilute to 200 ml., bring to the boil, and add 10 ml. of 3% quinaldinic acid solution (in approximately N/5 NaOH solution) dropwise. Stand in the warm for 20 minutes, filter on a tared sintered glass crucible (porosity 4), wash with hot water containing a few drops of acetic acid, dry for 1 hour at 125° C., cool and weigh as the complex Cu $(C_{10}H_6NO_2)_2 . H_2O$.

(complex × 0·149 = Cu.)

3. Precipitation as a complex by α-Benzoin-Oxime (*B.D.H. Book of Organic Reagents*, 1948; Silverman, *Ind. Eng. Chem.* (Anal. Edn.), 1940. **12.** 343)

This reagent forms a green precipitate with Cu in ammoniacal tartrate solution with most other common metals not interfering, but in mineral acid solution the reagent precipitates Mo, W, Pd, Cr^{VI}, V^{V}, Ta. This therefore gives a suitable method for determining Cu and Mo in steels containing these elements.

A neutral solution containing not more than 0·05 g Cu is treated with 10 ml. 10% tartaric acid solution and excess of a 2% alcoholic solution of the reagent. NH_4OH is next added until just alkaline. On boiling a green co-ordination compound is formed. This is filtered on to a tared sintered glass crucible washed with 1% NH_4OH then alcohol, finally hot water, then dried for 1 hour at 110° C., cooled and weighed as $C_6H_5CH(O)C(NO)Cu . C_6H_5$ which contains 22·02% Cu.

4. Titration of cupric salts in acetic acid solution with sodium thiosulphate in the presence of potassium iodide using starch as internal indicator

In only a few cases will it be found that a sufficiently pure copper solution exists from initial solution of the sample to enable a direct titration to be performed. These materials are usually copper-based alloys such as brasses (Pb and Fe free), bronzes, Cu/Ni, Ni silver and Al bronze (Fe free).

Note: For direct titration of Cu by this iodide-thiosulphate method, proceed as below—'Standardization of Thiosulphate' paragraphs (*a*) and (*b*).

In all other cases of alloys and ores especially there is usually sufficient Fe, As and Pb present to interfere. In these cases obtain an acid solution of the sample and then remove the copper by one of the following standard methods:

(A) As CuS by passing H_2S into the warm acid solution or boil with $Na_2S_2O_3$, and proceed as described in Method 1 (Note).

(B) As Cu by precipitation on Zn or Al by boiling a 15–20% H_2SO_4 solution of the Cu salt with As free rod Zn or $\frac{1}{16}$ in. sheet Al.

(C) As Cu by precipitation with hydrazine hydrochloride from a neutral solution containing tartaric acid.

(D) Electrolysis.

The following outlines of methods and references to full details of specific analyses will deal with these points in turn:

(A) *Precipitation as Sulphide, Conversion to Nitrate, then to Acetate, and titration with Potassium Iodide and Thiosulphate.*—This method is equally applicable to ores, alloys and most furnace products. Usually about 1 g of ore or 0·3–0·5 g of an alloy would be taken for each assay. The sulphide is best precipitated from a nearly boiling HCl or H_2SO_4 solution, by passing H_2S. In certain cases it is more conveniently precipitated from a tartaric solution made alkaline with NaOH, by means of sodium sulphide in boiling solution (As, Sb and Sn are not precipitated). In presence of bismuth, the separation by means of cyanide may be used (see Bismuth).

The sulphide (freed from interfering elements) is dried with the filter paper, ignited gently at the mouth of the muffle until carbon and excess sulphur have burnt off, then for a few minutes at a moderate red heat, and the residue dissolved in 5 ml. of conc. HNO_3. This is washed out into a suitable flask or beaker, and boiled to expel every trace of red fumes. It is now cooled somewhat, ammonia added in slight excess and the liquid again boiled

until the smell of ammonia is quite faint: 5 ml. of glacial acetic acid is added, and the mixture again boiled. It is then cooled to room temperature and 1–3 g of potassium iodide added, according to amount of Cu present.

The liberated iodine is at once titrated with standard sodium thiosulphate, until the brown colour of the iodine changes to pale yellow. Starch solution is then added and the titration continued cautiously, with agitation until the blue colour of the starch iodide disappears and the mixture has a pale yellowish or cream-coloured tint of cuprous iodide. The blue colour should not return on standing for several minutes. A rapid return of the colour generally indicates

(*a*) Presence of nitrous acid (overcome by addition of 0·2 g urea);
(*b*) Presence of ferric salts; or
(*c*) Undue dilution of the solution.

The volume of solution before titration should not exceed 75–125 ml.

The reactions are as follows:

$$Cu(C_2H_3O_2)_2 + 2KI = CuI + I + 2K(C_2H_3O_2)$$
$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6$$

From this it appears that 1 ml. N/10 thiosulphate (24·82 g $Na_2S_2O_3 . 5H_2O$ per litre) = ·006357 g Cu.

It is customary, however, to adjust the thiosulphate solution so that 1 litre represents some simple number of grammes Cu, thus if a solution be prepared containing 19·5 g $Na_2S_2O_3 . 5H_2O$ per litre, 1 ml. = 0·005 g Cu.

Standardization of the Thiosulphate.—Various methods are in use, but whatever method is used should correspond with the final treatment of the copper solution from the sample assayed.

For the method given above, the following are suitable:

(*a*) Dissolve 0·2–0·3 g pure copper foil, which has been exactly weighed, in 10 ml. HNO_3 (1 : 1), boil till all red fumes are expelled; cool, dilute slightly and add 0·2 g urea to neutralize nitrous acid thus: $2HNO_2 + (NH_2)_2CO = CO_2 + 2N_2 + 3H_2O$ and add ammonia till the precipitate formed just dissolves to a clear blue liquid. Boil gently till the smell of ammonia is faint, but no reprecipitation has occurred. Cool somewhat, add 5 ml. glacial acetic acid, again boil for a few moments. Cool thoroughly under the tap, to room temperature. Add 1–3 g KI (according to amount to be used in the assay) and titrate, as described above, with thiosulphate.

(*b*) Instead of neutralizing with ammonia, add a saturated solution of pure sodium carbonate in small quantities at a time,

until a slight blueish precipitate remains permanent and no effervescence is produced by further addition of Na_2CO_3. Dissolve in acetic acid and proceed as in (*a*).

(*c*) Dissolve 0·3–0·5 g pure copper foil in the minimum of HNO_3. Boil off all red fumes and evaporate to a small bulk. Cool, add a few drops conc. H_2SO_4 and boil down to strong white fumes. Cool, add 20 ml. of saturated zinc acetate; make up to 100 ml. To the cold solution add KI and titrate as in (*a*).

All those methods will give identical results, the choice being one of convenience. (*b*) is probably the simplest and most rapid.

(B) *Precipitation from Sulphuric Acid Solution on Zinc or Aluminium.*—The copper is obtained in solution as already described. If nitrates or chlorides, or free HCl or HNO_3 are present, add 10–15 ml. conc. H_2SO_4 and boil to strong white fumes. Cool, dilute with about 30 ml. water, boil (filter if necessary, to remove SiO_2 or $PbSO_4$). Dilute to about 75 ml. Add one or two pieces of stout sheet zinc or aluminium, bent at the corners or edges so as not to lie flat in the beaker. Boil 7–10 minutes or until the liquid becomes perfectly colourless, adding water if the volume becomes much reduced. The acid must not be so strong that the zinc or aluminium is violently attacked. At the end of the operation, H_2S added to the liquid should produce little or no discoloration. Decant the liquid through a filter, leaving the precipitate as much as possible with the remaining metal in the beaker ; wash with hot water and a little H_2S water until the filtrate runs off free from Fe (test with ferricyanide or $(NH_4)_2S$).

Now place a clean flask under the funnel, and pour 5 ml. of HNO_3 (1 : 1) over the metal in the beaker. Warm till the precipitated copper has dissolved, adding more HNO_3 if necessary ; pour through the filter, wash with hot water, passing all washes through the filter into the flask.

Boil to expel red fumes. If Sb or As are present, add Br water and boil off excess of Br. Proceed with determination by the iodide method, as described in Method A.

(C) *Precipitation in Alkaline Tartrate Solution by Hydrazine Hydrochloride.*—The alloy or other material is dissolved in *aqua regia* and filtered if necessary. For alloys of Pb, Sn and Sb, 2 g is suitable. Dilute with water to about 30 ml. If lead chloride separates, filter (best on paper pulp) and wash several times with small quantities of cold water. To the filtrate add 1 g tartaric acid and NaOH till nearly neutral. Boil and add this solution gradually to a hot solution of 20 g NaOH in 250–300 ml. water, containing

2–3 g hydrazine hydrochloride. Stir vigorously, heat for about 15 minutes till the precipitate of metallic copper settles in dense flocks without further evolution of gas. Filter (best on paper pulp), wash thoroughly with hot water. Redissolve in hot HNO_3 (1 : 1) and determine copper by the iodide method as in (A).

(D).—See Method 11.

Trivalent Fe and pentavalent As and Sb must be absent since these displace iodine from KI. Divalent Fe and trivalent As and Sb must be absent since these reduce iodine to HI. Best to inhibit Fe with sodium phosphate or citric acid before neutralizing with sodium carbonate. As and Sb should be removed by treating Group II sulphides as in (A). Bi, Ag and Pb are preferably absent since these form coloured iodides which mask the end point and consume KI.

(See also under 'Copper in Al Alloys; in Mg Alloys; in Steels; in White Metals; and Copper Alloys'.)

5. Titration with KCN of an ammoniacal copper solution

This is based on the fact that when KCN solution is added to a solution of cupric sulphate or nitrate in the presence of NH_4OH, the yellow cupric cyanide first formed rapidly decomposes with evolution of cyanogen and forms white cuprous cyanide. This in turn dissolves in one drop excess of KCN to give a colourless solution of potassium cupro-cyanide ($K_3Cu(CN)_4$.)

The copper may be present either in a nitric, sulphuric or hydrochloric acid solution, and should be free from other metals precipitated by H_2S in acid solution, also from Fe, Mn, Ni, Co and Zn. These are separated by the methods already described. A measured quantity of ammonia (in excess) is added to the cold solution, to produce a clear blue solution.

The solution is then titrated with a standard solution of pure potassium or sodium cyanide, simultaneously with one or more check solutions containing known amounts of copper and approximately the same amounts of HNO_3, HCl and NH_4OH as in the assay. The cyanide solution is run into each of the solutions to be tested until the blue colour becomes faint. A further quantity is then added, 1 ml. or 0·5 ml. at a time, until a pale violet tint is produced. This generally fades to a perfectly colourless solution on standing for a few minutes, in which case the assay is complete. If the colour does not fade, further small quantities of the cyanide solution are added. The check on which the calculation is based

should contain as nearly as possible the same amount of copper as the assay, hence a preliminary trial is often advisable.

The check solutions are prepared from pure copper foil dissolved in HNO_3.

The reaction is probably as follows :

$$Cu(NO_3)_2 + 5KCN = K_3Cu.(CN)_4 + 2KNO_3 + CN,$$

but other equations have been suggested.

In this method, consistent results are only obtained when the following conditions are adhered to during titration of assays and standards :

(1) approximately same temperature of solutions
(2) approximately same speed of titration
(3) approximately equal volumes of final solution.

The fading end point needs practice to observe and can be sharpened by the addition of a few drops of $AgNO_3$ solution and KI solution, the same quantities to each determination.

Here the turbidity produced by silver iodide is destroyed by one drop excess KCN thereby giving a sharper end point of a turbid solution turning clear rather than a blue solution fading to colourless or pale straw.

In the modified end point a dark tile (black) is recommended and the slight error due to KCN consumed to dissolve silver iodide can be ignored since it will apply in all cases of standards and assays and the error is then negligible.

6. Precipitation as cuprous thiocyanate and titration with potassium iodate (Low, Weinig and Schoder, *Technical Methods of Ore Analysis*, 1947)

Based on the reaction that a soluble thiocyanate when added to a solution of a cupric salt in the presence of a suitable reducing agent such as SO_2 will form first green cupric thiocyanate and this on heating is converted to white insoluble cuprous thiocyanate (CuCNS) which is titrated with standard potassium iodate solution. Alternatively we may ignite the CuCNS to cuprous sulphide.

Main reaction is :

$$2CuSO_4 + Na_2SO_3 + 2KCNS + H_2O = 2CuCNS + Na_2SO_4 + K_2SO_4 + H_2SO_4.$$

Take 0·5–5 g of ore and dissolve in 10–40 ml. conc. HCl and 5–25 ml. conc. HNO_3. To the solution of the ore add 5–10 ml. conc. H_2SO_4 and fume strongly. Cool and dilute with 50 ml. water, add a few mls. conc. HCl to precipitate any Ag as AgCl, bring to the boil and filter off any AgCl, $PbSO_4$ and insolubles. [If As, Sb and Sn are present, add 2 g tartaric acid to the filtrate, warm

and pass H_2S to precipitate Cu as CuS (this precipitation is also necessary if much iron is present). The sulphide would then be ignited to oxide which is dissolved in hot sulphuric acid, then proceed as follows.]

Assuming the copper is being treated directly in the filtrate from above, add NH_4OH until any iron is precipitated and the copper solution turns blue, then carefully clear the solution with 50% H_2SO_4 adding 2 ml. excess. Dilute to 100 ml., heat to boiling, add 1 g sodium sulphite in stages with stirring and warm until solution is reduced (blue colour again). Add slowly from a graduated pipette 5–15 ml. of a 10% KCNS solution and the copper is thrown out as a white precipitate according to the above equation.

Allow the precipitate to settle (preferable to stir in a little filter pulp) and filter off, washing with hot water.

Transfer precipitate on the filter to a flask and add 30 ml. conc. HCl, 20 ml. water and 5 ml. carbon tetrachloride. Shake well and titrate slowly with standard potassium iodate solution (29·455 g KIO_3/litre : 1 ml. = 0·005 g Cu) shaking well after each addition.

This reaction liberates iodine turning the solution brown:

$$10CuCNS + 14KIO_3 + 14HCl = 10CuSO_4 + 14HCl + 10HCN + 7I_2 + 2H_2O.$$

On continuing the titration the free iodine is converted to iodine monochloride thus :

$$2I_2 + KIO_3 + 6HCl = 5ICl + KCl + H_2O.$$

The function of the CCl_4 indicator is to dissolve elemental iodine which colours it reddish-brown and this colour is slowly discharged as the free iodine is converted to iodine monochloride at the end of the reaction.

7. Colorimetric method using ammonia

The general principle is to obtain the copper in a dilute nitric acid solution, add a slight excess of ammonia and compare the tint with that of standards of known copper contents containing as nearly as possible corresponding amounts of nitric acid and ammonia.

Difficulty is often experienced in obtaining the same shade of colour in the assay as in the standards. This may be due to the presence of traces of iron or of organic matter. The following procedure will often eliminate the trouble. Precipitate the copper as sulphide ; filter, wash, ignite. Dissolve the ash in a definite volume of dilute HNO_3 ; add a definite volume, in excess, of dilute ammonia, filter into a Nessler tube, wash with very dilute ammonia and make up to the mark (say 50 ml.). In a similar tube add the same volumes of dilute HNO_3 and NH_4OH, add standard copper nitrate solution until the colour matches that of the assay

when made up to the same volume. Where possible, the standard solution should be prepared from an ore or alloy of closely similar composition to the material to be assayed, the copper content of which has been determined by other methods. Standards containing larger amounts of copper may be prepared from this by adding the required amount of pure copper dissolved in dilute HNO_3. Quantities of copper ranging from 0·5–15 mg. may be estimated by this means.

(See also 'Cu in Steels and Cast-irons'.)

8. Colorimetric method using potassium ferrocyanide

Rather more useful for very small quantities of copper since the colour is more intense. Used with slightly acid or neutral copper solutions.

$$CuSO_4 + K_4Fe(CN)_6 = Cu_2Fe(CN)_6 + 2K_2SO_4$$

Procedure similar to previous method. Metals giving a coloured ferrocyanide should be absent or inhibited (e.g. Fe, using citric acid).

9. Colorimetric method using sodium diethyldithiocarbamate

This reagent is employed for detection and determination of much smaller quantities (1/10–1/100 mg Cu) than apply for methods 7 and 8.

In general, the solution of the alloy containing an amount of copper in the above range, is rendered alkaline with ammonia—2 g citric acid or 5 g tartaric acid having previously been added to keep Fe or Bi, Cd, Pb and Sn in solution where necessary.

Dilute solution to 70 ml., add 10 ml. of 0·1% aqueous solution of the reagent dilute to 100 ml. and compare the brown colour with that of standards containing known amounts of copper; all contained in Nessler glasses or by using a Lovibond tintometer.

(See also under 'Cu in Al alloys'.)

10. Photometric method using sodium diethyldithiocarbamate

Procedure is similar to that previously described, but the final intensity of colour is measured more accurately against standards using a Spekker absorptiometer.

(For full details see 'Copper in Al Alloys'.)

11. Electrolysis from acid solution

This method in many laboratories has replaced the iodide-thiosulphate titration for routine copper analyses in copper-based

materials and light alloys. However, initial outlay for Pt apparatus is costly and represents much capital locked up in a static condition.

The method is very accurate and may be carried out with either a sulphuric, nitric or mixed solution of these acids. The nitric acid present becomes ammonia during electrolysis and addition of fresh acid may be necessary to maintain slight acidity. The field of application is wide and includes Cu estimation in steels, cast irons, white metals and zinc diecasting alloys as well as those stated above.

The electro-deposition of copper is usually carried out in nitric acid solution. The copper is brought into solution by one of the methods previously given. The only ordinary metals that need be separated by a previous operation are tin and antimony.

Fe, Co, Ni, Zn and Bi do not interfere ; Pb and Mn are precipitated as peroxides on the anode.

The copper may be precipitated either on a stationary or on a rotating cathode.

The procedure is similar in all cases and generally requires a final electrolyte containing 3–10% by volume of total acid present and electrolysis is carried out usually at room temperature with current densities of 2–5 amps. at 2–6 volts when the usual Pt alloy gauze cylindrical cathodes and thimble-shaped rotating anodes are used. (The speed of rotation is usually about 200 r.p.m.) Time for electrolysis depends on many factors but these are usually adjusted to give complete electrolysis in 15–60 minutes.

The usual precautions regarding washing and removing electrodes before switching off the current, and drying in alcohol should be observed.

The completeness of the precipitation may be ascertained by testing a little of the solution with potassium ferrocyanide, which gives a brown coloration if copper is present.

(For specific details see elsewhere in this book under the respective headings: 'Copper in Al Alloys'; 'Copper in Steels'; 'Copper in Zinc Base Alloys'; 'Copper in Copper Alloys'. In particular the short section on electrolysis and electrolytic apparatus at the beginning of the section on copper and copper alloys should be studied.)

GALLIUM

(Ga) Atomic Weight = 69·72

Metallurgical Occurrence

Small quantities or traces in certain minerals such as zinc blende, germanite, bauxite etc.
In certain coal ashes
Gallium—cadmium alloys (used for arc lamp work)

Source of Metal for Standards

Gallium metal 99·9% (New Metals & Chemicals Ltd., London).
(but owing to great scarcity and cost of this material it is never used)

Methods of Estimation

GRAVIMETRIC

1. *Precipitation with cupferron and ignition to oxide*
   (for ores, ash etc.)
2. *Precipitation with tannin and ignition to oxide*
   (for ores, ash etc. and Ga/Cd alloys).
3. *Precipitation with ammonium bisulphite and ignition to oxide*
   (applicable as above).
4. *Precipitation as a complex by 8-hydroxyquinoline, dry and weigh as such*
   (only for solutions from which all heavy base metals Fe, Mn, Ni, Co, Ti, Cd, Zn, also Mg and Al have been removed).

ELECTROLYTIC

5. *Electrolytic deposition from a dilute alkaline sulphate solution*

METHODS

1. Precipitation with cupferron and ignition to Ga_2O_3 (Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements*)

This method is based on the fact that hydrated gallium oxide is precipitated from slightly acid solution by means of sodium thiosulphate in the presence of aniline. Heavy base metals which are liable to precipitate under similar conditions, are first removed by boiling the dilute solution of the ore [(50–100 g) in *aqua regia* (300 ml. conc. HCl + 20 ml. conc. HNO_3 added later and evaporated to a syrup) then dilute to 200 ml. with water] in contact with a strip of pure zinc, when these are deposited as a sponge.

Ignite the thiosulphate precipitate to oxide and fuse with potassium bisulphate, extract as gallium sulphate with 5% H_2SO_4 solution. Neutralize with NaOH solution and pour into an excess of NaOH solution (1%). Filter off $Fe(OH)_3$. Wash with 2% $NaNO_3$ solution. The filtrate containing gallium is just acidified with H_2SO_4, boiled and made just ammoniacal to cresol red. The precipitate of hydroxide is filtered, washed with hot 2% Na_2SO_4 solution then redissolved in 10% H_2SO_4, diluted to 200 ml. with water and to the *cold* solution, 6% cupferron solution is added until the white flocculent precipitate ceases to form. Stir in some filter pulp and filter off the coagulated precipitate washing with cold 2% H_2SO_4. Ignite in a porcelain crucible first at low temperature and then about 1000° C., cool and weigh as Ga_2O_3.

(Factor: Ga_2O_3 to Ga = 0·744.)

2. **Precipitation with tannin and ignition to Ga_2O_3** (Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements*)

About 20–100 g mineral (e.g. bauxite) is fused with potassium bisulphate and the melt leached with warm 5% H_2SO_4. In the presence of much iron the solution is treated with excess NaOH and $Fe(OH)_3$ is filtered off. The filtrate is just reacidified with dilute H_2SO_4, 2 g NH_4NO_3 added, then ammonium acetate added until neutral. To the boiling solution, a 1% tannin solution is added to excess (10 × weight of Ga present). The precipitate is filtered, washed with 1% NH_4NO_3 solution and ignited to Ga_2O_3. Cool and weigh as such.

In the presence of much Al, a separation of Ga from this element is necessary before the tannin precipitation. This is carried out as follows :

The filtrate from the caustic precipitation of iron is acidified with HCl to 25% conc. of the acid and a 5% solution of potassium ferrocyanide is added until no further white precipitate of gallium ferrocyanide is produced. The precipitate is ignited to the oxide in the presence of 2 g ammonium nitrate and the product fused with potassium bisulphate. The melt is leached with 5% H_2SO_4 and the tannin precipitation carried out as above.

3. **Precipitation as hydroxide and ignition to oxide** (Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements*)

The sulphate solution obtained by similar means to those described in previous methods is diluted to contain not more than 0·1 g Ga per 200 ml., then made ammoniacal to litmus. Boil for a few minutes after adding 10 ml. of ammonium bisulphite solution (made by saturating a 50% NH_4OH solution with SO_2), then make just alkaline to methyl red with dilute NH_4OH. The hydroxide precipitate is collected, washed with faintly ammoniacal 2% NH_4NO_3 solution and ignited to oxide as before.

All other metals giving hydroxide precipitate in alkaline solution must first be removed.

4. **Precipitation as a complex by 8-hydroxyquinoline, drying and weighing same** (Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements*; also Sandell, *Ind. Eng. Chem.* (Anal. Adn.), 1941. **13**. 844, and others)

As previously stated, most of the common metals should be absent or removed prior to this precipitation, since this reagent gives precipitates with all the metals mentioned.

To the faintly acid chloride or sulphate solution containing Ga, add 5 g ammonium tartrate and make faintly ammoniacal. Heat to boiling and add an excess of 5% solution of 8-hydroxyquinoline in 2N acetic acid (keep solution faintly ammoniacal with more ammonia if necessary). Collect the precipitate on a tared sintered glass crucible, wash with hot water and dry at 110° C. for 1 hour.

Weigh as $Ga(C_9H_6ON)_3$ which contains 13·88% Ga.

5. **Electrolytic method** (Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements*)

Ga is precipitated on a previously weighed copper-plated Pt gauze cathode from a weak sulphate solution of the metal (free from NH_4 salts) containing 1 g hydrazine sulphate and sufficient 10% NaOH solution to just redissolve the precipitate first formed. The electrolysis is carried out with a current of approximately 0·25–0·5 amp. for several hours. The cathode deposit is rinsed with hot water whilst the current is still on, then dried with alcohol and placed in a vacuum desiccator. No heat must be used as Ga melts at 30° C.

Note: Ga attacks Pt, therefore the necessity to copper-plate the cathode.

GERMANIUM

(Ge) Atomic Weight = 72·60

Metallurgical Occurrence

Minerals (Ge in small quantities often associated with zinc blende)
Flue dust from zinc extraction plants
Aluminium-magnesium-germanium alloys (in process of development)
Special rust-resisting steels (in process of development)

Source of Metal as Standard

Germanium metal = 99·9% Ge (New Metals & Chemical Ltd.). Rather rare, costly and not needed as an analytical standard.

Methods of Determination

GRAVIMETRIC

1. *Precipitation as a complex by tannic acid from acid solutions, followed by ignition to oxide*
   (suitable for all germanium-bearing materials).
2. *Precipitation as magnesium germanate by magnesium sulphate in the presence of ammonium salts*
   (suitable for most germanium-bearing materials).
3. *Distillation of germanium chloride followed by precipitation with tannin and finish as in* (1)
4. *Precipitation of cinchonine germanomolybdate by ammonium molybdate from nitric acid solutions*
   (for up to 0·005 g Ge in coal and plant ashes etc.).

METHODS

1. **Precipitation by tannin and ignition to oxide** (Davies and Morgan, *Analyst*, 1938. **63**. 388; also Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Metals*)

Under the conditions of precipitation, Mo, W, Ta, Nb may be co-precipitated and must therefore be absent—separation may be effected by using Method 3.

Solution of a suitable quantity of ore, etc. (1–100 g), is effected usually by attack with 50% HNO_3 with additions of 1–2 ml. conc. H_2SO_4—most sulphides respond to this treatment. The solution is evaporated and 'fumed'. This treatment should take into solution any GeO_2 produced by the action of nitric acid. The sulphuric acid solution is diluted to approx. N solution, about 10 g ammonium sulphate added, the solution heated to boiling and to it is slowly added 20–40 ml. 10% tannin solution with constant stirring. Finally a further 2–3 g ammonium sulphate is added and the solution allowed to cool by standing. The white precipitate is collected on a No. 40 Whatman paper, washed thoroughly with hot 5% ammonium nitrate solution (acidified with 5 ml. of 15% HNO_3/100 ml. solution) dried, ignited in a porcelain crucible at not more than 600° C. until all carbon has been removed. Cool, moisten with a few drops of conc. HNO_3, evaporate to dryness and reheat to 600° C. until precipitate is white, finally raise the temperature to 1000° C., cool and weigh as GeO_2.

(Factor: $GeO_2 \times 0{\cdot}694 = Ge$.)

The low temperature ignition and nitric acid treatment is to ensure that the carbon from the filter paper does not reduce the GeO_2 to GeO which is volatile above 700° C.

This method separates Ge from As, Cu, Cd, Zn, Fe, Al, Cr, Sb, Sn, Ca, Sr, Ba in one precipitation.

2. **Precipitation as magnesium germanate** (Davies and Morgan; Schoeller and Powell, loc. cit.)

Having obtained a dilute sulphuric acid solution of the material (as above), treat with 30 ml. 2N ammonium sulphate solution and add a slight excess of a N solution of $MgSO_4$ above that required to form Mg_2GeO_4 (about 10–20 ml. should be adequate). Add 20 ml. conc. NH_4OH, bring to the boil, boil 1 minute and allow to stand 4 hours. Collect the white precipitate on a tared Gooch crucible, wash with 10% NH_4OH solution, ignite and weigh as Mg_2GeO_4 which contains 39·2% Ge.

3. Distillation as chloride followed by tannin precipitation (Dennis and Johnson, *Jnl. Amer. Chem. Soc.*, 1929. **51.** 1459; also Schoeller and Powell, loc. cit.)

The material is attacked with 50% nitric acid only until decomposed, then the solution is evaporated to dryness in a porcelain dish. The dish and residue is then heated gradually in a muffle until all nitrates have been decomposed to oxides. The oxide cake is transferred to a distillation flask, 200 ml. conc. HCl added and chlorine is gently passed into the flask. The flask should carry a rectifying column connected to a condenser and a receiver cooled in ice-water. The solution in the distillation flask is gently boiled until half the liquid has distilled over. The solution in the flask is made up to its original volume with conc. HCl and the distillation process repeated—a third time if necessary. The final distillate may be tested for absence of Ge by the tannin reaction (Method 1).

The Ge in the chloride distillate may either be collected as sulphide by passing H_2S or preferably diluting with an equal volume of water, making *just* ammoniacal with NH_4OH (keep cool in ice-water), make just acid with acetic acid and proceed to add tannin as in Method 1.

4. Precipitation as cinchonine germanomolybdate (Davies and Morgan; also Schoeller and Powell, loc. cit.)

To about 50 ml. of a neutral solution containing germanium (up to 0·005 g) add 20 ml. 25% ammonium nitrate solution followed by 20 ml. 2% ammonium molybdate solution, 20 ml. 2N . HNO_3 and with stirring 10 ml. 2·5% solution of cinchonine in N/4 HNO_3. Allow to stand 2–4 hours and collect the white precipitate on a tared sintered glass crucible, washing with 2% ammonium nitrate solution containing 5 ml. 2N nitric acid per 100 ml. Dry at 160° C. for 2 hours, cool and weigh as $(C_{19}H_{22}ON_2)_4H_4$. $GeMo_{12}O_{40}$ which contains 2·385% Ge.

GOLD

(Au) Atomic Weight = 197·2

Metallurgical Occurrence

Native gold—nuggets and finely divided
Sulphide, arsenide and telluride minerals
Associated with Cu, Pb, Zn and Ni ores
In jewellery as carat gold alloys (with Ag and Cu), rolled gold, gold plating and white gold
Gold leaf and fine wire, also powder for pigments
Expensive dental alloys
Coinage, medals and trophies

Source of Metal as Standard

Electrolytic gold = 99·99% (Johnson Matthey, London)
(Derby & Co., London)

General Properties

Gold is classified as a noble metal, because it shows little or no tendency to combine with oxygen and is not readily attacked by any ordinary acids. It has some relationship to the platinum metals, and to a less extent, to silver and copper, but is not really closely connected with any other element. It is normally a triad, but in aurous compounds, which are unstable, it appears as a monad. The sulphides AuS and Au_2S are precipitated by H_2S from acid solutions and are soluble in alkali sulphides, thus placing gold in the same analytical group as As, Sb, Sn, Mo, Se and Te. The compound formed is a thioaurate, in which gold acts as a non-metal.

Several other cases are known in which gold forms part of a non-metallic radical, the most important being the double cyanides, such as $KAu(CN)_2$, formed by the action of cyanides on the metal in presence of oxygen:

$$2Au + 4KCN + O + H_2O = 2KAu(CN)_2 + 2KOH$$

Gold is also soluble in chlorine and bromine with formation of $AuCl_3$ and $AuBr_3$ respectively, and in mixtures which evolve Cl, such as *aqua regia* ($HCl + HNO_3$).

It readily combines with mercury, forming an amalgam.

For its separation in analytical work, use is commonly made of the readiness with which it alloys with lead, and subsequent separation therefrom by oxidation of the lead.

Methods of Determination

1. *Fire assays*
   (nearly all standard methods involve fire assaying to obtain a lead bead which has gold and possibly other precious (and base) metals in solution. This is followed by the usual procedure of scorification, cupellation and acid parting when the resulting gold button is weighed. Selected methods are given below for each of many specific cases.

GRAVIMETRIC

2. *Precipitation of metallic gold by evaporation or by metallic zinc or aluminium* (suitable for estimating gold [and silver] in cyanide solutions).
3. *Precipitation of metallic gold by a reducing agent from* aqua regia *solution* (used for gold alloys and bullion [alternative to (1)]).

COLORIMETRIC

4. *Qualitative test—the formation of purple-coloured colloidal gold, when a gold solution is added to stannous chloride solution*

METHODS

1. Various fire assaying methods

The Scorification Assay.—This is especially applicable to relatively high grade material. The quantity taken for assay may vary from 1–20 g, but it is usually from 5–8 g. This is mixed with grain lead, placed on a small fire-clay dish ('Scorifier') with a further quantity of grain lead and a small pinch of borax added as a cover. The total amount of grain lead is usually about 50 g and of borax 0·2–0·25 g. This is then placed in a muffle and the temperature gradually raised to bright redness until fusion is complete. The door of the muffle is then opened sufficiently to admit a good

current of air without unduly lowering the temperature. The lead oxidises to litharge, which forms a fusible silicate of lead with the silica of the ore, forming a ring round a bright central spot. The gold (and silver) combine with the unoxidized lead beneath. When the layer of slag has completely covered the central spot the assay is usually considered complete. The scorifier is then withdrawn from the muffle by suitable tongs and its contents poured into a conical or hemispherical iron mould. The fused slag solidifies rapidly, and is detached by hammering. The button of lead containing the precious metals, is then cleaned and hammered into compact shape.

The lead is then separated from the gold and silver by the process of cupellation. It is placed in the muffle on a previously heated 'cupel', or small vessel of some refractory porous material, which has a concave upper surface. Various different substances such as bone ash, magnesite and the material known as 'morganite' are used for cupels, but all have the property of absorbing the molten litharge while the small bead of gold, or gold-silver alloy, finally remains unabsorbed on the upper surface. The lead melts, and in a few moments, if the temperature is correct, brightens and exhibits a rotary movement. This appearance should continue until the cupellation is completed, usually in twenty to thirty minutes. The movement then ceases and the button, when the cupel is withdrawn from the furnace, suddenly solidifies. It is important to maintain a sufficient temperature throughout, so that there is no danger of the lead button 'freezing' or solidifying before the oxidation of the lead is complete, but the operation should be conducted at as low a temperature as possible, consistent with this requirement, in order to minimize losses by volatilization. A somewhat higher temperature is necessary for starting and also for finishing the cupellation than is needed during the remainder of the process.

The bead of gold-silver alloy is then removed by a small forceps or pliers, cleaned and weighed. If the proportion of silver in it is less than about 2·5 : 1, it should be recupelled with addition of the required amount of silver foil, the whole being wrapped in a small piece of lead foil. Alternatively, the necessary quantity of silver may be added to the charge in the scorifier.

When a bead has been obtained containing the necessary proportion of silver, it is flattened on a clean, well-polished steel anvil and 'parted' with nitric acid. This may be done in a small flask or test tube, or often quite conveniently in a porcelain crucible. The best strength of acid for ordinary assays is HNO_3 (1 : 4), i.e. 20% by volume, using 10–15 ml. of this acid. This is heated

very gently at first, then boiled gently till all red fumes are driven off. Except for large beads, a second parting with stronger acid is unnecessary. The acid is carefully decanted and replaced by distilled water, this being again poured off and the bead of gold finally carefully dried, and ignited until it assumes the natural yellow colour.

In the case of large beads, a second parting, with HNO_3 (1 : 1) is usually necessary.

When cold, the gold bead is weighed on a specially constructed sensitive balance (assay balance).

The Crucible Assay.—This is the method universally adopted for every kind of ore or product which is not of particularly high grade. The finely-ground ore is mixed with suitable fluxes, which include (1) an oxide of lead, to furnish an alloy of lead with the precious metals ; (2) a reducing agent to form metallic lead for the above purpose ; (3) a basic flux, to combine with the 'acid' ingredients of the ore (chiefly silica) and form a fusible slag with the same ; (4) an acid flux to combine with the base metals or their oxides. The fusion is carried out in a fire-clay crucible in a coke, coal, gas or oil furnace, and the molten charge poured into a suitable mould. The resulting lead button is then cleaned, cupelled and the gold-silver alloy parted as already described under scorification.

The nature and quantity of the fluxes to be used depends upon the chemical composition of the ore to be assayed. Only a few typical fluxes can be given here.

In general, it may be stated that highly siliceous ores require the largest amount of basic flux (generally sodium carbonate) ; basic or oxidized ores require more acid flux (borax), and also more reducing agents (charcoal, flour or argol) ; pyritic ores require less reducing agent, in some cases none, or even an oxidizing agent, such as nitre ; cupriferous, antimonial and telluride ores require a large amount of lead oxide.

In the following fluxes the weights are given in grammes. It is customary to weigh the ore on the 'assay ton' system, the ton usually referred to being the short ton of 2000 lb. Av. On this system, a weight of $29\frac{1}{6}$ g is called 1 assay ton (1 A.T.), and it will be seen that every mg. of gold or silver in the final weighing represents 1 oz. Troy of such metal per ton of 2000 lb. Av. (Where the 'long ton' of 2240 lb. Av. is used, the assay ton is $32\frac{2}{3}$ g. In this case 1 mg. in the assay represents 1 oz. Troy per ton of 2240 lb. Av. In countries where the metric system is in use, results are usually reported in grammes per ton of 1000 kilogrammes.)

Except where otherwise stated, the quantities given are for 1 A.T. of ore (29⅛ g).

TYPICAL FLUXES FOR CRUCIBLE ASSAYS (ORE, 1 A.T.)

(1) *Siliceous (Quartzose) Ores*

	A	B	C
Sodium Carbonate (g)	35	45	45
Borax Glass (g) ..	5	15	12
Litharge (g) ..	60	30	40
Charcoal (g) ..	1	1·25	1·2

(2) *Basic or Oxidized Ores*

	A	B	C
Sodium Carbonate (g)	18	20	20
Borax Glass (g) ..	12	20	30
Litharge (g) ..	40	45	30
Charcoal (g) ..	2·5	2	2·5

(3) *Slightly Pyritic Ores (without roasting)*

	A	B
Sodium Carbonate (g)	45	30
Borax (g)	15	30
Litharge (g)	50	150
Charcoal (g)	0·8 to nil	nil
Salt (g)	—	as cover

(4) *Moderately Pyritic Ores (fusion with iron)*

	A	B
Sodium Carbonate (g)	30	22
Borax (g)	10	15
Red Lead (g) ..	30	45
Hoop Iron (g) ..	2 or 3 pieces	2 to 3 pieces
Nitre (g)	—	7 (or as required)

(5) *Highly Pyritic (after roasting)*

Roast on clay dish with 15 g clean sand, then flux with

Sodium Carbonate (g)	60 (or less)
Borax (g)	30
Litharge (g)	50
Charcoal (g)	1·5 to 2·5

(6) *Highly Pyritic (fusion with nitre)*

A preliminary fusion is made with (say)

Ore, 0·25 A.T. (= 7·292 g)	
Sodium Carbonate	4 g
Litharge	60 g

The lead button obtained from this is used as a basis for calculating the nitre required to oxidize the surplus lead formed in the fusion and leave a button of suitable weight for cupellation. It is generally assumed that 1 g of nitre will oxidize 4 g of lead. Thus, suppose the weight of button from preliminary fusion on 0·25 A.T. was 'w', and that a final fusion is to be made on 1 A.T. we shall require $\frac{4w - 25}{4}$ g nitre, to produce a 25 g lead button.

The following fluxes may be used for the actual assay, on 1 A.T. ore :

	A	B
Sodium Carbonate ..	15 g	22 g
Borax	6 g	15 g
Red Lead	60 g	45 g
Nitre	(as indicated)	(as indicated)

(7) *Lead-Zinc Ores*

These are generally fused with addition of hoop iron, the amount of litharge or red lead being reduced or even omitted when much lead is present in the ore. Large amounts of zinc require increased soda and borax.

Flux as for moderately pyritic ores, with variations indicated by nature or ore. See (4) above. The hoop iron should be withdrawn after shaking and tapping, when fusion appears complete, and the crucible left in the furnace a few minutes longer before pouring.

(8) *Arsenical Ores*

These are generally best assayed after a preliminary roasting. The weighed portion of ore is spread out on a shallow, wide clay dish (roasting dish) with or without addition of silica as indicated by nature of sample. This is heated very gradually at the mouth of the muffle, with occasional stirring with a flattened iron rod, to prevent caking. When most of the sulphur is burnt off, the dish may be withdrawn and 1–3 g of powdered charcoal mixed with the charge. The roasting is then continued at a higher temperature till the sulphur is completely burnt out. The charcoal serves to decompose any arsenates that may be formed.

The roasted material, when cool, is mixed with a flux suitable for basic ore and a crucible fusion made.

Fusion with nitre should not be employed, as this would form arsenates which carry gold and silver into the slag.

(9) *Antimonial Ores*

Roasting is not generally advisable, owing to the fusibility of stibnite and consequent tendency to caking.

(*a*) Fusion with nitre may be made as follows :

Ore	1 A.T.
Sodium Carbonate ..	25 g
Borax	6–25 g
Red Lead	60 g
Nitre	15–25 g
	(as indicated by trial fusion)

Fuse very slowly at first. In some cases the addition of hoop iron is an advantage.

(*b*) Deflagration Method : A mixture of the ore with a large amount of nitre (30 to 40 g) and (say) 15 g clean sand is charged a little at a time into a previously heated empty crucible. Stir and mix well. When action has ceased, empty the contents on to an iron plate, mix with flux for basic ore (or flux given below), return to the same crucible and fuse at a low temperature.

Flux for antimonial ore after deflagration :

Sodium Carbonate ..	30 g
Borax	22 g
Red Lead	45 g
Charcoal	2 g
Strip of hoop iron.	

(*c*) Combined wet and dry method : The weighed charge of ore (1 A.T.) is treated with conc. HCl till action is complete, then diluted with water, a little tartaric acid added, settled, washed by decantation through a filter and the residue dried, the filter paper being burnt and the ash added. It is then fluxed with

Sodium Carbonate ..	25 g
Borax	5 g
Red Lead	30 g
Charcoal	1·5 g

(10) *Cupriferous Ores*

(*a*) Where the amount of copper is at all considerable, these are best assayed by a wet and dry method.

1 A.T. of ore is heated with conc. HNO_3, or a mixture of HNO_3

and H_2SO_4 until nitrous fumes are expelled. It is then diluted and allowed to settle thoroughly. Wash by decantation through a filter several times with hot water. (It is not necessary to transfer the bulk of the material to the filter.) Dry, flux the residue as for antimonial ores (*9c*) (wet and dry method).

When silver is to be determined, a separate assay should be made (e.g. by scorification). Attempts to precipitate the silver, either from the filtrate, or before filtration, by addition of chloride are not usually satisfactory.

(*b*) For ores containing only small amounts of copper, a direct fusion may be made by largely increasing the amount of lead oxide thus :

Ore	1 A.T.
Sodium carbonate ..	30 g
Borax	20 g
Red lead	100 g
Charcoal	1·5–3·5 g

A large lead button is produced, which must be reduced by scorification before cupelling.

(11) *Telluride Ores*

These require very fine grinding. No roasting or other oxidation process should be used, and the temperature of fusion should be raised very gradually. A large excess of lead oxide is required.

Ore	1 A.T.
Sodium Carbonate ..	30 g
Borax	10–12 g
Litharge	50–180 g (according to Te present)
Charcoal	If required
Salt	As cover

Some gold is generally carried into the cupels, and for exact assays these should be crushed and a fusion made to recover this. The ordinary fluxes are used, with addition of fluorspar.

Flux for Assay of Used Cupels.—The following may be used in ordinary cases :

Cupel (crushed fine) ..	1 A.T.
Sodium carbonate ..	20 g
Borax	15 g
Fluorspar	30 g
Charcoal	1·5 g
Litharge (a little extra if required, usually the cupel material contains sufficient)	

(12) *Other Classes of Ores*

The influence of the following metals is briefly indicated. Flux must be varied according to circumstances.

Bismuth—requires low fusion temperature. Causes absorption of gold by cupel.

Tin—requires low fusion temperature. Use considerable alkaline flux, as for zinc-lead ores. If reduced to metal, forms scoria in cupellation which ruins the assay.

Manganese—usually flux as for basic ores.

Assay of Gold Bullion

Sampling.—The most accurate method is to take a dip sample of the molten bullion immediately before pouring. This is taken out by means of a graphite dipper and poured into a suitable mould, or into water.

Samples are also taken by drilling at various points in the bar after casting. These should extend half-way through the bar, as there is often a difference of composition between the centre and the outer parts of the ingot. Any slag or dirt must be carefully removed.

Preparation of the Assay.—Usually 500 mg. is weighed out, either exactly or approximately, and the exact weight determined, say within 1/20 mg. This is wrapped in 2 g or more of pure lead foil, usually with the addition of 20–30 mg. of copper. When the bullion does not contain sufficient silver for parting (i.e. at least 2·25 times the weight of the gold), a sufficient amount of silver foil is added.

Checks.—In order to determine and correct the losses of gold and silver in cupellation, a number of check assays are weighed out consisting of approximately the same weight of gold as in the actual assay, and a weight of silver larger than that obtained in the preliminary assay by the amount which will probably be lost by volatilization and absorption in the cupel. These are wrapped in lead foil and cupelled simultaneously with the assays. Usually one check is placed in each cross-row of cupels in the muffle. Copper may also be added, as in the assays. A preliminary assay is generally made to determine the approximate composition of the bullion.

Cupellation.—The assay pieces, rolled up into small packets in lead foil, as described, are introduced into previously heated cupels, preferably after a small piece of pure lead foil has been placed in the cupels and has started to cupel freely. A uniform and moderate heat should be maintained throughout the operation, raising the temperature at the finish. The approaching end of the

operation is shown by a film of iridescent colours on the surface of the bead. The cupels should stand in the muffle for a few minutes longer, and should not be allowed to cool too suddenly, or particles of metal may be projected owing to the sudden ejection of absorbed oxygen on solidification. A momentary incandescence occurs as the beads solidify.

Weighing for Fine Metal.—The beads after cooling, are removed from the cupels by pliers, cleaned with a wire brush and flattened by hammering on a clean anvil. If no silver has been added, they are then weighed and the weight reported as 'fine metal', i.e. gold +silver. In this case, the requisite amount of silver is now added and the cupellation repeated. If silver has already been added, the beads are treated as described below, after weighing.

Annealing and Rolling.—The beads are then annealed by heating to dull redness (in a muffle, spirit or gas flame) and passed between smooth steel rolls, to form strips about 3 inches in length. The rolls are gradually tightened after each passage of the bead. The strips are then again annealed, and loosely coiled so that the rougher surface is at the outside.

Parting.—This is usually done in special flasks with a long, rounded bulb and a long, narrow neck (parting flasks), but large porcelain crucibles may also be used. The rolled strips ('cornets') are placed in these and about 15 ml. of pure dilute nitric acid (1 part HNO_3 to 4 parts water, by volume) is added. This is heated to boiling, allowed to remain hot for about twenty minutes, then again boiled till all red fumes are expelled. The acid is then poured off and a wash given with distilled water. A second acid treatment is then given with nitric acid (3 : 1) i.e. 75% HNO_3 by volume. This may require about 30 minutes, heating very cautiously at first, finally to boiling. After pouring off the strong acid, a final wash is given with distilled water, this being repeated at least twice. If 'parting flasks' have been used, these are simply filled to the top with water, an inverted 'annealing cup' (small crucible of unglazed earthenware) placed over the mouth, and inverted, allowing the gold to settle at the bottom. The flask is then gradually raised till the lip is level with the edge of the annealing cup, and withdrawn by a lateral movement. The surplus water is poured off and the crucibles or annealing cups dried and ignited until the gold assumes its natural colour.

Final Weighing.—The gold cornets are weighed when cold, and the weight corrected by means of the checks. Usually these show a slight increase in weight (surcharge) and the amount of this increase must be deducted from each of the corresponding bullion assays. It is generally assumed that each assay in the same cross-row

of the muffle has undergone the same losses or gains as the check. The increase is due to the fact that the weight of silver retained by the gold after parting is greater than the loss of gold in cupellation.

The fineness of the bullion is generally reported in parts of gold (or silver) per 1000 parts of bullion. If 500 mg. has been taken for the assay, the fineness is obtained by simply multiplying the corrected weight of the final assay in mg. by 2.

Special Procedure in Presence of Platinum.—When the bullion contains platinum, at least 3 parts of silver for each part of combined gold and platinum should be used in cupellation and, after parting, the cupellation repeated with a similar addition of silver, until the weight of the gold cornet is constant.

If the amount of platinum is also to be determined, it is necessary to part after the first cupellation with pure conc. sulphuric acid instead of nitric acid, as the latter, in presence of silver, dissolves some platinum. At least 2 parts of silver must be added before cupellation for each part of platinum. After a second treatment with sulphuric acid, the undissolved metal is free from silver, and the gold and platinum may be weighed together and parted, after cupellation with addition of silver, with nitric acid as described above.

2. Precipitation of metallic gold by evaporation or by metallic zinc or aluminium

In the cyanide process of extracting gold from ores it is a matter of importance to determine the amount of gold in the solutions, both before and after precipitation. As the percentage is usually small, it is generally necessary to operate upon a considerable volume of liquid. The following methods are recommended :

Evaporation with Litharge.—A measured volume of the solution is evaporated in a porcelain basin, at a moderate heat, without actual boiling ; 20–50 g of litharge or red lead is sprinkled over the surface of the liquid before evaporation. At the end, the residue must be allowed to dry slowly, without overheating. It is then scraped out and fluxed with the addition of a suitable mixture, such as the following :

Litharge (originally added)	45 g
Sodium carbonate ..	40 g
Silica	25 g
Borax	10 g
Charcoal	1 g

The resulting lead button is cupelled and parted in the ordinary way.

Precipitation with Zinc.—Acidify a measured volume strongly with H_2SO_4. Add about 5 g zinc (dust or shavings), a little at a time, to the boiling solution, allowing action to cease before the next addition is made. When zinc has dissolved, add a few drops of lead acetate, agitate, filter, and rinse precipitate out on to the filter. Allow to drain, then scorify the filter paper with residue, adding grain lead (litharge and charcoal if necessary). Cupel resulting lead button.

Many modifications of this process have been suggested, but the above will generally be found quite satisfactory.

Precipitation with Copper Salts.—Take 10 A.T. (or 300 ml.) of the solution, add 3 ml. of 5% potassium ferrocyanide (if little free cyanide is present, add also a small quantity of KCN), then 10 ml. of 15% copper sulphate; follow with 10 ml. of 25% sodium bisulphite ($NaHSO_3$); and finally, 5 ml. of sulphuric acid (1 : 9) agitating after each addition. Allow to settle, for about half an hour, filter, scorify filter paper and residue, or fuse with the following flux:

Sodium carbonate ..	10 g
Borax	5 g
Litharge or red lead ..	10–15 g
Charcoal	0·2 g

This method has the advantage that the precipitation may be made in a cold solution. It is not necessary to wash the precipitate on the filter, or to dry before fusion.

Note: Precipitation by Al (Chiddey's method) is carried out in a similar manner to that described for zinc.

3. Precipitation of metallic gold from 'aqua regia' solution using a reducing agent

The usual reagents employed are SO_2 or $FeSO_4$ but oxalic acid may be used. For a product of highest purity SO_2 or oxalic acid should be used as with $FeSO_4$ iron salts are liable to contaminate the gold powder.

The scrap gold or bullion is dissolved in *aqua regia* to give the chlorides of gold and other metals present. Evaporate with HCl to displace HNO_3 and filter off any silver chloride precipitated after dilution. It may be necessary to dilute to a great volume (5–20 litres) and allow to stand for several days to enable all the AgCl to settle. Syphon or filter off the clear solution and saturate with SO_2 or stir in $FeSO_4$ or oxalic acid solution to precipitate the gold as a brown powder. Allow to settle for a few days, syphon off clear solution after testing that all Au has been deposited,

finally filter off the gold, dry and melt in a clean crucible. Weigh the bead.

$$2AuCl_3 + 3H_2SO_3 + 3H_2O = Au_2 + 6HCl + 3H_2SO_4$$

Platinum may be co-precipitated in traces but no Pd is deposited.

(See also under 'Estimation of Gold in Carat Golds'.)

Note: For straight binary Ag/Au alloys a simple parting in nitric acid is adequate. (For details see 'Estimation of Gold in Standard Gold Alloys'.)

4. Colorimetric test for gold

The material is taken into solution with *aqua regia* and evaporated with HCl to remove most of the nitric acid. This auric chloride solution is then poured into a saturated solution of stannous chloride in HCl and if gold is present a purplish coloured precipitate of colloidal gold is produced. ('Purple of Cassius'.)

INDIUM

(In) Atomic Weight = 114·76

Metallurgical Occurrence

In flue dust from zinc extraction processes
Associated with Bolivian tin ores
Special dental alloys
As a tarnish resisting plating on dental work, on silver, cadmium alloy bearings and as an impregnating medium for copper-lead bearings
Fusible alloys

Source of Metal as Standard

Electrolytic indium = 99·99% (Johnson Matthey & Co. Ltd., London). In general, no standards are used in the analyses.

Methods of Estimation

GRAVIMETRIC

1. *Precipitation as hydroxide and ignition to oxide* (suitable for most materials).
2. *Precipitation by 8-hydroxyquinoline in acetic acid solution* (heavy base metals should be absent or removed).

ELECTROLYTIC

3. *Electrolysis of a neutral sulphate solution* (for small quantities in solutions free from heavy base metals).

METHODS

1. Precipitation as hydroxide and ignition to oxide

(Schoeller and Powell, loc. cit.)

Owing to the small quantity of indium likely to be present in ores (less than 0·5%), large samples of about 100 g may be necessary. For alloys, take smaller samples in proportion to their indium

content. Concentration of the indium present in ores is usually a necessary preliminary, and is effected by solution of the ore in conc. HCl followed by dropwise addition of conc. HNO_3; alternatively a potassium bisulphate fusion may be carried out (particularly on iron ores). The HCl solution is evaporated to a syrup, then diluted to about 800 ml. with hot water and insoluble silicates are filtered off. Strips of pure electrolytic zinc are placed in the solution, which is gently boiled. Indium is precipitated as a metallic sponge on the zinc. When precipitation is complete, the sponge is dissolved in 50% HNO_3 and the solution evaporated to dryness and diluted with 5% ammonium nitrate solution; meta acids of Sn and Sb and the basic nitrate of Bi are precipitated and are filtered off. To the filtrate, containing In in nearly neutral nitrate solution, add 5 g ammonium nitrate, a little filter pulp and *either* add NH_4OH until slightly alkaline and boil until the hydroxide is precipitated, *or* instead of NH_4OH, boil and add a 2% solution of hexamethylenetetramine until no further precipitate forms. Filter, wash the precipitate with 2% ammonium nitrate solution and it is usually advisable to redissolve in 50% HNO_3 and reprecipitate with ammonia. The final hydroxide precipitate is ignited at lowest temperature possible until all carbon has been removed. At no time should the ignition temperature exceed 800° C. since In_2O_3 is easily reduced to metal or to In_3O_4 at 850° C.

Cool and weigh as In_2O_3 containing 82·71% In.

2. Precipitation by 8-hydroxyquinoline (Geilmann and Wrigge, *Zeitsch. anorg. Chem*, 1932. **209.** 129)

The neutral chloride solution is treated with 2 g sodium acetate and 2 ml. acetic acid, diluted to 100 ml., heated to 70° C. and a 5% solution of 8-hydroxyquinoline in 30% acetic acid is added until no further precipitate forms. Stand 10 minutes at 40° C., then filter through a tared sintered glass crucible under suction. Wash with warm water and dry at 105–120° C. for 1 hour. Cool and weigh as $(C_9H_6OH)_3In$ which contains 20·97% In.

As this reagent will give precipitates with many of the common base metals, these (Fe, Mn, Ni, Co, Ti) should be removed prior to the precipitation of In. Also Mg, Be, Al, Zn and Cd are liable to interfere and should preferably be absent. For full details of separation procedure when these metals are present, see the original paper (above) or *B.D.H. Book of Organic Reagents*, 1948.

3. Electrolysis

To a sulphate solution of indium, freed from the presence of

common base metals, add NH_4OH until a permanent precipitate is just avoided. Add 10 g ammonium sulphate and electrolyse at 0·2 amps and about 1 volt using a rotating Pt gauze cathode and a Pt spiral anode. After about 8–12 hours, remove the cathode with the current still on, wash with water, then alcohol. Dry and weigh as the metal.

IRIDIUM

(Ir) Atomic Weight = 193·1

Metallurgical Occurrence

Electrolytic slimes from Cu and Ni refining
Native osmiridium
Iridium-platinum alloys

Source of Metal as Standard

Purified iridium = 99·98% (Johnson Matthey & Co. Ltd., London). Rarely used as standards.

Methods of Determination

All usual methods of determination are gravimetric. As explained in the chapter on 'Platinum Metals', the method to adopt for any determination is largely governed by the presence or absence of other metals of the Pt group. In this section, therefore, will be presented selected methods under specific conditions.

GRAVIMETRIC

1. *Lead fusion followed by parting in* aqua regia
   (for Ir-Pt alloys, Ru and Os absent).
2. *Precipitation as ammonium chloriridate*
   (for materials with Pt and preferably Pd absent).
3. *Precipitation as hydroxide following bromate hydrolysis*
   (most reliable method for alloys. Rh and Pd must be removed however).
4. *Precipitation as metallic iridium by means of hydrazine hydrochloride*
   (less accurate than 3, mainly applicable to 'clean' Ir solutions).

METHODS

1. Lead fusion followed by parting in 'aqua regia'

The lead fusion breaks up the alloy and facilitates subsequent acid solution. Pb is removed as $PbSO_4$, and the Pt dissolved out by *aqua regia* to give chloroplatinic acid, leaving Ir which can be cleaned and weighed. Ruthenium and osmium would also appear in the residue and must be absent.

$$Pt + 2HCl + 2Cl_2 = H_2PtCl_6.$$

2. Precipitation as ammonium chloriridate

Although NH_4Cl will precipitate Pt and Pd as well as Ir from solutions of their hexachloro acids, both the Pt and Pd can be

removed at the initial stages of *aqua regia* attack to form the subgroups of the Pt metals. A chloride solution of Ir may be obtained by adding *aqua regia* to the solution obtained by a caustic fusion on the initial residue from *aqua regia* attack. To this chloride solution, addition of a saturated solution of NH_4Cl will precipitate ammonium chloriridate, as a black crystalline precipitate. It is advisable to evaporate the filtrate with a crystal of sodium chlorate to precipitate last traces of Ir which being present as ammonium chloriridite had not precipitated. Combine precipitates and ignite, finally reduce to metal by heating and cooling in a stream of hydrogen.

3. Precipitation as hydroxide following bromine hydrolysis

Ir (Rh and Pd) hydroxides are produced as a result of boiling a neutral solution of their chlorides in the presence of sodium bromate ('bromate hydrolysis'). The washed hydroxide precipitate is dissolved in conc. HCl., Pd is removed as the dimethylglyoxime complex, the filtrate, treated with HNO_3 and then fumed with H_2SO_4, is diluted, and Rh is precipitated as metal sponge by titanous sulphate solution from a 40% H_2SO_4 solution of Rh and Ir. (Ir is not precipitated, merely reduced to the iridous state.) Ir in the filtrate is precipitated as hydroxide by bromate hydrolysis as before, after Ti has been removed by cupferron. Ignite and reduce to metal as in (2).

4. Precipitation as metallic iridium by means of hydrazine hydrochloride

The diluted chloride solution (200 ml.) containing Ir (HNO_3 absent) is neutralized with NaOH solution and a slight excess of alkali added. To the heated alkaline solution, add a slight excess of 10% hydrazine hydrochloride solution. The metal sponge produced is filtered, leached with 5% HCl, filtered, washed with water, ignited, reduced (as above), and weighed as Ir metal.

(For full details of all methods see under 'Analysis of Standard Pt Alloys'.)

IRON

(Fe) Atomic Weight = 55·85

Metallurgical Occurrence

This element is found in a very wide variety of metallurgical materials and in particular: iron ores; coal; coke; slags; refractories (fireclay, chromite, dolomite, magnesite etc.); steel; cast iron; Ni/Cr/Fe resistance alloys; stellite; Al and Mg and their alloys; white metal and solders; zinc base die-casting alloys; nickel alloys; copper alloys of several types.

Source of Metal as Standard

Electrolytic iron, carbonyl iron powder (approximately 99·95% pure) (Murex Ltd., Rainham, Essex) or pure iron wire, but more convenient to use A.R. ferrous ammonium sulphate solution.

Methods of Determination

GRAVIMETRIC

1. *Precipitation as hydroxide by ammonia and ignition to ferric oxide*
   (not very reliable except in clean solutions, may be used for 1–10% Fe).
2. *Precipitation as basic acetate and ignition to oxide*
   (mainly used as a method of separation rather than estimation).
3. *Precipitation as hydroxide by means of zinc oxide or sodium hydroxide and ignition to oxide*
   (similar application as [2]).
4. *Precipitation as a red-brown complex by cupferron and ignition to oxide*
   (useful for separation but liable to contamination by certain metals. Used for up to 10% Fe in non-ferrous alloys)

VOLUMETRIC

5. *Titration with $KMnO_4$ in sulphuric acid solution after reduction by Zn, Al, SO_2 or H_2S*
   (widely used for all types of analyses but chlorides must be absent [see also 5a]).

5a. *Titration with $KMnO_4$ in HCl solution after stannous chloride reduction*
   (Zimmerman-Reinhardt Method—useful but not as accurate as [6])

6. *Titration with $K_2Cr_2O_7$ in HCl solution using either external or internal indicator*
   (universally employed for all types of metallurgical materials [ores, ferrous and non-ferrous alloys]).
7. *Titration with ceric ammonium sulphate in HCl solution after $SnCl_2$ reduction using internal indicator*
   (may be used instead of [6] and has the advantage that ceric salts do not have the intense colour of chromic salts from $K_2Cr_2O_7$ titration, thus the end point is clarified).
8. *Titration of ferric iron with titanous chloride solution*
   (not widely used owing to difficulty of storing $TiCl_2$—Is used in light alloy analyses).
9. *Titration of ferric iron with mercurous nitrate solution* (for plain carbon steels and cast irons).

COLORIMETRIC

10. *Based on the blood-red colours produced with thiocyanates in the presence of ferric iron* (widely used for small quantities [less than 1%] in light alloys, refractories, slag, ash etc.).
11. *Based on the purple-pink colours produced with thioglycollic acid in the presence of ferrous and ferric iron*
    (similar application to [10], probably a more sensitive test).

METHODS

1. Precipitation as hydroxide by ammonia and ignition to ferric oxide

This is the method usually adopted in qualitative analysis, and is frequently used in quantitative work, in spite of several serious drawbacks. The iron must be obtained in the ferric condition. If ferrous iron is present it is oxidized by the addition of nitric acid, bromine, hydrogen peroxide or other oxidizer. Hydrogen sulphide, if present, should be boiled off before adding the

oxidizer. The amount of NH_4Cl to be added will depend on the quantity of Mn, Ni, Co, Zn, Ca or Mg in the solution, the addition of this substance being designed to prevent the precipitation of these metals as hydroxides. In an assay on 1 g ore, 10 g NH_4Cl will usually be sufficient.

Ammonia is then added until the solution is distinctly, but not strongly alkaline, and the liquid is boiled for about 2 minutes. The precipitate should be flocculent, reddish-brown, and settling rapidly. Too long boiling tends to produce a slimy or gelatinous precipitate, which will not filter rapidly, or which passes through the filter as a colloidal suspension. It is best filtered on a Buchner funnel under vacuum.

When the amount of iron, or of other elements such as Cu, Mn, etc., is at all considerable, the precipitate must be redissolved in hot dilute HCl, and reprecipitated by NH_4OH with a further addition of NH_4Cl. The precipitate tends to carry down and occlude considerable quantities of these elements, even when they are not precipitated by NH_4OH themselves. (This is particularly noticeable in the case of cobalt, large quantities of which may, under some conditions, precipitate as a cobaltamine compound.) Aluminium, titanium and chromium (in chromic salts) are completely precipitated with the iron ; Be, Ce, Mo, As, Nb, Ta, Th, U, V and Zr are likewise precipitated as hydroxides by NH_4OH and NH_4Cl.

The precipitate is washed with hot water, to which a few drops of dilute ammonia are added, until free from soluble chlorides, then dried and ignited with the paper, in a porcelain or platinum crucible ; this is placed at the mouth of the muffle and allowed to heat gradually until the carbon of the paper is burnt off ; finally at a moderate red heat and weighed as Fe_2O_3.

($Fe_2O_3 \times 0{\cdot}6994 = Fe.$)
($Fe_3O_4 \times 0{\cdot}7236 = Fe.$)
(See also 'Iron in Fireclay'.)

2. Precipitation as basic acetate and ignition to oxide

This method serves to separate iron, together with Al and Ti, from Cr, Mn, Co, Ni, U and Zn. The procedure has been fully described under 'General Methods of Separation and Solution'.

3. Precipitation as hydroxide by means of zinc oxide or sodium hydroxide and ignition to oxide

The method serves to separate iron (Al and Ti) from Mn, Ni, Co and some other metals. The details are given under 'General

Methods of Separation'. The method is not very suitable if a gravimetric determination is to be made, as the precipitate of $Fe(OH)_3$ is mixed with the excess of insoluble ZnO or $Zn(OH)_2$, which must be separated before the Fe_2O_3 can be ignited and weighed, but if a volumetric method is to be used, the presence of the zinc compound is immaterial.

When caustic soda is used as the precipitant Cr, Al and Mo are also separated from the iron (useful in nitrided steels, etc.). In the absence of Mn, vanadium is also separated, otherwise it is co-precipitated as manganese vanadate.

4. Precipitation of a red-brown complex by cupferron and ignition to ferric oxide

Based on the reaction :

$$FeCl_3 + 3(C_6H_5N \,.\, NO \,.\, ONH_4) = Fe(C_6H_5N_2O_2)_3 + 3NH_4Cl.$$

This method serves to separate iron from Al, Cr, Ni, Co, Zn, Mo and Cd. The reagent also precipitates Hg, Pb, Bi, Sn, Ag, V, Ti, U, Zr so that these elements should first be removed. Copper is completely precipitated but may easily be separated from the iron compound by means of ammonia, in which the copper compound is readily soluble, while the iron compound is not. The reagent is soluble in water, and is used in the form of a 6% solution, which is best freshly prepared, but keeps for about a week if not exposed to light.

The solution containing the iron is made up to, or concentrated to 100 ml. and 20 ml. conc. HCl added. The cupferron solution is then added gradually, in the cold, with constant stirring until precipitation is complete and the reagent begins to crystallize. A reddish-brown precipitate is produced (the copper compound is greyish-white). A further quantity of the reagent is now added, equal to one-fifth the volume of the solution, the precipitate allowed to settle for about 15 minutes, then filtered and washed first with cold 2N hydrochloric acid, then with ammonia (to remove Cu), and finally with water. The precipitate is then dried and ignited slowly and weighed as Fe_2O_3.

Notes:

(1) The Fe and Cu precipitates are only slowly attacked by 2N HCl in the cold, but are decomposed by hot acid. Cold dilute K_2CO_3 solution, or NH_4OH have no action on the Fe precipitate, but the Cu compound dissolves readily in NH_4OH. Alkaline hydroxides decompose them rapidly.

(2) Instead of igniting the complex to Fe_2O_3, it may be

dissolved in 20–50 ml. hot 50% HCl, reduced with $SnCl_2$ and titrated with $K_2Cr_2O_7$ as in Method 6.

5. Titration with $KMnO_4$ in sulphuric acid solution after reduction by Zn, Al, SO_2, or H_2S

When Ti, V, Cr, Mo, W and U are present, zinc should not be used for reducing the ferric salts since the above metals will also be reduced and then reoxidized later by $KMnO_4$ giving a high result. Instead, use SO_2 reduction when Ti or U are present or use Method 5a ; Cr and V do not interfere if Zn or Al reduction is used and titration carried out in the cold using 3 drops of Ortho-phenanthroline indicator (0·7 g $FeSO_4$ in 100 ml. water add 1·485 g ortho-phenanthroline and stir until dissolved)—colour change is orange-red to blue-green. Mo and W are best removed by a preliminary treatment of the ferric solution with ammonia when molybdates and tungstates go into solution leaving $Fe(OH)_3$.

The use of H_2S as a reducing agent is both certain and popular, and it is sometimes useful to pass H_2S into a tartaric acid solution of ferric salts when reduction to the ferrous state is obtained : $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$.

Then make the solution alkaline with ammonia and re-gas with H_2S. Ferrous sulphide will be precipitated under these conditions whereas any Al, Cr or Ti will remain in solution.

For this method, the iron is best obtained in a sulphuric acid solution free from other mineral acids, from organic matter and from other substances that react with permanganate in acid solution. It is possible to make the titration in a hydrochloric acid solution if a considerable quantity of manganous sulphate ($MnSO_4$) be added.

The iron must be in the ferrous condition ; if ferric iron be present, the solution must be reduced. This may be done in several ways as previously stated. One method is to boil the solution, which should contain a small amount of free H_2SO_4 (say 5–10 ml. per 100 ml. of liquid) with pure granulated metallic zinc, which should be free from iron. The solution is boiled gently, best in a flask with 'Bunsen valve' until a drop of the liquid no longer gives a red colour when tested with a thiocyanate, indicating that the iron is all in the ferrous condition. Any undissolved zinc, together with whatever deposit of lead, copper, arsenic or other metal has formed, is then filtered off as rapidly as possible (e.g. through a plug of glass wool and the residue well washed with

recently boiled cold distilled water. The cold solution is then at once titrated with permanganate, the reaction being as follows:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

The reaction is complete when a faint pink tint remains premanent for a minute or two after agitation.

1 ml. N/10 $KMnO_4$ (3·1606 g $KMnO_4$ per litre) = 0·005584 g Fe.

One may also use a permanganate solution which will give the percentage of iron with little or no calculation. Thus, a solution may be prepared containing 2·83 g $KMnO_4$ per litre, so that 1 ml. = 0·005 g Fe or 1% Fe on as assay of 0·5 g of material.

Whenever possible, it is advisable to prepare the permanganate solution a day or two before standardizing, using slightly more than the theoretical amount of $KMnO_4$, to allow for reduction by organic matter or other substances in the water.

Reduction with Aluminium

A convenient method of reducing the iron solution, which avoids the necessity of filtration, is to use stout sheet aluminium in a fairly strong (say 1 : 10) H_2SO_4 solution. The sheets are bent at the edges or corners so as not to lie flat on the bottom of the vessel. If, at the end of the reduction, the liquid be diluted and cooled sufficiently to stop the evolution of gas from the metal, it is unnecessary to remove the aluminium sheets before titration, unless a loose, black deposit has been formed. As an additional precaution against oxidation, a small pinch of Na_2CO_3 or a fragment of marble may be added, to produce an atmosphere of CO_2 in the flask.

Standardization of Potassium Permanganate

There are three methods in common use:

A. *With Iron Wire.*—The purest obtainable soft iron wire is used; this contains usually about 99·8% Fe. Weigh out 0·1–0·2 g exactly (after removing any rust or grease by means of cloth and emery paper), dissolve in a mixture of HCl and HNO_3, say 5 ml. of each; when dissolved, cool and add 5 ml. conc. H_2SO_4. Boil down to strong white fumes, cool, add 100 ml. H_2SO_4 (1 : 9) and 5–10 g pure granulated zinc (or one or two pieces of Al foil about 1 in. square) and boil till reduction is complete. Cool to room temperature under the tap. Dilute with about 100 ml. of boiled cooled distilled water and titrate at once with $KMnO_4$. (For exact work it is necessary to make a blank test, using the same amounts of all substances added, omitting the iron wire; this is put through

the same process and titrated with $KMnO_4$. The amount found in the blank is deducted from the previous titration. It is assumed that a similar method of reduction is to be used with the assay sample. (A correction must also be made for the actual Fe contents of the wire used; thus if this contains 99·6% Fe the amount weighed out is multiplied by 0·996 in calculating the standard.)

B. *With Ferrous Ammonium Sulphate* ($FeSO_4 . (NH_4)_2SO_4 . 6H_2O$).—This salt, when pure and dry, contains approximately one-seventh of its weight of iron (actually 14·24%). Weigh out 0·7–1·40 g of the salt, dissolve in a large volume (say 200–300 ml.) of water, acidify with 10 ml. conc. H_2SO_4, cool and titrate at once with $KMnO_4$. The weight of salt taken × 0·1424 = Fe.

C. *With Oxalic Acid* ($C_2H_2O_4 . 2H_2O$).—This method depends upon the reaction:

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 18H_2O,$$

from which it appears that 2 × 158·03 g $KMnO_4$ are equivalent to 5 × 126·046 g of crystallized oxalic acid ($C_2H_2O_4 . 2H_2O$) or 158·03 g $KMnO_4$ to 5 × 63·023 g oxalic acid. Since this same amount of permanganate is equivalent to 5 × 55·84 g Fe, it follows that 63·023 g oxalic acid are equivalent to 55·84 g Fe or 1 g to 0·886 g Fe. Thus the oxalic acid factor of the permanganate × 0·886 will give the iron factor. 1 ml N/10 $KMnO_4$ = 0·0063023 g oxalic acid ($C_2H_2O_4 . 2H_2O$.)

To standardize: weigh out 0·25–0·5 g pure crystallized oxalic acid, dissolve in hot water, with addition of about 10 ml. conc. H_2SO_4 (previously diluted), and titrate the hot solution with $KMnO_4$. The reaction is at first rather slow, but after 1 or 2 ml. of $KMnO_4$ have been added, it proceeds rapidly.

Note: With titaniferous ores (or even normal ores), sulphuric acid solution may be impossible. Either attack with HCl, or *aqua regia*, then remove these by fuming with H_2SO_4 or better, fuse 0·5 g ore with 5 g potassium bisulphate in a Pt or silica crucible. When cool, leach with dilute H_2SO_4 and reduce ferric iron by adding 5 g sodium sulphite to a faintly acid solution. Warm until solution is colourless, dilute to 200 ml. add 5 ml. H_2SO_4, boil out SO_2, cool and titrate with $KMnO_4$ as before. (For non-titaniferous ores, the leached melt may be reduced with Zn or Al in the normal way.)

(See also 'Iron in Zinc Base Alloys'.)

5a. Titration with $KMnO_4$ in HCl solution after reduction with stannous chloride (Zimmermann-Reinhardt Method)

When it is unavoidable to have HCl or chlorides present in

solution or when time does not allow removal of HCl by H_2SO_4 fuming, this method may be used. Some analysts claim that it is less accurate than either the normal $KMnO_4$ titration or the $K_2Cr_2O_7$ titration.

From 0·25–0·5 g of the finely-ground ore is boiled with 10–25 ml. of HCl (1 : 1) with the addition of about 3 ml. of a concentrated solution of stannous chloride in HCl. A large excess of $SnCl_2$ must be avoided; if too much has been used, strong $KMnO_4$ should be added drop by drop till the yellow colour reappears, then $SnCl_2$ is added carefully till the solution is just decolorized. Most ores are rapidly dissolved in this way. Cool to room temperature, add about 15 ml. of a saturated solution of mercuric chloride, and pour into 400 ml. of cold (recently boiled) distilled water containing 5–25 ml. of a special manganese sulphate solution described below, and titrated slowly with $KMnO_4$.

Special manganese sulphate solution:

Manganese sulphate	100 g	} diluted to 1 litre
Phosphoric acid (d. 1·7)	175 ml.	
Sulphuric acid conc. (d. 1·84)	175 ml.	

The function of this solution is as follows:

Dilute $KMnO_4$ solution will not oxidize cold diluted HCl and liberate chlorine unless ferrous iron is present, it is thought to be due to the intermediate formation of an iron peroxide Fe_2O_5 which oxidises the HCl according to the following equation:

$$Fe_2O_5 + 10HCl = 2FeCl_3 + 5H_2O + 2Cl.$$

When manganous salts are present, this reaction is prevented by the Mn reacting preferentially with the $KMnO_4$ forming MnO_2 which in turn oxidizes the ferrous iron and thereby prevents decomposition of the HCl. When all ferrous irons have thus been oxidized, no further MnO_2 is produced.

The phosphoric acid present forms ferric phosphate with the ferric iron produced, and being nearly colourless, renders the end point more distinct.

6. Titration with $K_2Cr_2O_7$ in HCl solution, using either external or internal indicators

Originally this method although very convenient and accurate had the disadvantage of requiring an external indicator (approx. 1% potassium ferricyanide). In more recent years various internal indicators have been developed such as diphenylamine (1% in conc. H_2SO_4), barium or sodium diphenylamine sulphonate (0·25% in water) and o-phenanthroline (approximately 1·5% in

0·7% $FeSO_4$ solution). The first named although still commonly used has the disadvantage of being relatively insoluble in aqueous and diluted acid solutions and does not keep whereas the barium, and sodium salt and the last named are both water soluble and relatively stable.

Any of the methods mentioned in (5) may be used for the reduction of ferric iron but since in this case we have a hydrochloric acid solution it is much more speedy and effective to use stannous chloride as the reducing agent, a few ml.s being dropwise added to the hot solution of the ferric iron until the ferric ion colour has been discharged. Two drops excess is advisable and any surplus is rendered innocuous by the subsequent addition in the cold of 15–25 ml.s saturated mercuric chloride solution. The resulting products have no effect upon the titration.

The respective actions of the indicators mentioned above are as follows:

(*a*) *Potassium Ferricyanide* (external)—this produces an intense blue coloration or precipitate of ferrous ferricyanide with ferrous iron, and the disappearance of this colour marks the completion of oxidation of all ferrous iron by $K_2Cr_2O_7$ during titration (see equation (iv) below).

(*b*) *Diphenylamine* (internal).—$(C_6H_5)_2NH$ is an aniline derivative which on oxidation gives a deep violet coloration; thus the change is from green to violet. Has the disadvantage of first having to be made up in conc. H_2SO_4 in which its solubility is not very great and then the titration should be carried out in fairly strong acid solution (say 20–40% acidity) otherwise the indicator is not held in solution.

Mainly for this reason, after reduction to ferrous iron by $SnCl_2$ and treatment with $HgCl_2$ about 20 ml. of a sulphuric-phosphoric acid mixture is added (1 volume conc. H_2SO_4 and 1 volume syrupy phosphoric acid plus 8 volumes water) followed by 5 drops of indicator and the titration then performed in the cold.

The presence of the phosphoric acid is for the same reason as quoted in Method 5a and also to diminish the oxidizing effect of ferric iron on the indicator, since the indicator is subject to selective oxidation by the $K_2Cr_2O_7$ in so far that the indicator is not permanently oxidized to the violet-blue dyestuff until all ferrous iron has been oxidized.

The presence of some HCl in the solution prior to titration is found to sharpen the end point.

(*c*) *Barium or Sodium Diphenylamine Sulphonate* (internal).—These salts give a much more stable aqueous solution than we have with diphenylamine and are to be recommended. As before

a H_2SO_4–H_3PO_4 solution plus some HCl is added prior to titration but in this case the optimum acidity of the solution is N–3N. Colour change as with diphenylamine.

(*d*) *Ortho-Phenanthroline* ($C_{12}H_8N_2$. H_2O)—*Ferrous Sulphate Mixture* (*Jnl. Amm. Chem. Soc.*, 1933. **55**. 2649).—This internal indicator is sometimes used as an alternative to (*b*) or (*c*) and has a colour change from orange to green in sulphuric solutions and from orange-red to yellow in HCl solutions. Phosphoric acid may be present as before.

With indicators (*b*), (*c*) and (*d*), since the colour change is due to oxidation of the reagent, 0·05 ml. should be deducted from the titration reading to allow for this.

Titration in Hydrochloric Acid Solution by Potassium Dichromate

Solutions Required

(*a*) *Stannous Chloride.*—30 g pure tin or 60 g crystallized stannous chloride dissolved in 550 ml. conc. HCl, and diluted to 1 litre. A stick of pure tin is kept in the solution to prevent oxidation.

(*b*) *Mercuric Chloride.*—Saturated solution in water.

(*c*) *Potassium Ferricyanide* (Indicator for Ferrous Iron).—1 g in 100 ml. water. Best prepared in small quantity as required.

Treatment of Ore.—The iron is obtained in solution by the methods already described. If completely soluble in HCl it is unnecessary to treat with H_2SO_4. If no HCl is present in the final solution add 5 ml. conc. HCl.

The solution may be reduced to ferrous state by any of the methods previously given, or by boiling with (say) 20 g of granulated test lead, which precipitates any Cu, As or Sb that may be present. Filter while hot into a vessel containing 2 ml. of the above stannous chloride solution (with 5 ml. HCl if necessary) and wash thoroughly with hot water. The $SnCl_2$ prevents any oxidation during this process. To the filtrate add 10 ml. of the mercuric chloride solution, cool and titrate at once with standard potassium dichromate containing 4·3905 g $K_2Cr_2O_7$ per litre.

1 ml. $K_2Cr_2O_7$ = 0.005 g Fe.

With external indicator, the end of the reaction is found by testing a drop of the solution, after mixing thoroughly, by adding it to a drop of the ferricyanide indicator on a porcelain plate. So long as an excess of ferrous salt is still present, a blue colour will be produced. When this colour becomes faint or only forms slowly, run in the $K_2Cr_2O_7$ in smaller quantities at a time, and continue to test until a drop taken out develops no blue colour for thirty seconds. The reaction is then complete.

The following reactions take place :

(i) $FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$.

(ii) $SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$.

(iii) $6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2CrCl_2 + 2KCl + 7H_2O$,
(from which 1 g $K_2Cr_2O_7$ = 1·1389 g Fe.)

(iv) $3FeCl_2 + 2K_3Fe(CN)_6 = Fe_3(Fe(CN)_6)_2 + 6KCl$.

Precautions.—It is necessary to avoid a large excess of $SnCl_2$, otherwise there may be a precipitate of metallic mercury by the reaction $SnCl_2 + HgCl_2 = Hg + SnCl_4$, giving a grey or black discoloration, which if not immediately removed by addition of more $HgCl_2$, vitiates the assay. The precipitate formed on adding $HgCl_2$ should be quite white.

For detailed procedures see also under : 'Iron in Magnesium Alloys', 'Iron in Steel and Stellite', 'Iron in Ironstone and Slags', 'Iron in Whitemetals', and 'Iron in Copper Alloys'.

Note: In the case of iron ores, it may be necessary to determine ferrous iron and total iron in order to ascertain the proportions of ferrous and ferric compounds.

Ferrous Iron is determined by dissolving a sample in HCl or dilute H_2SO_4 (whichever is more convenient) in a flask with Bunsen valve attached and with 1–2 g sodium carbonate in the flask to generate an inert atmosphere. When sample is dissolved, cool and titrate at once with $K_2Cr_2O_7$ or $KMnO_4$ respectively. Refractory ores may be given a bisulphate fusion, leached and titrated with $KMnO_4$ similarly.

Total Iron is determined by any of the normal methods outlined previously or subsequently and ferric iron is thereby obtained by difference with little loss of accuracy.

7. Titration with ceric ammonium sulphate in HCl solution, after $SnCl_2$ reduction, using an internal indicator

As mentioned previously, the only advantage of this method over Method 6 is that no dark green chromic compounds are formed to mask the end point since cerous salts are colourless.

Ceric ammonium sulphate is more stable than the straight ceric sulphate and is used in an identical fashion to the $K_2Cr_2O_7$ solution in Method 6. A modification is to titrate with the ceric solution to the violet end point of the internal indicator, add a small known excess (2–5 ml.) and back titrate to the green change point with a standard ferrous ammonium sulphate solution.

Convenient solution strengths are : N/10 ceric ammonium

sulphate ($Ce(SO_4)_2$. $2(NH_4)_2SO_4$. $2H_2O$) = 64 g/litre of 5% H_2SO_4. N/10 ferrous ammonium sulphate ($FeSO_4$. $(NH_4)_2SO_4$. $6H_2O$) = 39·2 g/litre of 5% H_2SO_4.

1 ml. = 0·005585 g Fe.

8. Titration of ferric iron with titanous chloride solution

This method is not so popular as any of the foregoing but is nevertheless accurate under carefully controlled conditions. The main source of error is the instability of the titanous chloride solution which must be stored under hydrogen, nitrogen or CO_2.

This process depends upon the reaction $FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4$, which takes place in the cold.

The solutions required are:

(*a*) *Titanous Chloride.*—The concentrated solution may be prepared for use by mixing with an equal volume of conc. HCl and diluting to the required volume with boiled water. The solution is a powerful reducing agent and must be preserved and used in an atmosphere of H_2 or CO_2. The bottle in which it is stored should be connected with the burette and with a Kipp generating H_2 or CO_2.

(*b*) *Ferric Chloride* (for standardizing).—A convenient solution is made by dissolving 10·03 g iron wire (99·8% Fe) in HCl with addition of $KClO_3$, boiling off chlorous gases, and diluting to 1 litre.

1 ml. of this solution = 0·01 g Fe.

The $TiCl_3$ solution may be adjusted to correspond to this.

Determination of Iron.—The iron is obtained in the ferric state, in H_2SO_4 or in HCl solution, and the titanous chloride added slowly, with constant stirring, a current of CO_2 being passed through the liquid at the same time. When the yellow colour has nearly disappeared, a drop of KCNS solution is added and the titration continued until the red colour just disappears.

1 ml. N/10 $TiCl_3$ = 0·005585 g Fe.

Oxidation to the ferric state is best carried out with $KClO_3$ in HCl solution or $KMnO_4$ in H_2SO_4 solution.

The addition of potassium thiocyanate acts as an indicator showing the presence of ferric iron by a blood-red coloration $Fe(CNS)_3$. KCNS gives no coloration with ferrous iron.

(See also 'Iron in Aluminium Alloys'.)

9. Titration of ferric iron with mercurous nitrate solution

(*Jnl. Soc. Chem. Ind.*, May 1940; and Pigott, *Chemical Analysis of Ferrous Alloys*)

This lesser known method overcomes the disadvantages encountered in the previous method of titrating with an unstable

reducing agent. Here the iron is obtained in the form of a ferric salt, converted to ferric thiocyanate and titrated in the cold to the disappearance of the red colour, with mercurous nitrate solution which is quite stable.

It is preferable to work in diluted HNO_3 solution since HCl and H_2SO_4 tend to give slightly high results which difficulty is easily overcome by running alongside standards of known iron content.

In general, obtain an acid solution of the material, fume with H_2SO_4 (remove Pb and SiO_2 if present). Treat the diluted solution with 3% $KMnO_4$ until MnO_2 is just precipitated on boiling, clear with drops of sodium nitrite solution (10%), boil out NO_2, dilute to 200 ml. with cold water, add 20 ml. 10% NH_4CNS solution and titrate to a colourless end point with N/5 mercurous nitrate solution. N/5 approximately = 59·5 g $HgNO_3 . H_2O$/litre 5% HNO_3.

1 ml. = 0·011 g Fe (approximately).

Standardize under similar conditions against a standard of known iron content.

10. Colorimetric—thiocyanate method

This is one of the best methods for estimating very small quantities of iron.

The iron should be in the ferric state and in HCl solution. If ferrous iron or reducing agents are present a slight excess of $KMnO_4$ may be added and the liquid boiled, then slightly acidified with HCl.

Solutions Required

(*a*) *Potassium Thiocyanate.*—60 g per litre.

(*b*) *Ferric Chloride.*—10 mg. Fe (as wire, or an equivalent amount of ferrous ammonium sulphate) dissolved in HCl, diluted, $KMnO_4$ added till just coloured pink, and diluted to a litre.

The test may be made as follows :

In each of a number of Nessler tubes add 10 ml. of the thiocyanate solution, and an equal amount of dilute HCl (1 : 5). To one of these add the solution to be tested, mix and make up to 50 ml. To another add the ferric chloride solution until the colour matches that of the assay, finally making up to 50 ml., adding more ferric chloride if there is now a difference of intensity. The colour is best observed by looking down the tubes, which should be placed on a white background.

Conditions as to acidity, temperature and dilution should be the same in all tests.

1 ml. ferric chloride (as above) = 0·01 mg. Fe.

It is possible to estimate quantities from 0·001 mg. to about 1 mg. Fe by this means. With larger quantities the intensity of colour is too great for small differences to be perceptible.

Fluorides, phosphates and arsenates tend to affect the colour produced and should be absent, similarly elements giving coloured solutions.

This method has more recently been adapted to routine photometric analyses for such materials as Al alloys.

(For specific analyses see also 'Iron in Al and Mg Alloys' and 'Iron in Clays, etc.'.)

11. Colorimetric—thioglycollic acid method

This reagent (CH_2 . SH . (COOH)) when added to an ammoniacal ferrous solution gives a purple pink coloration in proportion to the amount of iron present. It is an extremely sensitive test detecting 1 part of iron in 5 million parts of solution.

The test is not appreciably affected by the presence of Pb, Ag, Hg, Cu, Cd, Cr, Al, Ca, Mg, Na or K salts or by sulphates, phosphates and nitrates, but zinc depresses the intensity of the colour produced and sulphides tend to bleach and both should be removed.

Thioglycollic acid reduces ferric iron to the ferrous state and therefore small quantities of iron present in both the ferrous and ferric states may be determined in the same solution as follows:

Ferric iron first determined in acid solution by Method 10, neutralize the solution with ammonia (this destroys the blood-red colour of ferric thiocyanate, then add 3 drops of thioglycollic acid followed by 3 ml. of conc. NH_4OH. This will give total iron, ferrous iron being obtained by difference.

Standards of known iron content made up from ferrous ammonium sulphate or iron wire should be used at the same time. (See also 'Iron in Pure Copper'.)

LEAD

(Pb) Atomic Weight = 207·2

Metallurgical Occurrence

Ores (often associated with Cu, Ag, Au, Sn, Zn etc.)
White metal bearings, solders and type metals
Leaded brasses, bronzes, drosses, residues
Leaded steels (approximately 0.25% Pb)
Accumulator plates, sheeting, roofing, guttering, acid resisting (Sb/Pb tank linings, pipe and ducting, cable sheathing
Al and Al alloys
Zinc base diecasting alloys
Alloys with Ca, Cu, Te etc.

Source of Metal as Standard

Assay pure lead foil = 99·99% Pb (approximately) (Johnson, Matthey & Co. Ltd., London) or 'pure' lead sulphate

Methods of Determination

GRAVIMETRIC

1. *Precipitation as sulphate, either dry and weigh as such or ignite and weigh as sulphate*
   (may be used for 0.25–5% Pb in non-ferrous alloys such as brass, bronze, gunmetal, also Al alloys, steels etc. Less accurate than [2]).
2. *Precipitation as sulphate, conversion to molybdate, ignite and weigh as such*
   (suitable for lead in steels, copper and copper alloys and most other cases where present up to about 5%).

VOLUMETRIC

3. *Precipitation of sulphate, solution in ammonium or sodium acetate and titration with ammonium molybdate*
   (external indicator: 0·5% tannic acid solution.) (Suitable for most materials of high Pb content—ores, Pb base alloys etc.).
4. *Precipitation of sulphate, solution in ammonium or sodium acetate, precipitation as chromate, conversion to chromic acid, allowing this to displace iodine from potassium iodide and titration of the iodine with sodium thiosulphate (using starch solution as internal indicator)*
   (suitable for lower grade ores [5–25% Pb] and lead in tin-base bearing alloys.) Alternatively titrate chromic acid by adding known excess of standard ferrous ammonium sulphate and back titrating with standard $K_2Cr_2O_7$.

COLORIMETRIC

5. *Based on the comparison of brown colours produced by lead sulphide in the assay and standard lead solutions*
   (only for traces [less than 0·1% Pb] but not as accurate as Method [8]).
6. *Based on the comparison of colours of the red complex formed by the addition of a chloroform solution of diphenyl-thiocarbazone in the presence of KCN*
   (useful for isolating traces [up to 0·1% Pb]. Colorimetric estimation may follow using this reagent or Method [5]).
7. *Precipitate electrolytically as PbO_2, solution of this in 2% solution of tetramethyldiaminodiphenylmethane in glacial acetic acid and comparison of the blue colour with standards similarly prepared*
   (useful for traces [up to 0·1% Pb] in light alloys).

ELECTROLYTIC

8. *Electrolytic precipitation as PbO_2 from nitric acid solutions*
   (for trace quantities in Cu, Zn, die-casting alloys, light alloys).

DRY ASSAYING

9. *Fusion of lead ores or residues with sodium carbonate, iron and carbon in the presence of suitable fluxes*

METHODS

1. Precipitation of lead sulphate, dry or ignite and weigh as such

The separation of lead in ordinary ores has been described in 'General Methods of Solution and Separation'. By the treatment there detailed, the lead is obtained as $PbSO_4$ mixed with silica, and perhaps some undecomposed silicates of Fe, Al, Mg, etc., or with $BaSO_4$.

The solution, diluted to 30–50 ml. is heated to boiling, then

allowed to stand till quite cold, and filtered, washing first by decantation through the filter, with cold 10% H_2SO_4 (i.e. H_2SO_4, 1 : 9); usually about 100 ml. of this is sufficient, but the filtrate should be tested with KCNS or $K_4Fe(CN)_6$, and washing continued until no reaction for Fe is obtained. In cases where the amount of lead is small, add, before settlement and filtration, about one-third the volume of alcohol, stir and settle, and give a final wash of alcohol after filtering. ($PbSO_4$ is less soluble in alcohol than in water.)

Wash the precipitate off the paper into the vessel originally used for the precipitation, using a fine jet of hot water and diluting as little as possible. Add about 3–5 g of sodium or ammonium acetate, and pass some hot conc. solution of the same through the filter, collecting with the bulk of precipitate. Digest this for some time nearly at boiling point, with frequent agitation, until everything, except the siliceous residue and possibly $BaSO_4$, appears to have dissolved. Filter again on the same paper, and wash thoroughly, first with hot conc. ammonium acetate and finally with hot water until the washings give no reaction when a drop is tested with potassium chromate. If some lead sulphate reprecipitates as the solution cools this is of no consequence.

To the filtrate add 5–10 ml. of conc. H_2SO_4, evaporate down cautiously, with frequent agitation to prevent bumping, till strong white fumes are evolved. Cool, add 30 ml. water and 10 ml. of absolute alcohol. Agitate, settle and allow to stand until the liquid is perfectly clear. Filter on a Gooch crucible (previously ignited and weighed). Wash first with H_2SO_4 (1 : 9), finally with absolute alcohol, dry, ignite at a very moderate red heat and weigh as $PbSO_4$.

Alternatively dry the lead sulphate precipitate at 110° C. for 30–50 minutes, cool and weigh.

($PbSO_4 \times 0{\cdot}6831 = Pb$.)

Modification in Presence of Barium or Calcium.—In the case of ores containing much barium, it is preferable to add 5–10 ml. of HCl to the $PbSO_4 + SiO_2$, etc., after filtering to remove Fe, and to boil down to a small bulk, before adding the ammonium acetate, otherwise proceed as above.

Alternatively with Ca present the lead may be removed as PbS by passing H_2S into the initial acid solution of the material as in next method. (See also under 'Lead in Steels'.)

2. Precipitation of lead molybdate, igniting and weighing as such

The lead is separated, and obtained in ammonium acetate as described above, or in absence of iron and other interfering metals,

the solution may simply be made slightly alkaline with ammonia and then acid with acetic acid. Add 3–5 g of ammonium chloride, heat to boiling, then add ammonium molybdate as long as a precipitate forms, boil for a short time and allow to settle. Filter, preferably on paper pulp, wash with hot dilute ammonium acetate. Ignite, gently at first, at the mouth of the muffle, finally at a temperature not exceeding 650° C., and weigh as $PbMoO_4$.

($PbMoO_4 \times 0{\cdot}5643 = Pb$.)

If only a single precipitation is made, this method usually gives somewhat high results owing to co-precipitation of MoO_3 (or an acid molybdate of lead). It is therefore advisable to redissolve the ignited precipitate in HCl with a little HNO_3, add NH_4OH till a faint turbidity is formed, then HCl till clear, and neutralize exactly to methyl orange by addition of ammonium acetate. Boil, settle, filter, wash and ignite as before. The final precipitate should be pure $PbMoO_4$.

The following modifications are necessary in the analysis of certain metals and alloys thus :

In steels, particularly with Cr content over 0·5% it is advisable to remove Pb, from the initial solution of the sample in HCl, by passing H_2S through the solution. The PbS being then dissolved in nitric acid, fumed with H_2SO_4 to convert to $PbSO_4$ and then proceed as above.

Alternatively, having removed lead as PbS (usually contaminated with a little iron sulphide) and redissolved in nitric acid, add 2–3 g tartaric acid (to hold up iron) followed by ammonia to neutralization then precipitate Pb molybdate as above.

$$PbSO_4 + 2NH_4(CH_3COO) = Pb(CH_3COO)_2 + (NH_4)_2SO_4$$
$$7Pb(CH_3COO)_2 + (NH_4)_6Mo_7O_{24} \cdot 4H_2O =$$
$$7PbMoO_4 + 6NH_4(CH_3COO) + 8CH_3COOH.$$

In both Methods 1 and 2 final ignition of the $PbSO_4$ or $PbMoO_4$ precipitates if contained on filter paper or filter pulp should be conducted with care since excessive temperatures before all carbon has been oxidized may lead to fusion and reduction of the compound to metallic Pb which in turn may oxidize to PbO and this will flux the porcelain or silica crucible resulting in a ioss. Any re-treatment of such silicates with $HNO_3 + H_2SO_4$ does not often successfully recover the desired metal. (See also under sections : 'Lead in Steels', 'Lead in Copper and Copper Alloys'.)

3. Titration with ammonium molybdate of an acetic acid solution of lead

This method is based on the quantitative precipitation of lead

molybdate by titration under similar conditions to that outlined above for the gravimetric estimation of the same compound. The end of the titration is shown by the presence of a yellow or brownish flocculation in a spot of clear tannic acid solution used as an external indicator; brought about by the slightest excess of a soluble molybdate.

Certain metals interfere with the titration, particularly calcium which forms an insoluble molybdate during titration, therefore giving a high result, and iron which may contaminate the original lead sulphate precipitate—this element and copper may also give a coloration with tannin causing erroneous results.

To overcome these effects the lead is precipitated as PbS from original solution of the ore, this sulphide is then converted to sulphate in a similar manner to that described for Cr steels in Method 2.

Tungsten may also interfere by precipitating tungstic acid during 'fuming' with H_2SO_4. This tungstic acid is soluble in ammonium acetate to give ammonium tungstate which colours the indicator. Best to remove W as tungstic acid by treating the ore with HCl and/or HNO_3 and evaporating to low bulk without H_2SO_4. The tungstic acid may then be filtered off after diluting and boiling. The filtrate is evaporated and 'fumed' with H_2SO_4 as usual to form $PbSO_4$.

The reaction between lead acetate solution and ammonium molybdate solution is rather sluggish at room temperature and therefore the titration is best carried out with frequent shaking at a constant high temperature (for standards and assays) which is conveniently just short of the boiling point of the solution.

Pyritic lead ores with calcium negligible or absent are best attacked with 80–90% HNO_3 with a little $KClO_3$ or HCl if necessary. If calcium has to be removed it is essential that only HCl be present prior to passing H_2S.

The lead is obtained in solution as sulphate dissolved in ammonium acetate, as described in previous method. (Sodium acetate may, if desired, be used in place of ammonium acetate.) Heat to boiling and titrate while hot with a standard solution of ammonium molybdate, stirring constantly, and testing a drop of the liquid from time to time with a solution of tannin on a white porcelain plate. When the soluble molybdate is in excess an immediate brown colour is produced.

It is best to reserve a portion of the assay solution and, after the end-point has been passed, add a part of the reserved solution, titrating with continually smaller quantities of standard solution and adding the reserve until all has been used.

A blank test should be made with the same reagents and volume of solution, heated to boiling, but without addition of lead compound, and the amount of standard molybdate required to give a colour deducted from that found in the assay.

Solutions Required

Ammonium Molybdate.—4·26 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ per litre, 1 ml. = 0·005 g Pb.

Tannin ($C_{14}H_{10}O_9$).—0·5 g in 100 ml. of water.

The reaction is as follows :

$$(NH_4)_6\ Mo_7O_{24} + 7Pb(C_2H_3O_2)_2 + 4H_2O = 7PbMoO_4 + 6NH_4(C_2H_3O_2) + 8CH_3COOH.$$

Standardization of the Ammonium Molybdate.—Dissolve 0·2 g pure lead foil in 10 ml. HNO_3 (1 : 4), boil to expel nitrous fumes, cool, add 5 ml. conc. H_2SO_4, boil to strong white fumes, cool, filter, wash with 100 ml. H_2SO_4 (1 : 9), then with minimum 5% alcohol/water mixture until free from acid. Dissolve in ammonium acetate as described under gravimetric method, add acetic acid and titrate with standard ammonium molybdate.

As an alternative to using pure lead foil for standardization, 0·3 g 'pure' lead sulphate may be used and immediately dissolved in about 100 ml. 25% ammonium acetate solution made acid with 2–3 ml. acetic acid, warmed and titrated as before. This reduces the time of the operation by eliminating the solution and fuming stages necessary with lead foil.

Procedure in Presence of Large Amount of Calcium.—Dissolve the ore in HCl, with as little HNO_3 as possible, evaporate to a small bulk, dilute, heat and pass H_2S. Filter off the PbS, etc., wash. Dissolve in HNO_3.

In absence of interfering elements, add excess of ammonia to the HNO_3 solution, then excess of acetic acid, heat to boiling and titrate direct with ammonium molybdate.

Where the sulphide precipitate contains Cu, Bi, or other elements which might interfere with the molybdate titration, add 5 ml. conc. H_2SO_4, boil to strong white fumes, cool, dilute, filter, wash with H_2SO_4 (1 : 9) and proceed as before to dissolve the $PbSO_4$ in ammonium acetate, and titrate with molybdate.

4. Precipitation as lead chromate from acetic acid solution, conversion to chromic acid and titrating the iodine liberated from potassium iodide with sodium thiosulphate solution

Suitable weights of the ore or other material should be taken to contain approximately 0·05–0·1 g Pb (say 0·5 g ore). Dissolve in

25 ml. conc. HCl, adding 5 ml. conc. HNO_3 if necessary to obtain solution. Cool, add 5 ml. conc. H_2SO_4 and fume strongly. Cool, dilute with 75 ml. water and boil, cool, add 10 ml. ethyl alcohol (to render $PbSO_4$ insoluble in the dilute H_2SO_4 solution) and stand several hours. Filter off $PbSO_4$, wash with 5–10% alcohol/water solution until free from acid. Dissolve in 100 ml. 25% ammonium acetate solution (containing 10 ml. glacial acetic acid) by pouring this solution hot, through the filter.

[*Note:* If calcium is present the precautions should be taken as outlined previously. Bismuth also interferes by forming an insoluble chromate. This is prevented by the addition of about 2 g of citric acid to the acetate solution just prior to addition of potassium chromate. Under these conditions bismuth chromate is rendered soluble].

To the lead acetate solution heated to boiling, add 10 ml. of a saturated solution of potassium chromate or dichromate. Boil gently for about seven minutes. The $PbCrO_4$ settles as a dense orange-coloured precipitate, which can be readily filtered and washed. Filter; wash with hot water till free from soluble chromates, as shown by filtrate coming through colourless. Redissolve precipitate in a mixture of saturated NaCl and HCl or (perhaps better) in HCl (1 : 1), which should be quite cold. Wash with cold water. (It is unnecessary to dissolve all of the $PbCl_2$ formed, provided all yellow stain is removed from the paper.) Add 1–3 g KI and titrate the liberated iodine with standard thiosulphate, adding starch near the finish. The end-point is shown by the change from blue to pale green, and is quite sharp. The thiosulphate should be added rather slowly towards the finish.

1 ml. N/10 thiosulphate = 0·0069 g Pb.

(See remarks on standardization below.)

Reactions:

(i) $Pb(C_2H_3O_2)_2 + K_2CrO_4 = PbCrO_4 + 2KC_2H_3O_2$

(ii) $PbCrO_4 + 2HCl = PbCl_2 + H_2CrO_4$

(iii) $H_2CrO_4 + 3KI + 6HCl = CrCl_3 + 3KCl + 4H_2O + 3I$

(iv) $2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$

Hence $Pb = 3I = 3Na_2S_2O_3 . 5H_2O$.

The precipitation of lead by the chromate solution does not proceed exactly according to equation (i), as the precipitate formed contains a slight excess of chromic acid, and the factor of the thiosulphate solution is therefore generally less than that given. Hence it is always necessary to standardize the thiosulphate on metallic lead which has been treated by a similar process to that used in the assay.

Standardization.—Dissolve 0·2 g pure lead foil as in standardizing for molybdate titration. When a solution of $PbSO_4$ in ammonium acetate is obtained, acidify with acetic acid, add a slight excess of K_2CrO_4, or $K_2Cr_2O_7$ and proceed exactly as in the assay, adding the same amounts of HCl and KI, and titrating in the same manner with the thiosulphate solution.

Theoretically, 3·5934 g $Na_2S_2O_3$. 5HO should be equivalent to 1 g Pb, hence if a solution be prepared containing 35·934 g of thiosulphate per litre, 1 ml. = 0·010 g Pb, or of 17·967 g per litre 1 ml. = 0·005 g Pb.

The constant constitution of the lead chromate produced is of vital importance and the conditions set out above have been found to give consistent results.

Note: An alternative finish to the chromate estimation of lead is as follows :

Dissolve the precipitate of lead chromate in 25 ml. of the following acid mixture (100 ml. phosphoric acid + 180 ml. conc. H_2SO_4 diluted to 1 litre), add 5 g NH_4Cl and dilute to about 125 ml. To the chromic acid produced, add a measured excess of N/20 ferrous ammonium sulphate and back titrate with N/20 potassium dichromate using diphenylamine or barium diphenylamine sulphonate as internal indicator (see also under 'Iron'). 1 ml. N/20 ferrous ammonium sulphate solution = 0·00345 g Pb.

For the application of this method to the estimation of lead in tin base white metals, the initial solution of the alloy is best carried out with 50 ml. of a mixture of bromine and hydrobromic acid (1 : 9) which volatilizes Sn, Sb and Bi as bromides, the residue is then dissolved in 20 ml. 50% HNO_3 and boiled to expel bromine. After neutralizing with ammonia then acidifying with 5 ml. acetic acid the solution is diluted to 125 ml., heated to boiling and 10 ml. saturated solution of potassium chromate added just as described above. (See section on 'White Metal Analysis', also Technical Bulletin A.55—International Tin Research and Development Council.)

5. Colorimetric—sulphide method (British Aluminium Company's Publication No. 399 and other authorities)

The Al alloy (5 g) or other material is taken into solution by any of the normal methods (100 ml. 20% NaOH solution for Al and its alloys) and the lead is obtained as sulphate by fuming with H_2SO_4 (with Al alloys, add to the caustic solution 20 ml. 15% Na_2S solution, dilute to 500 ml., boil, allow precipitate to settle, filter, wash with hot water, dissolve in 50% HNO_3, add 3 ml. conc. H_2SO_4 and fume). The $PbSO_4$ precipitate is extracted with

20 ml. 10% ammonium acetate solution slightly acidified with acetic acid and diluted to 100 ml. Pipette an aliquot portion into a 100 ml. Nessler glass, add 3 drops 50% HNO_3, 1 ml. 50% sucrose solution and 50 ml. water. Add 5 ml. of fresh saturated H_2S water, mix well and compare the brown colour with that produced in a series of standards under similar conditions.

Standard solution suitable is made from 'Analar' grade lead nitrate or acetate dissolved in water, so that :

1 ml. lead salt solution = 0·0001 g Pb.

6. Colorimetric method using diphenylthiocarbazone (Biefield and Patrick, *Ind. Eng. Chem.* (Anal. Edn.), 1942. **14.** 275 ; *B.D.H. Book of Organic Reagents*, 1948)

Most of the heavy metals in slightly alkaline aqueous solution, form co-ordination compounds with a chloroform solution of the above reagent but if KCN is present, only Pb, Tl and Bi give a compound, which is red in the case of Pb (assuming Tl and Bi absent).

7. Electrolytic—colorimetric method using tetramethyldiaminodiphenylmethane

The principle of this method is to dissolve the light alloy or other material in HCl adding HNO_3 if necessary, then precipitating Pb, Cu and Zn as sulphides from the solution which now contains ammonium tartrate and formate as a buffer. The sulphides are ignited to oxides, dissolved in HNO_3 and the diluted solution is electrolysed to deposit the lead as PbO_2 on the Pt anode. This deposit (still on the anode) is dissolved in 5 ml. of the above organic reagent. The blue colour produced is matched in Nessler glasses with standards produced in a similar manner by electrolysing a standard solution of lead in nitric acid and proceeding as above. (For full details see 'Pb in Al Alloys'.)

8. Electrolytic precipitation as PbO_2 and weighing as such

Lead may be precipitated electrolytically from a solution made rather strongly acid with nitric acid, the metal being deposited as peroxide on the anode. The most satisfactory method is to use gauze electrodes revolving at about 300 r.p.m. Copper, if present, is simultaneously precipitated on the cathode. If sufficient nitric acid be added, there is no precipitation of manganese peroxide on the anode. For small quantities of lead the solution may be neutralized with ammonia and 5% HNO_3 added in excess. To precipitate 0·1 g Pb a concentration of 10% HNO_3 is required, this being increased with increasing quantities of lead up to 50% or more for 0·5 g Pb.

The suitable conditions (for revolving electrodes) are C.D. 1·0 to 2 amps., E.M.F. 3–4 volts. Quantities up to 0·4 g may be deposited in one hour, but it is preferable to work for a longer time with lower amperage. The completeness of deposition is tested by removing a drop of the liquid and adding Na_2S, or (when copper is present) NH_4OH or $K_4Fe(CN)_6$.

The deposit of lead peroxide (PbO_2) is washed with cold water, then with absolute alcohol, dried for ten minutes at 200° C. and weighed. As it is always impure, an empirical factor is used, varying under different conditions, usually about 0·853. Better results are said to be obtained by igniting and weighing as PbO.

Theoretically, $PbO_2 \times 0{\cdot}8662 = Pb$

$PbO \times 0{\cdot}9283 = Pb.$

9. Dry assay of lead ores and residues

This method serves as a useful guide to the results which may be expected from smelting. It may also be employed for concentrating the metal in lead ashes and residues, and for obtaining approximate results in the case of lead slags and lead glass.

Methods depend on: Reduction of lead from ore by the action of Na_2CO_3, Fe and C (from the argol), fluxing of siliceous and oxidized gangue by Na_2CO_3 and $Na_2B_4O_7$ respectively, and weighing the resultant lead button as such.

The ore, which should be ground to pass a 60 mesh, is mixed with the following charge:

	Sulphide Ore (Galena)	*Oxidized Ore (Lead Sulphate)*
Ore	30 g	25 g
Sodium carbonate	25 g	20 g
Argol	3 g	3 g
Borax	5 g	15 g
Iron	*ad lib*	—

	Lead Silicate or Lead Glass	*Lead Fume*
Ore	10 g	20 g
Argol	5 g	7 g
Sodium carbonate	30 g	25 g
Fluorspar	—	5 g

Use the borax as a cover, insert a piece of hoop iron into the charge and place the crucible in a moderately hot fire. Raise the temperature gradually until a dull red heat is obtained. When the charge has become 'tranquil', stir with the hoop iron and remove

the same, shaking back into the crucible any particles of metal or slag. Raise the temperature and when the charge is perfectly fluid, pour into mould, cool, break off slag, hammer the button to an octagonal shape, brush and weigh.

If arsenic is present a 'speiss' will be formed. This may be reduced or prevented by working at a low temperature and reducing the amount of argol.

Note: The success of the assay depends to a large extent on furnace temperature control. If an iron crucible is used a slightly higher result is obtained.

Should there be a large quantity of zinc or copper in the ore or residue the following 'combined wet and dry' method is advisable :

Take 10 g of the finely-powdered material, dissolve in *aqua regia*, cool, add H_2SO_4, evaporate to small bulk, cool, dilute, filter and wash. The residue consists of $PbSO_4$ and insoluble matter ; this is dried, and run down with the charge for an 'oxidized' ore.

MAGNESIUM

(Mg) Atomic Weight 24·32

Metallurgical Occurrence

Ores and minerals (magnesite, dolomite etc., spinels, talc.)
In the gangue associated with other metal minerals
Slags
Clays
Light alloys
Zinc base diecasting alloys
White metals
Sea-water (as $MgCl_2$)

Source of Metal as Standard

Redistilled magnesium = 99·99% but standards are rarely used since gravimetric determinations are invariably performed

Methods of Determination

GRAVIMETRIC

1. *Precipitation of magnesium ammonium phosphate and ignition to magnesium pyrophosphate, weigh as such*
   (suitable for all materials containing magnesium in excess of approximately 0·25%).
2. *Precipitation of magnesium quinolate by 8-hydroxyquinoline from alkaline tartrate solution containing potassium cyanide. Dry and weigh as oxinate or finish volumetrically using bromate-bromide solution and sodium thiosulphate*
   (suitable for materials such as limestone, dolomite, magnesite, and cement, Al alloys etc., in which interfering elements [see text below] are in small proportion or absent).

COLORIMETRIC

3. *Photometric estimation using titan yellow*
   (for routine estimation in light alloys).

METHODS

1. Precipitation as magnesium ammonium phosphate and ignition to the pyrophosphate

Undoubtedly the most accurate method for estimating magnesium. Most of the common elements do not interfere with the precipitation provided the usual group separations with H_2S; $NH_4Cl + NH_4OH$; and $(NH_4)_2S$ have been carried out carefully.

Phosphorus, arsenic, calcium and barium are said to interfere (after Low), and the alkali earth metals when being precipitated as carbonate or oxalate appear to carry some Mg with it. Calcium would cause co-precipitation of calcium phosphate (see 'Treatment in Presence of Calcium'). Majority of Ba can be removed as $BaSO_4$ at a very early stage of the metal separations.

Precipitation is effected equally well with either dibasic sodium or ammonium phosphate from alkaline solution, using about 0·5 g of the phosphate salt per 0·010 g Mg present.

The ore is treated by the methods described under 'Separation and Solution', for removal of silica and all metals precipitated by H_2S and by $NH_4OH + NH_4Cl$. The alkaline earth metals (Ba, Ca, Sr) are removed by precipitation as carbonate or oxalate and the filtrate from these evaporated to dryness and ignited to expel ammonium salts and organic matter.

The residue left after ignition is taken up with dilute HCl, nearly neutralized with NaOH, and sodium phosphate (Na_2HPO_4) or micro-cosmic salt ($NaNH_4HPO_4$) added gradually with constant agitation, till this produces no further precipitate. The solution is then mixed with one-third of its volume of 10% NH_4OH (1 : 9), when the magnesium will be precipitated as $MgNH_4PO_4$. If the solution be vigorously shaken for 5 minutes and allowed to settle for half an hour it may then be filtered. (If not agitated in this way it is better to allow the mixture to stand [covered] overnight.)

It is advisable to transfer the whole of the precipitate to the filter by means of portions of the filtrate, without addition of water, allow to drain and then wash with the smallest amount of dilute ammonia (2·5% by volume, i.e. NH_4OH [1 : 39]) necessary to remove the sodium salts. Washing is continued until a drop of the filtrate shows no turbidity with $AgNO_3 + HNO_3$. Usually about 100 ml. of wash liquor is sufficient.

The precipitate is then dried, on the paper, wrapped up in the same, and ignited slowly at first (at the mouth of the muffle or over a Bunsen flame) till carbon is completely burnt off, finally at bright redness for 10–20 minutes and weighed as $Mg_2P_2O_7$.

A platinum or porcelain crucible may be used.

If the residue after ignition appears grey it may generally be converted into a pure white pyrophosphate by moistening with conc. HNO_3, evaporating cautiously to dryness and re-igniting—

$$2MgNH_4PO_4 \cdot 6H_2O = Mg_2P_2O_7 + 2NH_3 + 13H_2O$$

$$Mg_2P_2O_7 \times 0{\cdot}2184 = Mg$$
$$Mg_2P_2O_7 \times 0{\cdot}3621 = MgO$$

(For details of methods for individual materials, see also under Mg in Light Alloys, in Slags, Clays, Iron Ores, White Metals and Zinc Base Diecasting Alloys.)

Treatment in the Presence of Calcium (greater than 0·1%).—The precipitate of calcium oxalate invariably carries down some magnesium. The quantity so precipitated is reduced by diluting the solution considerably (say to 300 ml.) and adding 3–4 g of ammonium chloride. Oxalic acid is then added, and the solution gradually neutralized by addition of dilute ammonia to the hot liquid. After settling for an hour it may be filtered and treated as above. When much magnesium is present it is best to add at first only sufficient oxalic acid to precipitate the calcium, neutralize with NH_4OH and allow to settle 10 minutes; a further quantity of oxalic acid, equivalent to the magnesium, is then added, made alkaline with NH_4OH, stirred and allowed to settle for an hour. With very large quantities of magnesium a double precipitation is necessary.

The filtrate should be evaporated and ignited as described above.

2. Precipitation as Mg quinolate and weighing as such or finishing volumetrically (Low, Weinig and Schoder, *Technical Methods of Ore Analysis*, 1947; British Aluminium Company's Publication No. 399, 1941)

8-hydroxyquinoline unfortunately forms precipitates with most of the common metals: (1) Sb, Bi, Cd, Cu, Pb, Hg, Ag, Sn; (2) Al, Be, Fe, Ti, Zr, Th; (3) Co, Ni, Mn, Zn, V, U; (4) alkali earth metals.

Group (1) above is best removed by H_2S from acid solution; Group (2) by the normal ammonia—NH_4Cl group precipitation; Group (3) by ammonium sulphide and Group (4) by precipitation as oxalates.

For Al Alloys.—Attack 0·25–2 g with 20–40 ml. of 20% NaOH solution. When no further action occurs, dilute to 200 ml. and

warm. Filter off residue, wash with hot water and dissolve this in hot *aqua regia* (3 HCl : 1 HNO_3 : $4H_2O$), add 10 ml. 10% H_2SO_4, evaporate and fume for 5 minutes, cool, dilute to 100 ml. with water and filter off SiO_2 washing with hot water. Evaporate to about 50 ml., cool, add 25 ml. 20% neutral sodium tartrate solution, dilute to 100 ml., add 60 ml. 2N. NaOH solution followed by 10 ml. 30% KCN solution. Add with constant stirring 15 ml. (for 0·5% Mg) or 30 ml. (for more than 1% Mg) of a 2% alcoholic solution of 8-hydroxyquinoline solution. Stand half an hour, filter off the precipitate, washing with cold 1% sodium tartrate solution containing 0·1% NaOH. Dissolve and reprecipitate the quinolate by treatment with 25 ml. hot 20% HCl and follow with 15 ml. of the tartrate solution, 5 ml. of the 8-hydroxyquinoline solution, 60 ml. of 2N . NaOH solution and 10 ml. of the KCN solution. Finally redissolve precipitate with HCl as before, add 2 ml. of the organic reagent, dilute to 200 ml., bring to the boil and reprecipitate the quinolate with 30 ml. of concentrated NH_4OH. Stand half an hour. Filter on a tared sintered glass crucible, wash with hot water, and dry at 105° C. for 2 hours to constant weight. Weigh as $Mg(C_9H_6ON)_2 . 2H_2O$ containing 6·98% Mg. Alternatively, drying at 160° C. gives the anhydrous complex which contains 7·68% Mg.

Note: Under these conditions of precipitation, no heavy metals or Ca are co-precipitated, Al and Zn have already been removed by the caustic attack initially.

For Mg Ores and Cement, etc.—0·5 g samples are dissolved in 20 ml. 50% HCl with gentle heating. Dilute to 150 ml. with hot water, add 3 drops methyl red (0·02% alcoholic solution) and follow with NH_4OH solution until distinctly alkaline (yellow). Add filter pulp and heat to boiling. Boil 2 minutes, allow precipitate of Al and Fe hydroxides, etc., to settle and filter rapidly washing with hot 2% NH_4Cl solution. Make the filtrate just ammoniacal and heat to boiling, whilst boiling add 25 ml. of 5% ammonium oxalate solution and boil 2 minutes. Stand at 90° C. for 15 minutes and filter off alkali earth oxalates washing with 1% NH_4OH solution. Cool the filtrate to 70° C. and add a slight excess of 2% 8-hydroxyquinoline reagent in 3% acetic acid solution (about 25–40 ml. should be sufficient) to precipitate all the Mg and follow with 5 ml. conc. NH_4OH per 100 ml. of solution. Stir and allow to stand 15 minutes. Filter and wash with 2% NH_4OH solution. Dry and weigh as above.

The Volumetric Finish is Conducted as Follows.—Dissolve the washed quinolate precipitate in 25 ml. hot 50% HCl and wash through with 30 ml. water. Cool to room temperature, add a

measured excess of N/10 potassium bromate-bromide solution (2·784 g $KBrO_3$ + 12 g KBr/litre) followed by 10 ml. 20% KI solution. Mix well and titrate the liberated iodine with N/10 sodium thiosulphate solution (24·8195 g $Na_2S_2O_3 . 5H_2O$/litre) using starch solution as indicator. The end point is the disappearance of the blue starch-iodide colour. The difference between the thiosulphate equivalent for the total KBr–$KBrO_3$ added and the final thiosulphate used for titration, gives the Mg equivalent. Under these conditions, 1 ml. N/10 sodium thiosulphate equals 0·0003 g Mg.

The effect of adding the bromate-bromide solution to the Mg quinolate precipitate is first to convert it to 5 : 7 dibromo-8-hydroxyquinoline. The excess bromate-bromide then reacts with the KI present to liberate iodine.

The equations of the reactions are as follows (after Low):

$$KBrO_3 + 5KBr + 6HCl = 6KCl + 3H_2O + 3Br_2 \quad (1)$$
$$2Br_2 + C_9H_7OH = C_9H_5OH . Br_2 + 2HBr \quad (2)$$

excess bromate-bromide gives Br_2 as in equation (1) which reacts with potassium iodide thus:

$$2KI + Br_2 = 2KBr + I_2$$
$$\text{then } 2Na_2S_2O_3 + I_2 = 2NaI + 2Na_2S_4O_6.$$

3. Photometric estimation using titan yellow

See references under 'Mg in Al Alloys—(Note 3)' or Stross, *Analyst*, 1942. **67**. 317.

MANGANESE

(Mn) Atomic Weight = 54·93

Metallurgical Occurrence

Manganese ores (pyrolusite)
Manganiferous iron ores
Clays and slags
Al and Mg alloys
Steels, cast irons and ferro-alloys
Stellite
Cu base alloys (high tensile brasses, aluminium bronzes, etc.)

Source of Metal as Standard

Elctrolytic manganese = 99·9% Mn (Johnson, Matthey, Ltd., London) (Murex Ltd., Rainham, Essex) but more usual to use 'Analar' potassium permanganate solutions.

Methods of Determination

GRAVIMETRIC

1. *Precipitation of hydrated manganese dioxide by bromine and ammonia, followed by ignition to* Mn_3O_4.
   (applicable to all materials, particularly in the presence of Fe, Al, Zr, Ti which are removed by basic acetate separation—see under 'Methods of Solution and Separation' and 'Manganese in Steels').

VOLUMETRIC

2. *Direct oxidation to permanganate, by means of sodium bismuthate, followed by titration with standard ferrous ammonium sulphate solution*
   (suitable for Al and Mg alloys [Cr absent] ; cast irons, steels (Cr, Co and U absent) ; ferro-alloys [ferromanganese, spiegel, silico-spiegel] ; ores

2a. *Modification of* (2)*—zinc oxide separation (of Cr), with* H_2O_2 *treatment for V and oxidation with sodium bismuthate as before*
   (for high Cr alloys, Co absent ; Co when present calls for a modified procedure).

2b. *Volhard method—ZnO separation and titration with potassium permanganate*
   (for high grade Mn ores)

3. *Chlorate method—precipitation of* MnO_2 *by* $KClO_3$ *in nitric acid. Solution of* MnO_2 *in standard oxalic acid or ferrous ammonium sulphate and titration with standard* $KMnO_4$
   (applicable to all steels and most materials).

4. *Persulphate method—oxidation of Mn to permanganate followed by titration with standard sodium arsenite solution*
   (suitable for steels and cast irons with Cr less than 0·5% ; also blast furnace slag, ironstone etc.).

COLORIMETRIC

5. *The permanganate colour produced from the Mn salt by action of sodium bismuthate or ammonium persulphate, or potassium periodate is compared with the colour of standard* $KMnO_4$
   (for less than 0·5% Mn in light alloys, steels, ores etc.).

6. *Available Manganese* (MnO_2 content of manganese ores). *Oxalic acid method—solution of pyrolusite in known excess of standard oxalic acid solution in the presence of sulphuric acid. Titration of excess oxalic acid with standard potassium permanganate solution.*

METHODS

1. Precipitation as hydrated MnO_2 and ignition to Mn_3O_4

Although this procedure was at one time standard for Mn in steels, it has largely been superseded by one of the many volumetric estimations which are in general more rapid and have a high degree of accuracy.

1–5 g of material (3–5 g of steel drillings) are dissolved in about 20–50 ml. conc. HCl with an eventual addition of 5 ml. conc. HNO_3 to oxidize iron. The basic acetate separation for Fe, Al, Ti, Zr and Cr (up to 5%) is performed (see references above) giving a filtrate containing Mn, Zn, Ni, Co, Mg. Dilute to 1 litre and filter off a fraction, add 10 ml. bromine water and 30 ml. conc. NH_4OH. Heat to boiling until all Mn is precipitated as hydrated dioxide. Filter, wash with hot water, dry and ignite at about 800° C. to Mn_3O_4.

The final precipitate is often contaminated by traces of Fe_2O_3, this can be estimated by dissolving the weighed precipitate in 10 ml. conc. HCl and carrying out a colorimetric determination of the iron by the thioglycollic acid method. (See under 'Iron', Method 11.)

This method of determining Mn should in theory separate Cr completely from the Mn, but in practice this appears so only with low Cr contents (up to about 4%)—(Gregory and Stevenson). With high Cr values, the ZnO separation is more reliable.

The equation for the reaction is :

$$MnCl_2 + 4NH_4OH + 2Br = MnO_2 . H_2O + 2NH_4Cl + 2NH_4Br + H_2O.$$

2. Direct oxidation to permanganate by sodium bismuthate, followed by titration with standard ferrous ammonium sulphate and potassium permanganate solutions

This method depends on the fact that manganous salts are oxidized to permanganate by sodium bismuthate, in presence of free nitric acid :

$$2Mn(NO_3)_2 + 5NaBiO_3 + 14HNO_3 = 2NaMnO_4 + 5Bi(NO_3)_3 + 3NaNO_3 + 7H_2O.$$

The solution must be free from every trace of chlorides, and nitrous acid must also be absent. As applied to steel and similar alloys the process is as follows :

Dissolve 1 g of the drillings in 50 ml. HNO_3 (1 : 3), cool and add 0·5 g sodium bismuthate. Heat till the pink colour disappears. If a precipitate of manganese hydroxide appears, add a reducing agent (such as SO_2, $FeAmmSO_4$, or $Na_2S_2O_3$) until this dissolves. Boil off nitrous fumes. Cool to about 15° C., add 2–3 g of sodium bismuthate and agitate, without further warming, for a few minutes. Add 50 ml. of HNO_3 (3% by volume), filter through ignited asbestos, with slight vacuum, and wash with 50–100 ml. of the same acid, which must be cold. Add a measured quantity (in excess) of standard ferrous ammonium sulphate and titrate to faint pink with standard $KMnO_4$.

The reactions for this titration have already been given (see under 'Iron'). As this method is generally used for small quantities of manganese, it is convenient to use weak standard solutions.

Permanganate.—1 g $KMnO_4$ per litre ; 1 ml. = 0·000348 g Mn.

Ferrous-Ammonium Sulphate.—12·4 g $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$ and 50 ml. conc. H_2SO_4 made up to 1 litre. 1 ml. =

0·000347 g Mn. These solutions should nearly correspond. The reaction is as follows:

$$2HMnO_4 + 10FeSO_4 + 7H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O$$

from which $Fe \times 0{\cdot}1967 = Mn$.

Standardization.—These solutions should be standardized as nearly as possible under the conditions of the assay. A mixture is made containing the same amounts of HNO_3 and sodium bismuthate, diluted to the same degree, and filtered through asbestos. To this a measured volume of the ferrous ammonium sulphate is added, and titrated with the standard permanganate. Or add a known volume of ferrous ammonium sulphate solution to a finished assay solution and titrate with standard $KMnO_4$.

As a check the permanganate may be standardized on metallic iron in the ordinary way and the factor given above applied.

Special Precautions.—In cases where small quantities of chlorides are present, these may be removed by adding a few drops of silver nitrate solution, the excess of which does not interfere with the titration.

The filtrate must be perfectly clear as any bismuthate present will oxidize some of the ferrous salt and vitiate the result.

The titration with permanganate must be made in the cold and immediately after adding the ferrous salt, as the latter rapidly reduces HNO_3 with production of HNO_2.

In the presence of vanadium, there may occur a slowly fading end point just prior to the true end point; this is due to the slow oxidation of vanadyl sulphate to metavanadic acid thus:

$$10VOSO_4 + 12H_2O + 2KMnO_4 = 10HVO_3 + K_2SO_4 + 2MnSO_4 + 7H_2SO_4.$$

The reaction does not appreciably affect the accuracy of the titration if this be conducted as rapidly as possible to a pink end point persisting for at least half a minute.

Chromium interferes in a similar manner but to a greater extent than vanadium, since sodium bismuthate oxidizes it to sodium chromate, then becomes reduced to the chromous state by the ferrous solution and is re-oxidized to chromate by the titrating potassium permanganate. However if the Cr content does not exceed 0·5% its effect is very slight provided the filtration and subsequent titration is carried out rapidly. For Cr contents in excess of 0·5%, use Method 2a, whereby Cr is removed in the ZnO separation.

Cobaltous salts are oxidized by sodium bismuthate in nitric acid solution and the resulting cobaltic solution is in turn reduced

and re-oxidized by the ferrous and permanganate titrating solutions respectively.

This interfering element would give a high result by this method, so when present it is preferable to use Method 2a—modifications in the presence of Co ; or Method 3.

Notes:

(1) Oxidation of Mn by sodium bismuthate is effective quantitatively only when the nitric acid concentration is between 10 and 25% by volume, the solutions are quite cold, and 25–30 times as much bismuthate is added as Mn present.

(2) For materials rich in Mn it is advisable to fractionate the solution prior to titration (say at the permanganate stage) or even prior to oxidation with bismuthate. Alternatively a small initial sample may be taken (about 0·1 g).

(3) If N/10 ferrous ammonium sulphate and potassium permanganate solutions are used for titration, then 1 ml. = 0·0011 g Mn. (See also under 'Mn in Al Alloys' and 'Mn in Steels'.)

2a. Zinc oxide separation followed by sodium bismuthate treatment as before (Pigott, *The Chemical Analysis of Ferrous Alloys*)

By this method, Fe, Cr, Al, Ti, Zr, Cu, V, Mo, U and Be are precipitated as hydroxides by the zinc oxide, while Ni, Co, Mn, Mg stay in solution as sulphates.

It is essential to have ammonium chloride or sulphate present to ensure that Ni and Co are not precipitated, if these elements are required in the filtrate.

The presence of vanadium may cause loss of Mn in the precipitate as basic Mn vanadate unless the V is first treated with hydrogen peroxide to produce pervanadic acid prior to the zinc oxide treatment.

Nitric acid is added to the manganous sulphate filtrate to ensure complete oxidation to permanganate by sodium bismuthate.

In the presence of cobalt (which will appear in the filtrate, with the Mn, from the zinc oxide separation and produce a pink coloration) a slight modification is necessary, since otherwise the cobaltous salt would be oxidized to the cobaltic state by the sodium bismuthate then be reduced by the excess ferrous solution which is added to the permanganate and finally be re-oxidized by the titrating potassium permanganate solution, thus giving an erroneous result.

The modified procedure is to precipitate the Mn from the zinc oxide filtrate by bromine and ammonia as in Method 2, the

hydrated manganese dioxide produced is then ignited to Mn_3O_4 and either dissolved in a mixture of nitric and sulphurous acids or nitric acid (30 ml.) with the addition of 2 g sodium nitrite. A third alternative is to dissolve the ignited residue in 20 ml. conc. HCl and fume with 5 ml. conc. H_2SO_4. Add HNO_3 to 20% concentration and follow with sodium bismuthate as before.

(For full details of procedure see under 'Manganese in Steel'.)

2b. Volhard's Method

According to Low, no common metals interfere with this method which gives accurate results on materials rich in manganese.

For purposes of calculation, the reaction may be regarded as producing hydrated manganese dioxide (see below), but it has been found (Low) that the reaction between manganous salts and potassium permanganate in the presence of calcium or zinc (here present from the zinc oxide separation) may result in the formation of manganites thus :

$$4KMnO_4 + 5ZnSO_4 + 6MnSO_4 + 14H_2O$$
$$= 4KHSO_4 + 7H_2SO_4 + 5(Zn(OH)_2 \cdot 2MnO_2).$$

However, whichever is the case, inspection of both equations of reaction shows that the valency of the Mn is similar as is the ratio between manganous salt and $KMnO_4$. This is a simple and comparatively rapid method, applicable when considerable quantities of manganese are present.

Dissolve 0·5–1 g of the ore in HCl, adding HNO_3 if necessary. Add 5–7 ml. conc. H_2SO_4 and boil to strong white fumes. Cool, add 25 ml. water, boil, dilute further, and (if much free acid is still present) partly neutralize by addition of Na_2CO_3 or NH_4OH. Add zinc oxide, or an emulsion of $Zn(OH)_2$ until the iron is completely precipitated as $Fe(OH)_3$, adding the ZnO in small quantities at a time, with agitation, until some remains undissolved. Dilute in a stoppered flask to a definite volume (say 500 ml.) mix thoroughly, and allow to settle. Filter off (or draw off with a pipette) portions of (say) 100 ml., heat to boiling, add a few drops of HNO_3, and titrate with standard permanganate until, on shaking and settling, the supernatant liquid shows a pink colour, which persists after shaking and settling a second time. The solution should be titrated as hot as possible, but it is not advisable to boil (as sometimes recommended) after the permanganate has been added in slight excess. The reaction is probably as follows :

$$3MnSO_4 + 2KMnO_4 + 7H_2O$$
$$= 5MnO_2 \cdot H_2O + K_2SO_4 + 2H_2SO_4$$

From which it appears that 1 ml. N/10 $KMnO_4$ (3·16 g per litre) = 0·001648 g Mn.

If the permanganate solution be standardized on iron or ferrous ammonium sulphate, then the manganese standard is found by multiplying the iron standard by 0·2951, since by the equations $3 \times 54{\cdot}93$ parts Mn are equivalent to $10 \times 55{\cdot}84$ parts Fe.

The most satisfactory way of carrying out this titration is to determine the end-point approximately, on an aliquot part of the solution by running in the $KMnO_4$ (say) 5 ml. at a time, until the end point is obviously passed. Another portion is then taken out, heated to boiling, and slightly less than the required amount of $KMnO_4$ added at once, finishing 1 ml. at a time until the end-point is again passed. In subsequent tests the end-point may then easily be determined with greater approach to accuracy, perhaps within 0·1 ml.

Re-boiling of the solution after titration causes a continual disappearance of the pink tint, and may thus give much too high a result.

Acetic acid may be added, in place of HNO_3, to promote the settlement of the precipitate.

3. Precipitation of MnO_2 by means of potassium chlorate in nitric acid solution

This method is based on the fact that potassium chlorate in nitric acid solution (similar to ammonium persulphate or potassium permanganate in sulphuric acid solution and to bromine in ammoniacal solution) will precipitate hydrated MnO_2 from solutions of a manganous salt according to the equation:

$$Mn(NO_3)_2 + 2KClO_3 + H_2O = MnO_2 . H_2O + 2KNO_3 + 2ClO_2.$$

The filtered and washed precipitate may be dissolved in a known excess volume of either N/10 ferrous ammonium sulphate or oxalic acid (acidified with sulphuric acid), the excess being back titrated with N/10 $KMnO_4$ solution.

No common metals interfere with this method. If the material treated is high in silicon or contains tungsten or both, it is better to remove as silica and tungstic oxide by treating the initial solution of the sample (which has been evaporated almost to dryness) with 50 ml. 5% HCl to digest the soluble salts, filter off WO_3 and SiO_2 and evaporate the filtrate twice with HNO_3 additions to ensure removal of HCl which may subsequently hamper the precipitation of MnO_2.

(For full details of method see 'Mn in Steel—Chlorate Method'.)

4. Persulphate—arsenite method

Dissolve 0·25–1 g of material (1 g for steels) in 10–30 ml. of 30% HNO_3 (for materials rich in Ni and Cr dissolve in 30–50% H_2SO_4 instead followed by oxidation with 3 ml. HNO_3) dilute to 100 ml., filter off any graphite and add to the filtrate 5 ml. 1% $AgNO_3$ solution followed by 10 ml. 25% ammonium persulphate. Boil for 30–60 seconds only, cool to 20° C., add 50 ml. cold water and 5 ml. 1% NaCl solution. Titrate at once with standard sodium arsenite solution to a yellow-coloured end-point (pink colour of permanganic acid is converted to a yellowish colour probably due to the formation of manganous nitrate and finely divided MnO_2 from the unstable manganic nitrate first produced).

A convenient strength of sodium arsenite solution to use is approximately N/10 made up by dissolving 7 g sodium arsenite and 15 g ammonium carbonate (or sodium bicarbonate) in warm water and diluting when cold to 1 litre. Although this solution should have the equivalent value of 0·0011 g Mn for each 1 ml., it is advisable to run standards alongside assays, these standards being similar materials of known manganese content.

The effect of ammonium persulphate (in the presence of the catalyst silver nitrate) on the manganous solution, is to convert to permanganic acid—it is thought that this is brought about by oxygen liberated from the unstable silver peroxide as an intermediate product from the ammonium persulphate and silver nitrate present thus :

$$(NH_4)_2S_2O_8 + 2AgNO_3 + 2H_2O = Ag_2O_2 + (NH_4)_2SO_4 + H_2SO_4 + 2HNO_3$$

then

$$5Ag_2O_2 + 2Mn(NO_3)_2 + 6HNO_3 = H_2Mn_2O_8 + 10AgNO_3 + 2H_2O.$$

The reaction during titration with sodium arsenite is uncertain but may be represented empirically as follows :

$$Mn_2O_7 + 2As_2O_3 = \underset{\text{(unstable)}}{Mn_2O_3} + 2As_2O_5 \quad \text{(Pigott)}$$

$$\downarrow$$

$$MnO + MnO_2$$

Notes:

(1) 5 ml. of syrupy phosphoric acid may be added, with advantage, prior to the oxidation with ammonium persulphate. It has the effect of stabilizing permanganic acid.

(2) The oxidation process will also cause oxidation of Cr, V, Co, Ce, and U salts but it appears that sodium arsenite will selectively reduce only manganese. Nevertheless owing to the uncertain

constitution of the reaction products it is not recommended to use this method in the presence of these interfering metals if their proportion singly exceeds 0·5–1%.

(See also under 'Mn in Steel'—Bismuthate-Arsenite Method and 'Mn in Al Bronze'.)

5. Colorimetric methods

For small quantities, the pink permanganate colour produced by either sodium bismuthate (from HNO_3 solution); ammonium persulphate (from H_2SO_4 or HNO_3 solution), or potassium periodate (KIO_4) from $HNO_3 + H_2SO_4$ solution is matched visually or photometrically with standards produced from similar materials under identical conditions.

Methods for bismuthate and persulphate oxidation have already been described. The periodate method is carried out as described under 'Mn in Light Alloys'.

6. 'Available manganese'—oxalic acid method

To 0·5 g of finely crushed pyrolusite add 30 ml. 20% H_2SO_4 and a known volume (or weight) of oxalic acid or sodium oxalate, such that a small definite excess is present (1–1·5 g of oxalic acid or oxalate should suffice for 0·5 g of high grade Mn ores). Warm and agitate until dissolved. Dilute to 250 ml., filter if much iron is present, take an aliquot portion, add 5 ml. 50% H_2SO_4, warm to about 60° C. and titrate *slowly* with standard $KMnO_4$ solution (N/10 or N/5) to a pink flush.

The reactions are as follows:

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

$$\text{Excess } H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O.$$

From the first equation: 126 g oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) or 134 g sodium oxalate ($Na_2C_2O_4$) = 87 g MnO_2.

MERCURY

(Hg) Atomic Weight = 200·61

Metallurgical Occurrence

Native mercury and mercury ores
Amalgams (with Sn, Ag, Cu, Au)
Alkali-earth hardened lead bearing alloys (up to 0·25%)

Source of Metal as Standard

'Analar' grade mercuric chloride or oxide

Methods of Determination

GRAVIMETRIC

1. *Decomposition of the ore by heating with iron, the volatilized mercury being condensed on to a gold or silver plate*
   (Eschka's method.) (Suitable for low-grade ores intended for extraction by distillation. Not a very accurate method.)

VOLUMETRIC

2. *Conversion to mercuric nitrate and titration with potassium thiocyanate*
   (suitable for ores and other materials rich in Hg).
3. *Conversion to mercuric nitrate and titration with KCN and $AgNO_3$ solutions*
   (similar to [2] but less popular method).
4. *Conversion to mercuric nitrate and titration with KI using starch as external indicator*
   (*similar to* [3]).

ELECTROLYTIC

5. *Electrolysis from sulphuric acid solution*
   (suitable for special lead base bearing alloys).

METHODS

1. Eschka's method

A mixture of 0·2–5 g of the ore with a rather larger weight of clean iron filings is heated gently in a porcelain crucible which is covered with a closely-fitting lid of thin sheet gold or silver, the upper side of which is concave and kept filled with water during the operation. The gold or silver lid is carefully dried and cleaned, and weighed before use. The crucible may conveniently be supported on a sheet of asbestos in which a circular hole is cut, so that about a third of the crucible passes through the hole, the flame being applied only to the bottom of the crucible. The decomposition should be complete in ten to thirty minutes.

$$HgS + Fe = FeS + Hg.$$

The mercury volatilizes and is condensed on the under side of the gold or silver plate, which is then dried without heating and weighed, the increase of weight representing the mercury.

If desired, the plate may be washed successively in water, alcohol and ether before weighing.

This method cannot be regarded as a very accurate one, but it serves a useful purpose in the evaluation of ores from which mercury is to be extracted by a distillation process. Care should be taken that the iron filings are thoroughly freed from grease or other organic matter before use. A correction for losses of mercury amounting to one-tenth to one-sixtieth of the amount found is sometimes made.

The presence of much sulphur or moisture will interfere with the effective condensation of the mercury on the silver or gold plate. Gold is less affected than silver.

2. Conversion to mercuric nitrate and titration with potassium thiocyanate

This method is suitable for the rapid determination of mercury in cinnabar and the like, none of the usual impurities interfering. With certain modifications it may be applied to the titration of mercury in preparations containing iodine.

0·3 to 0·5 g of the ore, finely powdered, is heated with 1 to 1·5 g potassium nitrate and 5 to 10 ml. conc. H_2SO_4 in a flask or large test tube provided with a long straight leading tube (about 18 inches), which serves as a condenser for any volatile mercury salts. This is connected by means of a perforated rubber stopper. (A ground glass connection would be preferable.) The mixture is boiled gently until all red particles have disappeared and the mineral is completely decomposed. This takes usually about 15 minutes.

After cooling, the contents of the flask are diluted with about 50 ml. of water, the stopper and leading tube being rinsed with water into the same or another vessel. Potassium permanganate (1 : 100) is then added drop by drop until the red colour is permanent, in order to oxidize any nitrous acid present. (Any excess of permanganate may be removed by cautious addition of dilute ferrous sulphate, but with care this is unnecessary.) A few millilitres of iron alum or ferric nitrate solution are now added and the mixture titrated, cold, with potassium thiocyanate until a reddish-brown colour is permanent:

$$Hg(NO_3)_2 + 2KCNS = Hg(CNS)_2 + 2KNO_3$$

1 ml. N/10 KCNS = 0·01003 g Hg
= 0·01163 g HgS

Halogens must be absent, since if $HgCl_2$ is formed, this is only partly decomposed to $Hg(CNS)_2$ by KCNS.

Modification for Substances Containing Iodine.—The substance is extracted with KI solution, and the extract made strongly alkaline with caustic alkali. After filtering, if necessary, the solution, containing KHgI, is mixed, with agitation, with a few millilitres of formaldehyde (30–35%) and 10–15 ml. of water, agitated gently for a minute and the precipitated mercury collected on a Gooch filter. After washing with water the mercury is extracted from the filter by pure conc. HNO_3, diluted to about 50 ml., $KMnO_4$ added and titrated with KCNS as previously.

Ag, Pd, Cu, Pb and Sn if present in quantity, may react with the thiocyanate to form insoluble compounds and should thus be removed by precipitating the Hg and above metals as sulphides

by H_2S from 10% H_2SO_4 solution, digesting with 50% HNO_3 to dissolve all sulphides except HgS and finally dissolving HgS in conc. H_2SO_4 containing KNO_3 as in above method.

3. Titration with excess potassium cyanide in cold solution and back titrating with silver nitrate

The following method was found by the authors to give very satisfactory results with chloride or nitrate solutions. The mercury must be in the mercuric condition and free from other elements that would react with cyanide, e.g. Zn, Cu, Ni, Co, Cd, Ag, Au.

Solutions Required

Mercuric Nitrate.—5·4 g pure HgO dissolved in 15–20 ml. HNO_3 and diluted to 1 litre.

1 ml. = 0·005 g Hg.

Potassium Cyanide.—3·25 g KCN (or an equivalent of NaCN) dissolved in water, $BaCl_2$ added to precipitate carbonates, filtered on Buchner funnel, and made up to 1 litre.

Silver Nitrate.—4·25 g $AgNO_3$ dissolved in distilled water, made up to 1 litre. This should correspond approximately with the cyanide solution, and if desired one or other of these solutions may be diluted so that they correspond exactly.

Potassium Iodide.—About 1 g in 100 ml. water (as indicator).

Sodium Hydroxide.—Pure moderately strong solution, exact strength immaterial.

Method.—The solution to be tested is made slightly alkaline with NaOH, so that the whole of the mercury is precipitated as $Hg(OH)_2$. Cyanide is then run in from a burette till a perfectly clear and colourless solution is obtained, and the volume of KCN which has been used is noted. A few millilitres of the potassium iodide indicator are then added, and the excess cyanide titrated by running in $AgNO_3$ until a distinct yellowish turbidity remains permanent. The equivalent in terms of KCN of the $AgNO_3$ added is then deducted from the total KCN used, the difference being equivalent to the mercury.

The method depends upon the fact that mercuric cyanide is not decomposed by silver nitrate. The reactions are as follows :

(i) $HgCl_2 + 2NaOH = Hg(OH)_2 + 2NaCl$
(ii) $Hg(OH)_2 + 2KCN = Hg(CN)_2 + 2KOH$
(iii) $2KCN + AgNO_3 = KAg(CN)_2 + KNO_3$
(iv) $AgNO_3 + KI = AgI + KNO_3$

The cyanide solution is standardized on the mercuric nitrate

solution given above, using precisely the same method. The exact relation between the silver nitrate and the cyanide should also be determined by titrating a measured volume of the cyanide solution, with KI indicator added, but no mercury salt, running in $AgNO_3$ until a permanent yellow turbidity is produced.

4. Titration with potassium iodide using starch as external indicator

This method depends upon the fact that mercuric chloride prevents the liberation of iodine from potassium iodide by nitrous acid, but when the reaction $HgCl_2 + 2KI = HgI_2 + 2KCl$ is complete, any further addition of KI causes a liberation of iodine, if HNO_2 be present.

$$KI + HNO_2 + HNO_3 = I + NO + KNO_3 + H_2O$$

Standard Solutions

Potassium Iodide.—8·3 g KI per litre.

Mercuric Chloride.—6·775 g $HgCl_2$ per litre.

A measured volume of the solution to be tested, containing mercury as $HgCl_2$, is mixed with 2–5 ml. of conc. HNO_3 containing a little HNO_2. (A convenient way of securing this is to add a few drops of a solution of SO_2.) The mixture is then titrated with the standard KI until a drop taken out gives a blue colour with a drop of starch solution on a porcelain plate.

The KI is standardized in the same manner on the mercuric chloride solution given above.

1 ml. KI = 0·005 g Hg.

5. Electrolysis from sulphuric acid solution

The lead base bearing alloy is attacked with nitric acid, any metastannic acid filtered off, the filtrate has Pb precipitated from it as $PbSO_4$ by an addition of H_2SO_4. Filter off and electrolyse the filtrate between Pt electrodes. (See under 'Hg in Alkali-earth Hardened Lead Bearing Alloys'.)

MOLYBDENUM

(Mo) Atomic Weight = 95·95

Metallurgical Occurrence

Ores
Cast irons
Steels
Ferro-molybdenum

Source of Metal as Standard

Molybdenum metal approximately 99·9% pure is obtainable, but when required as a standard, pure ammonium molybdate is more convenient. However, since most modern methods of estimation are gravimetric, pure metal standards are unnecessary

Method of Determination

GRAVIMETRIC

1. *Sodium hydroxide separation, followed by precipitation as lead molybdate, ignite and weigh same*
   (suitable for all ores and ferrous alloys but subject to interference from certain of the metals found associated with Mo, particularly W and V).
2. *Precipitation by alpha-benzoinoxime from dilute acid solution and ignition to the trioxide*
   (very suitable for low grade ores and alloys containing less than 5% Mo. This method is free from interference from most other metals if suitable precautions are taken).

COLORIMETRIC

3. *Reduction of iron by stannous chloride and conversion of molybdenum to the red oxythiocyanate which is compared with standards*
   (suitable for materials containing less than 0·75% Mo, preferably with copper and cobalt absent since these may interfere).

METHODS

1. Precipitation as lead molybdate and weighing as such, after ignition

This method depends on initial solution of the ore or ferrous alloy in HCl with HNO_3 additions to decompose complex carbides and to oxidize iron and tungsten, etc., to facilitate their removal at a later stage.

Evaporation to dryness followed by resolution in HCl allows silica and tungstic oxide to be removed by filtration. The filtrate is run *slowly* into a hot caustic soda solution, this prevents the possible formation of basic ferric molybdate and instead gives soluble sodium molybdate and a precipitate of ferric hydroxide together with the hydroxides of chromium (most), cobalt, copper and nickel, etc.

$$2FeCl_3 + H_2MoO_4 + 8NaOH = 2Fe(OH)_3 + Na_2MoO_4 + 6NaCl + 2H_2O$$

Any Al and V present would be present in the filtrate and cause contamination of the final precipitation of Mo by lead acetate for the following reasons: Al hydrolyses to give the hydroxide in ammonium acetate solutions, and vanadium would precipitate as a lead vanadate on adding lead acetate. For a similar reason, sulphates must be absent to prevent co-precipitation of lead sulphate.

As and P may also precipitate as lead arsenate and phosphate respectively but are inhibited by addition of ammonium chloride (10–20 gm) prior to the lead acetate addition.

In the Absence of Vanadium.—The filtrate (or an aliquot part) from the caustic separation, is neutralized with HCl or formic acid using methyl orange as indicator, add 5 ml. excess acid, add 2–5 ml. sulphurous acid (to reduce any residual chromate to the chromic condition, when it will not be precipitated by lead acetate) and boil out excess SO_2.

To the boiling solution about 50 ml. of a 20% ammonium acetate solution is added, followed by the lead acetate solution (15 ml. of an 8% solution for steels) until no further white precipitate of lead molybdate is produced. (*Note:* 1 ml. 8% lead acetate solution will precipitate 0·02 g Mo [Pigott].) Boil gently for about 10 minutes to convert the basic to the normal salt, filter, wash with 2% ammonium acetate solution slightly acidified with acetic acid and finally ignite at below 600° C. to prevent reduction (by carbon from the filter) of lead molybdate to PbO or Pb.

$$Pb(CH_3COO)_2 + Na_2MoO_4 = PbMoO_4 + 2Na(CH_3COO)$$
$$(PbMoO_4 \times 0{\cdot}2615 = Mo)$$

In the Presence of Vanadium.—A slight modification is necessary. To the filtrate from the caustic soda separation, neutralize with HCl (using methyl orange as before) and add a slight excess, neutralize with ammonia, add 5 ml. excess and follow with 10 g NH_4Cl and 1 g $MnCl_2$. Boil for 2–3 minutes and filter off yellow basic manganese vanadate (variable constitution) washing with hot water. The filtrate is then neutralized (to methyl orange) and slightly acidified using HCl, with ammonium acetate and lead acetate added to the boiling solution just as before. (For full details of method for ferrous alloys, see also under 'Molybdenum in Steels, Cast-irons and Ferro-molybdenum'.)

2. α-Benzoinoxime precipitation (Knowles, *Nat. Bur. Standards J. Research*, 9/1/1932; Pigott, *Chemical Analysis of Ferrous Alloys:* Low, *Technical Methods of Ore Analysis*, 1947)

This reagent in alcoholic or acetone solution can precipitate from dilute mineral acid solution: W, Pd, Ta, Cr, V, Cb as well as Mo, but under the conditions of precipitation quoted in the reference below, no contamination should be experienced.

The initial solution in HCl followed by oxidation with HNO_3 should be sufficient to decompose any complex carbides in the material (steels, etc.). The subsequent evaporation, baking and digestion in HCl effects precipitation of Si, W (also Ta and Cb) as insoluble oxides which are removed by filtration. The filtrate, apart from molybdic acid (H_2MoO_4), may contain Cr and/or V which will both be in the oxidized condition (chromic salts and

metavanadic acid) both of which would precipitate later with the α-benzoinoxime. The addition of a little ferrous sulphate has the effect of reducing these interfering metals to the chromous and vanadyl states in which they will not precipitate with the organic reagent.

The precipitation of Mo with α-benzoinoxime may be represented as follows:

$$H_2MoO_4 + 3(C_6H_5CHOH.CN.OH.C_6H_5) = Mo(C_{14}H_{11}O_2N)_3 + 4H_2O.$$

This reaction should be performed with very cold solutions in order to minimize any reduction of the molybdic acid by the reagent—the addition of a little bromine water helps in this respect.

It has been suggested (Low) that when Cr and/or V are present, the bromine water addition should be omitted for fear of co-precipitation by these metals in their oxidized condition. Instead, oxidize the cooled acid solution containing Mo with $KMnO_4$ solution until faintly pink, add 5 ml. H_2SO_3 (saturated solution) to reduce Cr and V and proceed with the Mo precipitation as before.

Ignition of the Mo complex to MoO_3 is performed below 525° C. since volatilization of the oxide commences about 550° C. The ignited oxide should be white or faintly greyish (due to partial decomposition to Mo_2O_3). If very grey or blue, continue heating at low temperature with free access to air to convert the residue to MoO_3.

If the residue is coloured yellow or brown, contamination with W or Fe respectively should be suspected. For Fe, treat the residue with 10 ml. 10% NaOH solution, boil for a few minutes to convert MoO_3 into soluble sodium molybdate, dilute, filter, wash with hot water, ignite the residue and weigh as Fe_2O_3 which should be deducted from the first weighing of the impure MoO_3. 10 ml. conc. NH_4OH may be used instead of the NaOH, in which case both Mo and W pass into solution leaving ferric hydroxide undissolved. Dilute the ammoniacal solution to about 150 ml., just acidify with tartaric acid and pass H_2S into the boiling solution. Filter off brown MoS_2 and ignite at 500° C. (max.) to MoO_3. (For full details of method see under 'Molybdenum in Steel'.)

3. Colorimetric method

The principles upon which this method is based are first initial solution of the Mo as chloride, followed by its separation from the other metals present (expecially Fe in steels, etc.) by means of the solubility of molybdenum oxythiocyanate in ether or butyl acetate.

In this case, the addition of the reducing agent stannous

chloride, in the presence of a soluble alkali thiocyanate, produces a blood-red solution of molybdenum oxythiocyanate $MoO(SCN)_3$ whereas iron, which would give a similar reaction and coloration if in the ferric state, does not interfere owing to its presence in the reduced (ferrous) condition.

On shaking the blood-red solution with butyl acetate and allowing separation of the ethereal and aqueous layers, all the Mo compound is found to be dissolved in the acetate layer and is almost entirely uncontaminated by any other metals present.

This procedure when repeated with standards of similar materials, but of known Mo content, gives a basis of estimation since the intensity of the red colour produced is a measure of the proportion of Mo present.

The stronger solution is diluted with butyl acetate until the colour intensities match.

Note: Solutions of molybdenum salts and molybdates with stannous chloride (in the *absence* of alkali thiocyanate) give a bright blue coloration described as 'molybdenum blue'—constitution doubtful but $MoO_2 . 4MoO_3 . XH_2O$ has been suggested (Pigott). (For details of method see under 'Molybdenum in Steels and Cast-iron'.)

NICKEL

(Ni) Atomic Weight = 58·69

Metallurgical Occurrence

Ores, mattes, speisses etc.
Aluminium alloys
Steels and cast-irons
White metals
Copper alloys
Nickel alloys

Source of Metal as Standard

Electrolytic nickel = 99·97% (invariably contains small proportions of Co [about 0·02%] and Fe [about 0·005%].) (The Mond Nickel Co. Ltd., London, W.1)

Methods of Determination

GRAVIMETRIC

1. *Precipitation as a red complex by means of dimethylglyoxime, finish by one of the three following methods*
   (*a*) dry and weigh the complex
   (*b*) ignite the complex to nickel oxide
   (*c*) dissolve the complex in HCl and titrate with KCN (as in Method 2)
   (suitable for all nickel-bearing materials).

VOLUMETRIC

2. *Titration in ammoniacal solution with excess KCN and back titration with* $AgNO_3$
   (suitable for materials with Cu and Co absent).

METHODS

1. Precipitation with Dimethylglyoxime

This organic reagent gives a yellow precipitate with Pd from acid solution and with Bi from slightly ammoniacal solution. This latter reaction is inhibited by the presence of tartrates. The value of this reagent is evident when estimating nickel in ferrous materials for it is unnecessary to remove the iron. It must however not be allowed to precipitate when the Ni solution is rendered ammoniacal and therefore tartaric (or citric) acid is added to keep the iron (ferric state) soluble in the form of a tartrate or citrate.

It has been stated (Pigott) that ferrous iron gives a red precipitate with the reagent in acid solution but that the complex is destroyed on adding ammonia.

Cobalt and copper do not interfere unless present in very large proportions when the former consumes reagent in being oxidized to the cobaltic state (overcome by preliminary treatment with ammonium persulphate or H_2O_2) and the latter tends to be occluded in the precipitate. The best procedure is re-precipitation when Co and Cu are present, although precipitation of nickel from an acetic-acetate solution instead of ammoniacal solution is preferred by many, with or without the reprecipitation.

Notes:

(1) For convenience in handling this bulky precipitate, it is advisable to take a weight of sample such that the nickel content does not exceed 0·05 g.

(2) With iron-rich materials the amount of tartaric acid used to inhibit precipitation of the iron should be approximately 10 g for each 0·5 g iron present.

(3) For each 0·01 g Ni present in the solution, add 4 ml. of a 1% alcoholic solution of the reagent plus an excess of 10 ml. per assay.

(4) The concentration of ammonia should not exceed 30% (by volume) otherwise the complex will become soluble, similarly its solubility in alcohol-water mixtures demands that the alcohol content (by volume) of the solution during precipitation should not exceed about 35–40%.

(5) In the presence of much Zn or Mn, about 2–5 g NH_4Cl should be added to keep these metals from precipitating on making the solution ammoniacal, otherwise there is usually sufficient of this ammonium salt present during the neutralization of HCl by NH_4OH.

(6) With ferrous materials, it is advisable to neutralize with NH_4OH a *cold* solution containing Fe, Ni, etc. (and of course tartaric acid). If the temperature of the solution rises above about 80° C. the ferric tartrate is liable to decompose and ferric hydroxide may be precipitated.

The precipitation may take place in presence of most other metals, so that in treating an ore it is often only necessary to remove silica and other matter insoluble in acids. In the presence of iron and aluminium, enough tartaric acid is added to prevent the precipitation of these metals by ammonia. If a precipitate is formed by ammonia which cannot be dissolved in tartaric acid, this should be filtered off before proceeding to precipitate the nickel.

The solution, if acid, is made faintly alkaline with ammonia; if alkaline, it is first acidified with HCl or HNO_3 and then made just alkaline with ammonia. A sufficient quantity of a 1% alcoholic solution of dimethylglyoxime ($C_4H_8N_2O_2$) is then added to precipitate the whole of the nickel according to the reaction

$$NiCl_2 + 2(C_4H_8N_2O_2) = Ni(C_4H_7N_2O_2) + 2HCl$$

The solution is warmed, not above 50° C., then a little more ammonia added (to neutralize the acid formed by the reaction), agitated and kept slightly warm for about 15 minutes, then filtered (best on paper pulp or on a tared Gooch or sintered glass crucible). It is then washed with warm water to which a small quantity of ammonium nitrate is added.

(*a*) The red complex may be dried at 110–120° C. to constant weight.

$$Ni(C_4H_7N_2O_2)_2 \times 0{\cdot}2032 = Ni.$$

(*b*) Since the complex tends to volatilize undecomposed above 250° C. it is advisable to wrap the precipitate in a moistened filter paper and to burn off most of the organic matter at as low a temperature as possible, finally ignite at 800° C. to NiO ($\times$ 0·7858 = Ni).

(*c*) Dissolve the complex in the minimum volume of *aqua regia*, evaporate to low bulk, dilute to 200 ml. with water, make just ammoniacal and titrate with KCN and $AgNO_3$ as in Method 2 below. (For detailed methods see also under 'Nickel in Al alloys, Cu alloys and in Steels'.)

2. Titration with KCN and $AgNO_3$ in ammoniacal solution

In this method, Cu and Co must be absent (as must Ag and the precious metals) since these will react with KCN in a similar manner to Ni.

Fe, Al, Cr, Ti, Mo must be retained in solution by the addition

of tartrates or citrates (prior to making ammoniacal). Tungsten should be removed at an early stage in the form of WO_3 from an oxidized HCl solution of the material. The presence of NH_4Cl (2–5 g) is required for preventing the hydroxide precipitation of Mn and to keep Zn in the form of a complex ammine.

During titration the observation of the appearance and disappearance of the turbidity is considerably helped by the use of a black tile.

Solutions Required

(*a*) *Potassium Cyanide.*—This may be of any strength suited to the material to be tested. A N/10 solution contains 13·0226 g pure KCN, or an equivalent amount of pure NaCN, viz., 9·8026 g per litre.

1 ml. N/10 cyanide = 0·002934 g Ni.

As the strength of the solution does not remain constant, there is no object in adjusting it exactly, and it should always be standardized immediately before or after use on a silver nitrate solution of exactly known strength.

(*b*) *Silver Nitrate.*—A decinormal solution, containing 16·9888 g $AgNO_3$, dissolved in distilled water and made up to a litre, may be used; 1 ml. of this = 0·002934 g Ni.

If a solution be prepared containing 5·7903 g $AgNO_3$ per litre, 1 ml. = 0·001 g Ni.

If such a solution be used, the cyanide should be adjusted so that it corresponds approximately with this.

(*c*) *Potassium Iodide* (Indicator).—A 2% solution (or a small crystal may be added).

Method

The nickel is obtained in solution by any suitable means; copper and other metals precipitated by H_2S in acid solution are removed, and, preferably, Fe, Mn, Zn and Co. See section on Separations. (When the amount of Co does not exceed one-tenth of the amount of Ni it is approximately estimated in the titration as its equivalent in Ni.) The solution may contain HCl, HNO_3 or H_2SO_4, but the latter is preferable. Add ammonia until distinctly alkaline; (if no H_2SO_4 is present add 1–2 ml. of conc. H_2SO_4 before neutralizing). Add 5 ml. of the KI solution, or a small crystal of KI; run in a little $AgNO_3$ from a burette, noting the starting point, until a distinct turbidity of AgI is produced (about 0·5–1 ml. of $AgNO_3$ should be sufficient). Now add, in a rapid stream, standard cyanide from another burette until the precipitate of nickel cyanide $Ni(CN)_2$ first formed has completely

dissolved to a clear and colourless solution of potassium nickelocyanide ($K_2Ni(CN)_4$). Note amount of cyanide added. Now run in the $AgNO_3$ solution cautiously until a faint yellowish turbidity remains permanent on agitation.

Deduct the equivalent, in terms of KCN, of the total $AgNO_3$ added, from the amount of cyanide used; the difference represents the equivalent of the nickel.

The solution, before titration, should not contain more than 0·1 g Ni per 100 ml.

Standardization of the Cyanide Solution

A measured quantity of the cyanide solution (say 30 ml.) is diluted to 100 ml., 5 ml. of 2% KI added, and $AgNO_3$ run in until a permanent yellow turbidity is formed. The equivalent in terms of $AgNO_3$, and hence of Ni, is then calculated. If the metallic silver equivalent of the $AgNO_3$ is known, its value in terms of nickel is Ag × 0·272 = Ni.

The reactions are as follows:

(i) $Ni(NH_3)_6SO_4 + 4KCN = K_2Ni(CN)_4 + 6NH_3 + K_2SO_4$

(ii) $AgNO_3 + 2KCN = KAg(CN)_2 + KNO_3$

(iii) $AgNO_3 + KI = AgI + KNO_3$

The AgI formed by the first addition of $AgNO_3$ is redissolved by KCN as follows:

(iv) $AgI + 2KCN = KAg(CN)_2 + KI$

Hence at the end of the titration all the cyanide added has been converted either into the double nickel compound or the double silver compound, and the equivalent of the former is found by deducting the equivalent of the latter.

For details of methods for specific materials, also see 'Nickel in Al alloys and in Cu alloys'.

NITROGEN

(N) Atomic Weight = 14·008

Metallurgical Occurrence

Steels (mainly Bessemer steels and certain steel welds)
Slags (as nitrides and cyanonitrides)
Gases etc.
Nitrate minerals
Ammonium salts

Methods of Determination

GRAVIMETRIC

1. *Precipitation of nitrates with 'nitron'*
   (suitable for fairly small quantities of nitrates or nitric acid. Bromides, iodides, nitrites and chromates interfere and must be removed).

VOLUMETRIC

2. *Estimation of nitrates by oxidation of standard ferrous sulphate*
   (suitable for crude mineral deposits, e.g. nitre).
3. *Distillation of N_2 as NH_3 and titration with standard acid solution*
   (suitable for steels, cast-irons and other ferrous materials where the N_2 content exceeds 0·005%).
4. *Vacuum fusion followed by normal analysis of the gases produced*
   (suitable for steels and cast-irons [particularly those containing Ti and V], also other ferrous materials).
5. *Estimation of ammonia or the ammonium radical by caustic distillation, with collection of the distillate in excess standard acid*
   (suitable for most mixtures of ammonium salts with other inorganic or organic compounds).

COLORIMETRIC

6. *Estimation of ammonium salts using Nessler's solution*
   (suitable for very small quantities of ammonia or ammonium salts such as is obtained in the distillate from Method 3, or not more than 0·005% N_2).
7. *Nesslerization without distillation* (Newell's method)
   (suitable as an alternative to Methods 3 and 6).
8. *Estimation of nitrates using brucine*
   (suitable for traces in boiler water etc. Nitrites interfere).

METHODS

1. Precipitation of nitrates with 'nitron' (Diphenylendanilo-dihydro-triazole) (Heck, Hunt and Mealon, *Analyst*, 1934. **59**. 18)

Nitric acid may be estimated by weighing the fairly insoluble compound, 'nitron' nitrate, $C_{20}H_{16}N_4 . HNO_3$. The base also precipitates the following acids: nitrous, chromic, chloric, perchloric, hydrobromic, hydriodic, hydro-ferrocyanic, oxalic, picric and thiocyanic acids, hence these must be removed.

Procedure.—Such an amount of the substance as will contain about 0·1 g HNO_3 is dissolved in about 100 ml. of water, with addition of 10 drops of dilute H_2SO_4. The solution is heated nearly to boiling and about 12 ml. of nitron acetate solution added (10 g of nitron in 100 ml. of 5% acetic acid). The solution is cooled and placed in an ice pack for about 2 hours, and the compound then transferred to a weighed Gooch or Munroe crucible, and, after draining, it is washed with about 10 to 12 ml. of ice-water added in small portions. The precipitate is then dried to constant weight at 110° C. and weighed. Weight × 0·1653 = NO_3.

Note: Keep nitron reagent in a dark-coloured bottle.

Removal of Nitrous Acid.—Finely-powdered hydrazine sulphate

is dropped into the concentrated solution (0·2 g per 5 or 6 ml.).

Chromic Acid.—Reduced by hydrazine sulphate.

Hydrobromic Acid.—Decomposed by chlorine water added drop by drop to the neutral solution, which is then boiled till the yellow colour disappears.

Hydriodic Acid.—Add excess of potassium iodate to the neutral solution and boil till iodine is expelled.

2. Estimation of nitrates by oxidation of standard ferrous sulphate solution (Clennell, *Eng. Min. Jnl.*, 1918. **10.** 660)

Preparation of Sample.—Grind to 60 or 80 mesh. Weigh out 5–10 g, according to richness of sample in nitrate; boil with 100 ml. water, filter, wash three times with 25 ml. boiling water in each wash. Cool filtrate; make up to 200 ml. Take an aliquot part (5–25 ml.) for determination.

Salt samples free from earthy matter need only be dried below 200° C., crushed and mixed, and 2–10 g dissolved in water made up to 200 ml. and aliquot part taken.

Determination of the Nitrate.—This is made simultaneously with a check assay on a known quantity of pure KNO_3 or $NaNO_3$. Take 50 ml. of standard ferrous sulphate (see below), add 10–15 ml. conc. H_2SO_4 and cool. Add the measured volume of the nitrate solution to the above in a 300 ml. conical flask with Bunsen valve. Heat gradually to boiling. Boil gently till all trace of black or brown colour has disappeared, leaving a clear yellowish solution. Add 10 ml. of previously boiled and cooled distilled water. Cool and titrate excess $FeSO_4$ with $KMnO_4$.

Check Assay.—Take the same volume of a 1% solution of KNO_3 or $NaNO_3$ as was taken of the nitrate solution in the assay, add to the same quantities of $FeSO_4$ and H_2SO_4 as used in the assay, and proceed in the same way.

When the sample contains chlorides it is necessary to add in the check assay a quantity of NaCl equivalent to the chlorine found in the sample. (This may be determined by titration with silver nitrate and chromate indicator.)

Standardization of the Ferrous Sulphate.—Take 50 ml. of the standard ferrous sulphate; add volume of H_2SO_4 used in assay; add water equal to volume of nitrate solution used; boil, cool, add 100 ml. water and titrate with $KMnO_4$.

Standard Ferrous Sulphate.—Dissolve 50 g crystallized $FeSO_4 . 7H_2O$ in 500 ml. water, add 100 ml. conc. H_2SO_4, cool, make up to 1 litre.

Standard Permanganate.—3·3 g $KMnO_4$ per litre (or N/10 $KMnO_4$, 3·1606 g per litre).

Reactions.—$6FeSO_4 + 2NaNO_3 + 4H_2SO_4 = 3Fe_2(SO_4)_3 + Na_2SO_4 + 2NO + 4H_2O$.

Calculation of Results.—If the same volume of nitrate solution be used in the check as in the assay solution, the percentage of 'nitrate' (calculated as KNO_3 or $NaNO_3$ as desired) may be readily found as follows:

Let A = No. of ml. $KMnO_4$ used in assay
„ B = „ „ „ „ „ „ blank on $FeSO_4$
„ C = „ „ „ „ „ „ check
„ X = percentage of nitrate in assay solution.
Then $B - A$ represents $KMnO_4$ consumed by nitrate in assay
$B - C$ = $KMnO_4$ consumed by check.

Since the check assay is made on 100% nitrate,

$$B - A : B - C :: X : 100,$$

$$\text{or } X = 100\,\frac{(B - A)}{B - C}$$

3. Distillation of N_2 as NH_3 and titration with standard acid solution (United Steel Company's Method, 1945; Pigott, *Metallurgia*, Jan. 1948)

The principles employed in this method are firstly the solution of the sample in mineral acid, followed by distillation of ammonia, from the ammonium salts produced, by treatment with an alkali.

The main difficulties with chemical attack on the ferrous sample have been to obtain complete solution of some of the more stable nitrides (often coupled with carbides) of alloying elements. With plain carbon steels little trouble is encountered. It is primarily believed by many authorities that all chemical methods of attack on ferrous materials only determines the N_2 present as soluble nitrides (or other nitrogen-bearing constituents) whereas N_2 present as an occluded gas would be lost. Thus for a more complete determination, the vacuum fusion method is to be recommended, although gaseous N_2, when present, is usually negligibly small.

For a detailed study of the subject, it is suggested that the reader consult 'The Fourth Report of the Oxygen Sub-Committee of the Iron and Steel Institute' published in the Iron and Steel Institute's Journal, 1943. Volume 148. Pages 302–320.

The method given below was developed by the Central Research Department, The United Steel Company Ltd., Sheffield, who are represented on the above Sub-Committee.

1–2 g of washed and degreased sample are dissolved in 25 ml.

25% H_2SO_4 together with 2 g A.R. potassium bisulphate contained in a 250 ml. round bottom flask having a side arm leading to an 18-inch air condenser (ground glass points). Cover the flask and heat over a broad flame or electric hot plate until fuming commences. Attach the condenser and fume for 15–20 minutes. Cool, dilute with 30 ml. of ammonia free water.

Whilst this operation is in progress, the distillation apparatus is set up. This consists of a 750 ml. round-bottom flask having a ground glass stopper through which passes a tap-funnel reaching almost to the base of the flask. The side arm from the distillation flask has one or more bulbs totalling about 100 ml. capacity acting

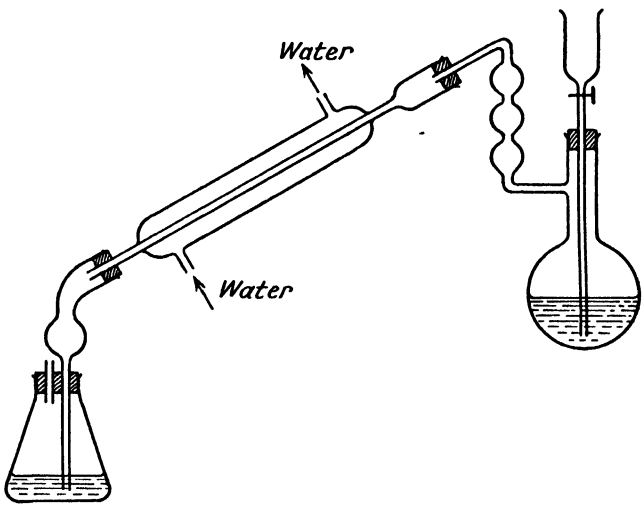


FIGURE 3

as an air condenser and a safety device. From here the side arm enters a cork fitted into one end of a water condenser. The far end of this condenser carries a glass adapter leading via a bulb to a conical corked flask acting as a receiver for the distillate. This flask carries about 25 ml. of ammonia-free water and the adapter tube should dip just below the level of this water.

To the distillation flask, add 75 ml. of 20% NaOH solution, 400 ml. of ammonia-free water, and a few pieces of short glass tube or beads, and distill the whole over a small broad flame until two successive 30 ml. fractions of condensate are ammonia free (by Nessler's reagent). Transfer the solution of the sample (with flask washings) to the tap funnel and slowly admit to the boiling

alkali solution so as to maintain boiling, rinse in last traces of sample solution with small washes of ammonia-free water. Continue the distillation for 45 minutes during which time about 150–200 ml. of condensate will have been collected.

Note: 45 minutes should be adequate for N_2 contents up to about 0·1%, for higher N_2 contents proportionately longer times should be given for the distillation.

To the distillate add 4 drops of indicator solution (0·125 g methyl red and 0·083 g methylene blue dissolved in 100 ml. of absolute alcohol by digesting at 50° C. until solution is complete; cool to room temperature) and titrate with N/200 HCl. This mixed indicator gives a sharp end-point.

1 ml. N/200 HCl = 0·00007 g nitrogen.

The reactions involved are:

$$Fe_4N + 5H_2SO_4 = (NH_4)_2SO_4 + 4FeSO_4 + 2H$$
$$Mn_3N_2 + 4H_2SO_4 = (NH_4)_2SO_4 + 3MnSO_4$$
$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_4OH$$
$$NH_4OH + HCl = NH_4Cl + H_2O$$

All reagents must be nitrogen free and made up with ammonia-free water. For ammonia-free water distil over sodium hydroxide solution containing a few drops of N/10 $KMnO_4$. The sulphuric acid used must be nitrate free, use 'Analar' grade and check with the brucine test (see Method 8 below). The determination should be carried out in an ammonia-free atmosphere.

It is advisable to do a 'blank' determination on the reagents used.

4. Vacuum fusion followed by normal analysis of gases produced

Here, the sample is melted (usually by high frequency methods) in a graphite crucible whilst the whole assembly is maintained under high vacuum. The evolved gases are collected and analysed by conventional methods.

References

Sloman, *Iron and Steel Institute Special Report.* No. **9.** 71.
Sloman, *Iron and Steel Institute Special Report.* No. **16.** 82.
Swindon, *Jnl. Iron and Steel Institute,* 1943. **148.** 303–6.
Hurst and Riley, *Jnl. Iron and Steel Institute,* 1948. June. 130–6.

5. Estimation of ammonia or the ammonium radical by caustic distillation with collection of the distillate in excess standard acid solution

This is a modification of Method 3 and when applied to

non-metallic materials merely involves the distillation with NaOH as described before. N/10 HCl or H_2SO_4 is a suitable medium for collecting the distillate and titration of excess acid is carried out with standard alkali (N/10 Na_2CO_3) in the presence of methyl orange.

1 ml. N/10 acid = 0·0017032 g NH_3 = 0·001804 g (NH_4)

6. Colorimetric estimation of ammonium salts using Nessler's solution

All reagents used must be made up with ammonia-free water and except for the standard ammonium chloride solution, all nitrogen compounds should be absent.

To the solution under test or the distillate from Methods 3 or 5 add sufficient ammonia-free water (produced as outlined in Method 3) so that not more than 0·00005 g NH_3 is present per 100 ml. of solution. For the standards, take an equal volume of ammonia-free water and add known quantities of standard NH_4Cl solution to give an ammonium content similar to the solution under test. Add 2 ml. of Nessler's reagent to both assays and standards, mix well, allow to stand 15 minutes for the full colour to develop, pour 50 ml. of test and standard solutions separately into Nessler glasses and match the colour intensities by diluting the more intense with ammonia-free water. Comparison may be carried out visually, by comparator, or photo-electric absorptiometer. The coloured compound produced is thought to have the formula $NH_2Hg_2I_3 \cdot H_2O$.

Nessler's Reagent.—Dissolve 35 g KI and 12·5 g $HgCl_2$ in 200 ml. ammonia-free water. To this solution (with constant stirring) add a cold saturated solution of $HgCl_2$ until a slight red precipitate is produced. Add 120 g NaOH dissolved in 120 ml. ammonia-free water, and finally add about 5 ml. saturated $HgCl_2$ solution until a slight permanent precipitate is produced, dilute to 1 litre with ammonia-free water, stand several hours and filter before use.

Standard NH_4Cl Solutions (either may be conveniently used)

(1) Dissolve 0·0382 g 'Analar' NH_4Cl in ammonia-free water and dilute to 1 litre. 1 ml. = 0·00001 g N_2.

(2) Dissolve 3·184 g 'Analar' NH_4Cl in ammonia-free water and dilute to 1 litre, take 10 ml. of this solution and dilute to 1 litre. 1 ml. of final solution = 0·0001 g NH_3.

7. Nesslerization without distillation (Newell, *J.I.S.I.*, 1945. **52**. 333–9)

The initial attack on the sample is very similar to that described

in Method 3, except that caustic soda solution is added, sufficient to precipitate all metals present as hydroxides and leave the solution alkaline. An aliquot portion is filtered off, Nessler's reagent added and also gum arabic solution (stabilizes the coloration produced). Standards are prepared from similar materials (N_2 free) and to the final alkaline solution, standard NH_4Cl solution is added, until the colour matches that of the solution under test. (For details of method see under 'Nitrogen in Steel'.)

8. Estimation of nitrates using brucine ($C_{23}H_{26}O_4N_2$) (B.D.H., *Book of Organic Reagents*, 1948)

This reagent may be used to detect nitrates or nitric acid present in very small quantities in boiler water, sulphuric acid, etc. In the latter instance it is of use in testing the suitability of a batch of sulphuric acid to be used in dissolving the ferrous alloy sample in Method 3 above.

Since nitrites give a similar effect (an orange coloration) with the reagent as nitrates, the former should be destroyed by boiling the solution under test with sodium azide thus :

$$N_3H + HNO_2 = N_2 + N_2O + H_2O$$

Any excess hydrazoic acid is volatilized during boiling. The cooled solution is treated with a few drops of a 0·02% solution of brucine in conc. H_2SO_4 (nitrate free) and the coloration matched with standards prepared from similar materials to which is added a known volume of a standard nitrate slution (e.g. 0·721 g 'Analar' KNO_3 per litre, then 1 ml. = 0·0001 g [NO_3])

OXYGEN

(O) Atomic Weight = 16·00

Metallurgical Occurrence

Oxide (and more complex oxygen-bearing) inclusions in irons, steels and ferro-alloys e.g. FeO, Fe_2O_3, MnO, Al_2O_3, SiO_2, TiO_2 etc. (oxygen content of 'killed' steels 0·002–0·03%)
Gaseous oxygen (pockets or adsorbed) in ferrous materials
Oxide inclusions in copper (Cu_2O) etc.

Methods of Determination

GRAVIMETRIC

1. *Aluminium Reduction*
   (suitable for plain C and low alloy steels and may be modified for pig irons).
2. (*a*) *Determination of oxide content by 'loss of weight in hydrogen'*
   (suitable for copper).
   (*b*) *As before but weighing the water produced.*

VOLUMETRIC

3. *Hydrogen reduction and analysis of gases produced*
   (an older and less reliable method than [1], [4] or [5] for ferrous materials).
4. *Vacuum fusion and analysis of gases produced*
   (most accurate and a standard method for all irons, steels and ferro-alloys. Hydrogen and nitrogen may be determined at the same time).
5. *Residue methods*
   (*a*) after alcoholic iodine extraction
   (*b*) after chlorine extraction
   (suitable for plain C and alloy steels with low Cr, V or Mo content and Ti absent. The C content should be less than 0·5%).

METHODS

1. Aluminium Reduction (Gray and Sanders, *J.I.S.I.*, 1938. **1.** 348; 1941. **1.** 321; 1944. **2.** 242; Gray and Sanders, Second Report Oxygen Sub-Committee, 1939. 103; Stevenson and Speight, *J.I.S.I.*, 1941. **1.** 326; 1943. **2.** 242; Pigott, *Metallurgia*, March and May, 1948)

Depends on the reduction of oxygen-bearing inclusions by heating to 1150° C. in contact with Al contained in a graphite boat either in H_2 atmosphere or under reduced pressure, followed by HCl solution of the Fe/Al alloy produced and the determination of Al_2O_3 present by filtration, ignition and weighing as such.

2a. 'Loss of weight in hydrogen' (Cartwright, Collier and Charlesworth, *Analysis of Non-Ferrous Metals and Alloys*)

A 20 g sample of copper in the form of thin sawn pieces is contained in a porcelain boat (previously heated empty in H_2) in a silica tube within a silica tube furnace and heated at 850° C. for 1 hour. A stream of pure dried hydrogen passes continuously over the sample and is burnt at the remote end of the tube. After 1 hour, remove the inner tube (containing boat and sample) from the furnace and allow to cool, with H_2 still passing. Reweigh the cold sample and report as 'loss in weight in hydrogen'.

2b. Weighing as water

The above set-up (but using 100 g samples) with an additional two U-tubes containing P_2O_5 at the H_2 exit end of the silica tube, may be used to absorb the steam produced which can then be weighed. The increase in weight of the U-tubes due to water absorbed can be related to the oxygen content of the sample thus: $H_2O \times 0{\cdot}8881 = O_2$.

3. Hydrogen reduction and analysis of gases produced (Pigott, *Metallurgia*, Feb. 1948)

The same principle as Method 2 applied to ferrous materials.

Here pure dry H_2 is passed over the sample heated to 1200° C. in a silica tube furnace. From the volumes of H_2O, CO and CO_2 produced, the oxygen content can be calculated.

4. **Vacuum Fusion** (Sloman, *J.I.S.I.*, 1941. **1.** 295 and Fourth Report of Oxygen Sub-Committee, *I.S.I.*, 1943. 235; Pigott, *Metallurgia*, Feb. and May, 1948)

This method is applicable to all ferrous materials, simple and complex and gives total O_2 (gaseous and combined). The sample, about 20 g, in rod form (1 in. × $\frac{3}{8}$ in dia.) is melted (by H.F.) in a degassed graphite crucible at 1600–1650° C. (usually) under a high vacuum (10^{-4} mm. Hg). In about 30–45 minutes most of the oxides present have reacted with the graphite and are liberated as CO (also N_2, H_2, methane and traces of O_2 are evolved). CaO, MgO and Al_2O_3 are more sluggish in their reaction and necessitate fusion for 2–3 hours. During the fusion under high vacuum some metals (Mn, Cu, Ni, Al and Mo) tend to volatilize and when condensed on the cooler parts of the apparatus give metal films which may absorb the liberated gases.

The use of a rod-like sample is necessary since milled, sawn or drilled samples occlude atmospheric oxygen on their large surface area.

A modification known as *Fractional Vacuum Fusion* is sometimes practised with a view to separating the various oxide constituents present. The process depends on the relative reducibility of the oxides by C with rising temperature, in the presence of tin as a flux. The general order of reduction of some of the more usual oxides are FeO (1050–1080° C.); MnO (1100° C.), SiO_2 (1300° C.); Al_2O_3 (1400–1600° C.). Tin, however, starts to volatilize and becomes troublesome above 1300° C.

5. **Residue Methods**

More lengthy and less reliable than Method 4, also less widely applicable. These methods depend on initial attack of the sample by a halogen and estimation of the residual oxides by microchemical or spectrographic methods.

(*a*) **Alcoholic iodine method** (Rooney, 1st–4th Reports of Oxygen Sub-Committee *I.S.I.*, 1937–1943; Pigott, *Metallurgia*, March and May 1948)

An 8–12 g sample, in the form of thin discs, is attacked at 60° C. with 70 g 'Analar' iodine dissolved in 600 ml. water-free methyl alcohol. The determination is carried out in an atmosphere of pure dry N_2 with constant stirring of the sample. The filtered residue is washed and examined by the methods outlined above.

(*b*) **Chlorine method** (Colbeck, *J.I.S.I.*, 1936. **2.** 251 ; 1st–4th Reports of Oxygen Sub-Committee *I.S.I.* ; Pigott, *Metallurgia*, March and May 1948)

The method depends on volatilizing the chlorides of the metals Fe, Mn, Si, etc., at a temperature (350° C.) which has little effect on oxide inclusions.

For high Cr steels, 500° C. is necessary for complete volatilization, or alternatively, reduction to chromous chloride (which is water soluble) by stannous chloride may be carried out.

The more usual oxide inclusions are appreciably unattacked below 700° C.

PALLADIUM

(Pd) Atomic Weight = 106·7

Metallurgical Occurrence

Ores, sweeps, residues of the precious metals
Certain dental and jewellery alloys
Certain electrical contact alloys
Palladium leaf and sponge
Palladium clad base metals for chemical plant

Source of Metal as Standard

Pd sponge = 99·98% pure is available but rarely used as standards (Johnson Matthey & Co.) (Mond Nickel Co. Ltd.)

Methods of Determination

GRAVIMETRIC

1. *Precipitation as a complex with dimethylglyoxime from acid solution*
   (applicable to most materials having up to 10% Pd—platinum metals and Ni do not interfere but gold should be absent or the method modified accordingly).
2. *Precipitation as ammonium chloropalladate*
   (suitable for Pd-rich materials).

COLORIMETRIC

3. *Comparison of the yellow colour produced with nitric acid with that from standards of similar composition*
   (suitable for estimating very small quantities, e.g. in parting beads).

METHODS

1. Precipitation with Dimethylglyoxime (Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements*)

The cold moderately (10%) acid chloride solution is diluted to about 200 ml. and should contain less than 0·1 g of the metal (for convenience in handling the bulky precipitate later) is treated with a slight excess of a 1% solution of dimethylglyoxime in 2% HCl (use weight of reagent about two and a half times weight of Pd present). Stand for half an hour, filter the orange-yellow

precipitate on a paper or a tared sintered glass crucible under suction. Wash with cold 1% HCl and finally hot water.

In the case of the filter paper, wrap up the precipitate and heat at the lowest possible temperature in a tared porcelain crucible until the paper chars. Then heat at about 800° C. to burn off the paper, finally heat the metal oxide produced, in H_2 at about 500° C. to reduce to the metal sponge, allow the temperature to fall to about 200° C. and cool off to room temperature in a current of CO_2. Weigh the residue as palladium metal.

Alternatively the precipitate on a tared sintered glass crucible can be heated at 110° C. to constant weight and weighed as the complex $[(CH_3)_2C_2NOH : NO]_2Pd$ (Complex weight : $\times$ 0·3167 = Pd).

Notes:

(1) Precipitation by dimethylglyoxime from sulphate solutions is not quite quantitative, but is completely precipitated from N/4 HCl or HNO_3 solutions.

(2) Gold is not co-precipitated if nitric acid is present in the solution before precipitation of the Pd. As an alternative therefore (in the presence of gold) precipitation of Pd from a 3% *aqua regia* solution is quite effective.

(3) If an alcoholic solution of the reagent is used, some Pt in the platinous state may be co-precipitated : the alcohol having effected the reduction.

(4) Large Pd precipitates are best redissolved in *aqua regia*, diluted to give 3% acid and reprecipitated as before. (For procedures with specific alloys consult the section on 'The Platinum Metals'.)

2. Precipitation as ammonium chloropalladate (Schoeller and Powell, loc. cit.)

For Pd-rich materials the preceding method would be unsuitable owing to the voluminous nature of the precipitate.

To the chloride solution of the metal, add 30–50 g NH_4Cl (unless already present) and slowly evaporate on a water bath with continual additions of nitric acid. This causes precipitation of the scarlet crystalline ammonium chloropalladate $[(NH_4)_2PdCl_6]$ and should leave a colourless solution when all the Pd has reacted. Cool, filter on paper washing with almost saturated NH_4Cl solution, wrap up the precipitate, heat gently to char the paper, burn off at about 700° C. and finally reduce to metal in H_2 cooling to room temperature in the process. Weigh as palladium sponge.

The final sponge should be grey in colour but may appear almost black due to superficial oxide films; in this case reheat to 200° C. under H_2 and cool, again under H_2.

The filtrate from precipitation should be tested for complete Pd removal by the dimethylglyoxime method previously described.

Since NH_4Cl also precipitates Pt and Ir as chloroplatinate (yellow) and chloroiridate (black) under similar conditions, separation is necessary—bromate hydrolysis or preliminary dimethylglyoxime treatment (see section on 'The Platinum Metals').

3. Colorimetric determination in nitric acid solutions (Schoeller and Powell, loc. cit.; Robinson, *Trans. Inst. Mining and Met.*, 1926. **35**. 423)

This method is suitable for routine determinations of minute quantities such as may be present in silver beads prior to parting. Palladium gives a yellow tint to nitric acid solutions due to the formation of palladous nitrate $Pd(NO_3)_2$. This coloration may be compared with similar solutions of known palladium content.

PHOSPHORUS

(P) Atomic Weight = 30·98

Metallurgical Occurrence

Iron ores, limestone, coke ash (as phosphates)
Pig iron, cast iron and steels (as phosphides)
Ferro-alloys
Copper and copper alloys

Source of Metal as Standard

Since most methods of estimation are gravimetric, phosphorus standards are never used except in the form of steels (and irons) of known phosphorus content

Methods of Determination

GRAVIMETRIC

1. (*a*) *Precipitation as ammonium phosphomolybdate and weighing as such* (may be used for P contents [up to 2%] in irons, ores etc., but more usual to use the volumetric finish as in Method 3).
   (*b*) *As* (1*a*) *but conversion of ammonium phosphomolybdate to lead molybdate, igniting and weighing same*
   (a more accurate method than [1a], suitable for most phosphorus-bearing materials, expecially those low in the element as in normal steels, etc.)
2. *Precipitation as magnesium ammonium phosphate and ignition to the pyrophosphate*
   (considered by many to be a very accurate method and less liable to interference from As, V, Si—suitable for all materials).

VOLUMETRIC

3. *Precipitation as ammonium phosphomolybdate, solution in excess standard alkali and titration of this excess with standard acid*
   (this is the usual routine method for P in ferrous and non-ferrous materials and may be applied to ores etc., where the P content is fairly low [say less than 5%]. For plain C and low alloy steels. Certain modifications necessary for high alloy content

METHODS

1a. Precipitation as ammonium phosphomolybdate and weighing as such

Most of the methods used for estimating phosphorus, make use of the precipitation of ammonium phosphomolybdate (yellow), somewhere in the procedure. Certain elements interfere in this precipitation, either by delaying same or by co-precipitation. Arsenic may co-precipitate as yellow ammonium arseno-molybdate when more than about 0·1% As is present, under such conditions it is better to remove the bulk of it from solution as arsine (AsH_3) by means of granulated zinc from HCl solution (original sample dissolved in *aqua regia* is evaporated, baked and dissolved up in HCl from which SiO_2 and WO_3 are filtered. Zinc is added to the filtrate). To ensure complete removal of As, the solution may be treated with ammonium bromide or hydrobromic acid which volatilizes As as the tribromide.

For the usual small amounts of As which may be present (up to 0·05%), no contamination will result if P is precipitated from a strong nitric acid solution (Pigott) of about 30% acid by volume (instead of the usual 7–10%) and with the temperature of the phosphoric acid solution below 35° C.

Tungsten unless removed prior to P precipitation would be carried down (as yellow tungstic acid) with the P precipitate. In any case if the W content is high, initial acid attack followed by baking may give tungstic acid which may hold up phosphoric acid or phosphates. This is overcome by taking up the baked residue in HCl, filtering off WO_3, SiO_2 + (P_2O_5) and treating with NH_4OH in the presence of a few mls. of 1% solution of a ferric salt (chloride or sulphate) if not already available. This NH_4OH treatment first dissolves WO_3 and P_2O_5 leaving SiO_2, then on reacidifying with HCl, adding the ferric salt and retreating with NH_4OH, WO_3 is dissolved as ammonium tungstate, but P is precipitated as ferric phosphate together with the excess iron (as hydroxide).

Silicon in normal amounts in steels does not appreciably interfere but it would then be preferable to finish the estimation volumetrically (Method 3) rather than suffer a high result due to SiO_2 present in the precipitate.

If SiO_2 is filtered off at the initial stages of acid attack and baking, it may be holding up phosphate and should be treated by H_2SO_4 and HF and any residue returned to the assay solution.

Alternatively if the solution of the sample from the initial *aqua regia* attack is not allowed to concentrate unduly, silicic acid will

be retained in its soluble form and will not contaminate the eventual P precipitate unless very prolonged standing is allowed (not more than 30 minutes is usually adequate) when contamination with gelatinous silico-molybdates is possible.

Vanadium is prevented from co-precipitation as ammonium phospho-vanadate by (*a*) reduction to the vanadyl state using 5 ml. saturated H_2SO_3 or 5 ml. 10% $NaNO_2$ solution, prior to P precipitation, (*b*) precipitating P from strongly acid solution (as is the case of As above), (*c*) removal of V (also Ti, Zr, Cb and Ta) by means of cupferron (for details of this procedure see Pigott, *Chemical Analysis of Ferrous Alloys.* p. 214).

Other points of importance in this method are :

(1) HCl should *never* be used above for initial solution, otherwise P may be lost as the volatile gas phosphine (PH_3), the usual presence of HNO_3 converts phosphides to phosphoric acid—complete conversion to orthophosphoric acid after treatment with $KMnO_4$, which also oxidizes any carbonaceous residue.

$$Fe_3P + 23HNO_3 = 3Fe(NO_3)_3 + H_3PO_4 + 14NO_2 + 10H_2O.$$

(2) Apart from the interfering elements quoted above, the presence of HCl or H_2SO_4 also retards precipitation of ammonium phosphomolybdate. Best removed by baking, or neutralize with NH_4OH. Free HNO_3 is essential for the precipitation as are ammonium salts.

(3) At no time after the addition of ammonium nitro-molybdate should the temperature of the solution be allowed to rise above about 80° C. otherwise there will be a possibility of the co-precipitation of yellow molybdic acid ($H_2MoO_4 . H_2O$).

(4) In the presence of high Cr and W contents (stainless and high-speed steels) and in the presence of Cb, treatment of the initial *aqua regia* solution with perchloric acid will take up refractory carbides and on fuming, will precipitate Si, W, Ta and Cb as their insoluble dehydrated oxides. (See procedure under 'Perchloric Acid Method for Steels'.)

Weight of sample taken should contain up to 0·05 g P. Ores are decomposed as much as possible by treatment with *aqua regia.* Any residue is filtered and washed with water. If this residue may retain any phosphorus compound, this may generally be rendered soluble by igniting, re-grinding and again igniting for a few minutes. The ignited residue may then be added to the filtrate and the whole evaporated to dryness. Add 25 ml. conc. HNO_3, boil down to about 12 ml., dilute with 12 ml. water, filter, wash and again concentrate, if necessary, to 50 ml. Heat (or cool) to 30° or 40° C. and add an excess of the ammonium-nitro-molybdate solution described below (usually 50 to 60 ml. is sufficient), also

previously heated to 30° to 40° C. Agitate thoroughly (best in a stoppered flask) for five minutes. Allow to settle 20–30 minutes. The reaction is as follows:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 23HNO_3 = [(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 2HNO_3 \cdot H_2O] + 21NH_4NO_3 + 11H_2O.$$

Filter on a sintered glass crucible that has been previously dried at 130° C. and weighed. Wash with 2% HNO_3 until free from iron. Then with 2% KNO_3 until free from acid. Dry at 130° C. weigh and continue drying and weighing at intervals, until weight is practically constant. $[(NH_4)_3 \cdot PO_4 \cdot 12MoO_3 \times 0{\cdot}0165 = P.]$

Ammonium-nitro-molybdate solution.—100 g molybdic acid (MoO_3) made into a paste with 265 ml. water. Add 155 ml. strong ammonia, and stir until everything dissolves. Add 66 ml. conc. HNO_3, stir, settle for an hour. Pour into a mixture of 395 ml. conc. HNO_3 and 1100 ml. water, with constant stirring. Allow to stand 24 hours and filter before use.

1b. Conversion of ammonium phosphomolybdate to lead molybdate, igniting and weighing same

Some degree of increased accuracy is gained by this method, since the conversion factor is much smaller than previously.

In the method given below, treatment of the ammonium phosphomolybdate precipitate with NH_4OH gives a solution containing ammonium phosphate and molybdate thus:

$$[(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 2HNO_3 \cdot H_2O] + 25NH_4OH = (NH_4)_2HPO_4 + 12(NH_4)_2MoO_4 + 2(NH_4)NO_3 + 14H_2O$$

On acidifying with HCl; orthophosphoric and molybdic acids are produced.

$$26HCl + (NH_4)_2HPO_4 + 12(NH_4)_2MoO_4 = H_3PO_4 + 12H_2MoO_4 + 26NH_4Cl.$$

When the lead acetate solution is added in the presence of ammonium acetate and ammonium chloride, first the ammonium acetate combines with any excess HCl to give acetic acid (in which lead molybdate is insoluble) and further the NH_4Cl added prevents the co-precipitation of lead phosphate.

Filtering and washing with hot water is necessary to keep in solution any lead chloride formed.

The main reaction is:

$$H_2MoO_4 + Pb(CH_3COO)_2 = 2CH_3COOH + PbMoO_4.$$

Proceed as before until the ammonium phosphomolybdate precipitate has been filtered off and washed with 2% KNO_3. Extract with a few mls. NH_4OH, washing out with hot water. To ensure complete extraction this solution may be passed again

through the filter and the residue again washed. Heat to boiling, acidify with about 10 ml. conc. HCl, add 10 ml. 4% lead acetate and pour into a mixture (also boiling) of 50 ml. saturated ammonium acetate and 10 g NH_4Cl. Filter hot, best on paper pulp, wash with *hot* water, drain, dry and ignite. Weigh as $PbMoO_4$. ($PbMoO_4 \times 0{\cdot}007 = P$.)

Remarks.—This method is only applicable for small quantities of phosphorus (not more than 2 mg). When larger quantities are present the ammoniacal solution of the phosphomolybdate may be made up to a definite volume, and an aliquot part treated as described. (See also under 'Phosphorus in Iron and Steels'.)

2. Precipitation as magnesium ammonium phosphate and ignition to the pyrophosphate

It is felt that some of the accuracy of this well known method is lost by the fact that the precipitate of magnesium ammonium phosphate sticks tenaciously to the walls of the vessel in which precipitation is performed—for that reason, scratched glassware should be avoided.

Also it requires time at high temperature to burn away the carbon filter from this precipitate before the latter is converted to magnesium pyrophosphate. Complete conversion should be tested by ignition until constant weight is achieved and then weighings should be conducted with rapidity owing to the hygroscopic nature of the precipitate.

The ore or alloy is obtained in solution with HCl + HNO_3, evaporated with HCl and filtered. The insoluble residue is ignited, extracted with HCl and the extract added to the previous filtrate. Metals of Group II are removed by H_2S and filtered off. The filtrate is boiled to expel excess of H_2S, oxidized with HNO_3, cooled and made alkaline with NH_4OH. If enough Fe is not present to precipitate all the phosphorus as ferric phosphate, add a little $FeCl_3$, again acidify with HCl and add slight excess of NH_4OH; repeat these operations until a reddish precipitate is formed. Now add acetic acid until distinctly acid, boil a few minutes, filter, wash once with hot water, redissolve in dilute HCl and reprecipitate with NH_4OH and acetic acid. Boil, filter and wash with hot water.

Dissolve the precipitate in warm dilute HCl, wash with hot water. Evaporate filtrate nearly to dryness, add 5–10 g citric acid[1] (dissolved in water and filtered). Add 5–10 ml. of 'magnesia

[1] Citric acid is added to keep Fe in solution; it is preferable to tartaric acid, since the latter tends to precipitate an insoluble magnesium tartrate which contaminates the NH_4MgPO_4.

mixture' (see below), and ammonia to slight alkalinity. Allow to stand in cold water (best on ice) until quite cold; add one-third volume of solution of strong ammonia, stir thoroughly at intervals for 15 minutes and allow to settle overnight. Filter, wash with NH_4OH (1 : 2) containing 2·5% NH_4NO_3.

Dry, ignite slowly at first, finally at 900–1000° C. until quite white. Weigh as $Mg_2P_2O_7$. ($Mg_2P_2O_7 \times 0{\cdot}2786 = P$.)

Magnesia Mixture

(*a*) Crystallized magnesium chloride, $MgCl_2 . 6H_2O$. Dissolve 110 g in water and filter.

(*b*) Ammonium chloride, NH_4Cl, 280 g, add a little Br water, then NH_4OH in slight excess and filter.

Add solution (*b*) to (*a*), then add :

(*c*) Ammonia, NH_4OH, to give a decided odour. Dilute to about 2 litres, shake vigorously, settle, and filter as required for use.

Smaller quantities can of course be prepared in the same proportions.

10 ml. of this solution precipitates about 0·15 g P_2O_5 or 0·066 g P.

3. Precipitation of ammonium phosphomolybdate, solution in excess standard alkali and titration of the excess with standard acid

A suitable weight of sample to contain up to 0·002 g P (for steels take 2 g) is dissolved in nitric acid 50 ml. (50%) or *aqua regia.* Proceed as in Method 1 to obtain a yellow precipitate of ammonium phosphomolybdate which is filtered, wash with 2% HNO_3 and then with 2% KNO_3 *until free from acid* (most essential otherwise a high result is obtained—test washings with litmus or methyl orange).

Digest the filter and precipitate (in the original vessel where the precipitate was carried out) with 50 ml. cold water and a measured excess of N/10 NaOH solution until the precipitate dissolves and gives a clear solution (about 10–25 ml. of alkali should be sufficient). Do not warm for fear that the ammonia present in solution be evolved before subsequent neutralization by the standard acid.

To the alkaline solution, add 2 drops of phenolphthalein solution (1% in 50% alcohol) and titrate with N/10 HNO_3 until the pink colour is discharged.

From the reaction :

$$2[(NH_4)_3PO_4 . 12MoO_3] + 46NaOH = 2Na_2HPO_4 + 3(NH_4)_2MoO_4 + 21Na_2MoO_4 + 22H_2O$$

(in the presence of excess NaOH)

$$3(NH_4)_2MoO_4 + 6NaOH = 3Na_2MoO_4 + 6NH_4OH$$

it appears that 1 ml. N/10 NaOH = 0·000135 g P.

The standard alkali should be checked against similar material as that of the assay except that the P content is known (e.g. a standard steel).

As an alternative the NaOH solution may be titrated against a known weight of benzoic acid or potassium acid phthalate.

N/10 NaOH.—Dissolve about 4·2 g 'Analar' NaOH in about 300 ml. water, add about 3 ml. of saturated $Ba(OH)_2$ solution to precipitate any carbonates, filter, dilute filtrate to 1 litre with boiled (to expel CO_2) and cooled water and titrate against benzoic acid (0·8 g in 20 ml. alcohol) or potassium acid phthalate (0·5 g in 100 ml. water) using phenolphthalein as indicator.

1 ml. N/10 NaOH = 0·020414 g $KHC_8H_4O_4$ (pot. acid phthalate)
= 0·012205 g $C_7H_6O_2$ (benzoic acid)

N/10 Nitric Acid.—7 ml. conc. HNO_3/litre, check against standardized alkali.

(For specific procedures see also 'Phosphorus in Iron and Steels' and 'Phosphorus in Cu and Bronzes'.)

PLATINUM

(Pt) Atomic Weight = 195·23

Metallurgical Occurrence

Native platinum ; minerals ; associated with base metal ores (e.g. Ni/Cu ores)
Jewellery, jewellers' scrap and sweeps
Certain dental and electrical alloys (contacts, sparking plugs and furnace windings Pt and Pt/Rh)
Precious metal thermocouples (Pt + Pt/10 or 13% Rh)
Catalysts for nitric and sulphuric acid making
Electrodes for electrodeposition

Source of Metal as Standard

Purified Pt sponge = 99·99% Pt is available, but rarely used as standard (Johnson Matthey & Co. Ltd., London)

Methods of Determination

GRAVIMETRIC

1. *Precipitation as ammonium chloroplatinate*
   (Ir, Rh and Pd should be absent or previously removed).
2. *Precipitation as metal by hydrazine hydrochloride*
   (with reduceable base metals absent there should be little or no contamination from Rh or Ir unless in preponderance—for small quantities of Pt)

3. *Precipitation as sulphide from HCl solution*
(not very accurate unless all Group II base metals are absent. Pd, Ru and Os may co-precipitate)

COLORIMETRIC

4. *The colour produced by reduction of chloroplatinic acid with stannous chloride is compared with standards*
(for very small quantities only and Pd should be absent).

METHODS

As mentioned in the section on the analysis of the Pt group metals, the materials submitted for analysis are usually complex in nature involving not only the Pt metals but frequently many base metals.

For accurate determinations of individual Pt metals it is usually very necessary to carry out preliminary separations firstly of the Pt metals sub-groups and then within each sub-group so that we then have the final estimation of the major metal in the presence (possibly) of small amounts of impurities.

Details of the usual methods of Pt group and sub-group separations will be found in the separate section on the subject.

In brief Pt may be separated most conveniently from its fellow members in the sub-group (Pd, Ir, Rh) by the method of bromate hydrolysis (given in 'Analysis of the Pt Group Metals') although the NH_4Cl process followed by chlorine treatment (see below) effects separation of small quantities of Pd and Rh only from Pt. Finally with Pd only to remove, the dimethylglyoxime precipitation of this metal is adequate (see also under 'Palladium').

Below are some standard methods of Pt estimation from fairly pure solutions of the metal—obtained from previous separation treatments.

1. **Precipitation as ammonium chloroplatinate** (Schoeller and Powell, loc. cit.)

About a 20% NH_4Cl solution is added to the warm Pt-bearing solution (from *aqua regia* attack or other source) slowly, to slight excess using continual agitation. Allow the solution to cool and add an equal volume of saturated NH_4Cl solution. Stand overnight and filter off the bulk of the Pt as the yellow precipitate—ammonium chloroplatinate which is washed with half-saturated NH_4Cl solution. Traces of Pt (also Ir) may remain in the filtrate which in this case should be carefully evaporated until NH_4Cl crystallizes out (a drop of 10% sodium chlorate solution being added in the process to ensure oxidation of any chloriridite). Add a little cold water to the concentrated solution so as just to dissolve the NH_4Cl crystals, stir well and stand overnight. A small dark

precipitate if formed will contain the residual Pt and all the Ir as ammonium chloriridate.

The first yellow precipitate of Pt may be ignited to the metal, but in the presence of quantities of Pd, Rh, and the base metals Fe, Ni, Cu and Bi it is advisable to purify by treatment with chlorine.

In this case the precipitate is washed off the paper with boiling water (about 150 ml. for each 1 g of Pt metals) slightly acidified with HCl, vigorously boiled and a current of chlorine gas passed through the solution (it is said that the chlorine must not be passed into a *cold* solution as there is a risk of explosion due to formation of nitrogen chloride) this rapidly dissolves the precipitate with the formation of chloroplatinic acid from which ammonium chloroplatinate is re-precipitated by evaporating to low bulk and adding NH_4Cl as before.

This precipitate is ignited (whilst wrapped in a wet filter paper to prevent spluttering) at very low temperature until all NH_4Cl is volatilized and the paper charred and burnt off (200–250° C.). After this, heat to about 700° C. for a few minutes. Although this ignition should leave Pt as a grey metal sponge, it is advisable to finish the ignition (cooling from 700–200° C.) with a hydrogen atmosphere and finally cooling to room temperature under CO_2. This ensures complete reduction to metal of any traces of contaminating Pt group metals.

2. Precipitation as metal by hydrazine hydrochloride (Schoeller and Powell, loc. cit.)

The chloride solution of Pt, free from HNO_3, is diluted to 200 ml., neutralized with sodium carbonate solution and boiled with a small excess of 10% hydrazine hydrochloride until the metallic Pt sponge has coagulated. Filter, wash with hot water and then hot 1% HCl (to remove any alkali). Ignite and reduce as in previous method.

3. Precipitation as sulphide from HCl solution (Schoeller and Powell)

A rapid stream of H_2S is passed into a hot 5% HCl solution of the Pt salt and allowed to cool whilst still passing the gas. The sulphide precipitate is filtered, washed with 1% HCl and ignited in a porcelain crucible to give the metal sponge. This should then be leached with 5% HCl, refiltered and ignited strongly to the metal sponge once more. The final residue may still contain about 0·0005 g S for each 1 g of metal weighed and it is impossible to remove it by further ignition.

It is frequently said that H_2S precipitation of the Pt group metals is unreliable owing to incomplete precipitation unless conditions of acidity, temperature, concentration and duration of 'gassing' are adequate. Because of these factors this method must *not* be considered one of great accuracy.

4. **Colorimetric method based on the reduction of chloroplatinic acid by stannous chloride** (Schoeller and Powell, loc. cit. 282 and Davis, *Tech Paper No.* 270, U.S. Bureau of Mines, 1921)

Reduction of chloroplatinic acid to chloroplatinous acid by stannous chloride gives a reddish-yellow coloration, the intensity of which varies inversely as the HCl concentration of the solution.

Thus both samples and standards should finally exist in about 2 ml. of 3% HCl (by volume) solution to which 2 drops of 50% stannous chloride solution (in 3% HCl) are added and the colours matched after standing 15 minutes.

The method is only suitable for quantities of Pt up to 0·0002 g and in the absence of Pd which gives a brown coloration under similar conditions.

POTASSIUM

(K) Atomic Weight = 39·096

Metallurgical Occurrence—of potassium compounds

Usually present in the gangue minerals of other metal ores as silicates, sulphates, chlorides etc.

Natural deposits of chloride, sulphate, and carbonates. Often found as an impurity in commercial sodium and other metal salts

Fluxes and salt baths—chloride, carbonate, borates, fluorides etc.

Source of Metal as Standard

Although potassium metal is available, it is never used as a standard because of its instability. 'Analar' standard potassium salts (e.g. KCl) may however find application

Methods of Determination

GRAVIMETRIC

1. *Precipitation as potassium chloroplatinate and weighing as such*
   (gives quite accurate results with mixtures of salts of the alkali metals [and Mg] but all other metals [and NH_4] should be removed. Suitable for small amounts of potassium).
2. *Calculation of alkali metals in mixtures of potassium and sodium chlorides after estimation of total chlorides*
   (a useful method for binary salt bath or flux mixtures or for treatment of final residues from other methods of estimation if in sufficient quantity).
3. *Determination in silicates and other insoluble material by ignition with calcium carbonate and ammonium chloride*
   (very suitable for silicate rocks, refractories etc.).

4. *Determination in silicates after decomposition with hydrofluoric acid* (an alternative to Method 3).
5. *Separation from sodium by precipitation as potassium perchlorate in strong alcohol solution*
(heavy metals, sulphates and ammonium salts should be absent. Suitable for small quantities of potassium).

METHODS

1. Precipitation as potassium chloroplatinate and weighing as such (Lindo-Gladding Method)

(A) *Chloroplatinic Acid.*—10 g platinum dissolved in HCl + HNO_3, is evaporated repeatedly on a water-bath with addition of HCl until free from HNO_3. Make up to 100 ml.

1 ml. = 0·10 g Pt.

(B) *Wash Solution.*—Dissolve 100 g NH_4Cl in 500 ml. water; add 1–2 g of powdered potassium chloroplatinate (K_2PtCl_6). Shake at intervals for 6–8 hours. Allow to settle overnight. Filter. (This gives a solution of NH_4Cl saturated with K_2PtCl_6, which cannot dissolve any further quantity of that salt, but is a solvent for Na_2SO_4 or Mg compounds which may be present and are only slightly soluble in alcohol.)

(C) *Alcohol.*—80 volumes absolute alcohol + 20 volumes water.

Preparation of Sample.—This must be free from all other metals except K, Na and Mg, and also free from NH_4. Dissolve a known weight in water and make up to a definite volume. In a normal case, 10 g of a salt (containing only soluble compounds of K, Na and Mg) is dissolved, made up to 300 ml. and boiled for a few minutes, cooled and made up to 500 ml. If turbid, filter through a dry filter.

Determination of Potassium.—Take 25 ml. or any convenient aliquot part of the prepared solution. Add an equal volume of water; acidify with a few drops HCl, and add enough of the chloroplatinic acid (A) to convert all the K and Na present into the corresponding chloroplatinates. If the quantities are not approximately known, assume that the whole of the substance is NaCl and calculate on the basis that 2NaCl (= 116·92) is equivalent to Pt (195·2) or 1 part NaCl requires 1·167 parts Pt. Mix the solutions in a small casserole or evaporating dish and evaporate on a water-bath almost to dryness. Remove from the bath and add 25 ml. 80% alcohol (C). Stir with glass rod to break up any large masses, and after about 5 minutes decant the clear liquid into a weighed alundum crucible. Treat the residue in the dish with three 10 ml. portions of 80% alcohol, stirring for several minutes after each addition, decanting as before and retaining the residue as much as possible in the dish. If the last liquor decanted shows a yellow

colour, repeat washing with alcohol until liquid is colourless. Finally, transfer all residue to the crucible by a jet of alcohol from a wash-bottle.

Wash the residue in the crucible (under slight vacuum) with 25 ml. portions of the wash solution (B), then with three 10 ml. portions of 80% alcohol. Dry the crucible for half an hour at 100° C. and weigh as K_2PtCl_6. It may be dried at 135° C. without decomposition. ($K_2PtCl_6 \times 0{\cdot}1608 = K$.)[1]

Note on the Properties of the Chloroplatinates.—At a temperature of 20° C. 1 part of K_2PtCl_6 requires about 98 parts of water, 26,400 parts of 80% alcohol, or 42,600 parts of absolute alcohol for complete solution. It is slightly soluble in ammonium chloride. When separated by evaporation of moderately dilute solutions, it is coarsely crystalline and does not contain either combined or occluded water. At temperatures above 135°–160° C. it slowly decomposes into KCl, Cl and metallic Pt. It is not appreciably hygroscopic.

$(NH_4)_2PtCl_6$ is almost insoluble in 80% alcohol.

Na_2PtCl_6 (both hydrated and anhydrous), and H_2PtCl_6 are readily soluble in 80% alcohol.

H_2PtCl_6 does not precipitate Mg from solutions of its chloride, nitrate, sulphate or other soluble salts.

2. Calculation of percentage of alkali metals in mixtures of potassium and sodium chlorides after estimation of total chlorides

The mixture, containing only the pure dry chlorides NaCl and KCl, is dissolved in water and made up to a definite volume. The chlorine is then titrated in an aliquot part (e.g. by silver nitrate with chromate indicator) and the percentage calculated.

The percentage of K may be calculated from the formula

$$K = 242{\cdot}864 - 4{\cdot}004c$$

where c = percentage of Cl.

Similarly, percentage of $Na = 3{\cdot}004c - 142{\cdot}864$.

These formulae are derived as follows :

Let a = percentage of K in the mixed chlorides
" b = " " Na " " " "
" c = " " Cl " " " "

c being known, it is required to find a and b.

[1] The factor $K_2PtCl_6 \times 0{\cdot}1603 = K$ is found to give a more correct result than the theoretical factor 0·1608 given above, owing to the formation of a certain proportion of $KHPtCl_5(OH)$ by hydrolysis of the precipitate.

Let c_1 = percentage of Cl as KCl
„ c_2 = „ „ Cl „ NaCl

Then $a : c_1 :: 39{\cdot}1 : 35{\cdot}46$,
and $b : c_2 :: 23 : 35{\cdot}46$,
or $c_1 = \frac{35{\cdot}46a}{39{\cdot}1}$ and $c_2 = \frac{35{\cdot}46b}{23}$

(i) Since $c_1 + c_2 = c$, therefore $\frac{35{\cdot}46a}{39{\cdot}1} + \frac{35{\cdot}46b}{23} = c$

(ii) Also $a + b + c = 100$

Eliminating b in equations (i) and (ii) we obtain :

(iii) $a = 242{\cdot}864 - 4{\cdot}004c$

Eliminating a in equations (i) and (ii) we obtain :

(iv) $b = 3{\cdot}004c - 142{\cdot}864$.

3. Determination in silicates and other insoluble material by ignition with calcium carbonate and ammonium chloride (J. Lawrence Smith's Method)

The finely powdered substance is heated in a platinum crucible (a long narrow form being most suitable) with an equal weight of NH_4Cl and eight times its weight of $CaCO_3$. Both reagents should be specially purified to free from alkali. In the case of silicates some such reaction as the following occurs :

$$2KAlSi_3O_8 + 6CaCO_3 + 2NH_4Cl$$
$$= 6CaSiO_3 + 6CO_2 + Al_2O_3 + 2KCl + 2NH_3 + H_2O.$$

A suitable charge is 0·5 g of the mineral. This is mixed first with the NH_4Cl, then 3 g $CaCO_3$ added and intimately mixed. The charge is then transferred to the crucible and the mortar in which the mixing took place is rinsed out with the remainder of the $CaCO_3$ (1 g), which is also transferred to the crucible. This is placed in an inclined position, with cover on, and heated very cautiously, as long as NH_3 is evolved (say for 15 minutes). It is then raised to a dull red heat and kept at this temperature for about an hour. When cool, the sintered mass is turned out into a large porcelain or platinum dish and heated with 50–75 ml. of water for half an hour, replacing water lost by evaporation. Any lumps are ground up by rubbing with a pestle.

Decant clear solution through a filter, wash by decantation with hot water, finally transfer to a filter and wash until practically free of chlorides. (If decomposition has been complete, the residue on the filter will be entirely soluble in HCl and free from alkali metals.)

To the filtrate add $NH_4OH + (NH_4)_2CO_3$, heat, filter, redissolve in HCl and reprecipitate with NH_4OH and $(NH_4)_2CO_3$. Evaporate the combined filtrates to dryness, heat for some time at

110° C., and ignite cautiously to decompose NH_4 salts. Cool, dissolve in a little water, and remove last traces of Ca by precipitation with NH_4OH and ammonium oxalate. Allow to settle thoroughly (best for 12 hours), filter, wash, evaporate filtrate with HCl in a weighed dish. Ignite and weigh. Again moisten with HCl, evaporate, ignite and weigh until constant weight is obtained. This is taken to represent NaCl + KCl.

The potassium may then be determined in this residue by any of the methods already given. When a fair amount of both chlorides is present, it may also be determined with sufficient accuracy for ordinary purposes by Method 2.

4. Determination in silicates after decomposition with hydrofluoric acid. [Berzelius (modified)]

Treat 1 g of the finely-powdered material in a platinum dish with a mixture of HCl and HF (or with H_2SO_4 and HF if the material is not decomposed by HCl). Warm gently, then evaporate on a water-bath.

If HCl has been used, evaporate to dryness. Add more HCl and again evaporate to dryness to expel excess of HF. If H_2SO_4 has been used, the mixture is evaporated to a small bulk, but not to dryness, until excess HF is expelled.

Dissolve residue in hot water, add sufficient $Ba(OH)_2$ to precipitate any magnesia and any sulphates that may be present. (If H_2SO_4 has been used, precipitate first with $BaCl_2$ so as to obtain the metals as chlorides, then add $Ba(OH)_2$.) In either case avoid a large excess. Filter and wash with hot water :

$$Ba(OH)_2 + MgCl_2 = Mg(OH)_2 + BaCl_2.$$

Heat filtrate to boiling and add $NH_4OH + (NH_4)_2CO_3$ to precipitate Fe, Al, Ca and any excess of Ba which has been added. Digest on water-bath, filter and wash with hot water. Evaporate filtrate to dryness and ignite below redness, to expel NH_4 salts. Redissolve in water and add NH_4OH, $(NH_4)_2CO_3$ and $(NH_4)_2C_2O_4$ in small amounts (to remove traces of Ba and Ca). Digest on water-bath, settle thoroughly for some hours, filter and wash with hot water.

Evaporate filtrate to dryness, and ignite at dull redness to expel ammonium salts. Dissolve residue in a little water and filter into a weighed platinum dish. Evaporate to dryness and ignite at dull redness. The residue should be white and completely soluble in water. If any insoluble material is found it must be filtered off, washed and the filtrate again evaporated to dryness and ignited, weighed and heated again, cooling in a desiccator, until constant weight is obtained.

The residue is then assumed to be NaCl + KCl and the amount of K may be determined by the methods already given.

5. Separation from sodium by precipitation as potassium perchlorate from strong alcohol solution

This method is applicable in the presence of chlorides, nitrates, alkaline earths and magnesium, and in the presence of phosphates. Sulphates and ammonium salts must be absent. Sulphates may be removed by cautious addition of N/2 $BaCl_2$, but an excess of this reagent must be avoided. Ammonium compounds are removed by evaporation and ignition.

A quantity of the substance containing about 0·15 g K is dissolved in 20 ml. hot water, and 5 ml. of 20% $HClO_4$ added. Evaporate, with stirring, on a water-bath to a syrup, add a little hot water and continue evaporation with stirring until white fumes appear. If no fumes are formed, add a little more $HClO_4$ until heavy fumes of $HClO_4$ are given off. Cool and stir with 97% alcohol (20 ml.), to which 0·2% of $HClO_4$ has been added. The crystals should be broken up somewhat, but not finely crushed, or some may pass through the filter.

Decant through a weighed Gooch crucible, which has been washed before weighing with 97% alcohol containing 0·2% $HClO_4$ and dried at 100° C. Wash the precipitate by decantation, transfer it to the filter and wash on the filter with the above alcoholic $HClO_4$ solution; finally wash with pure 97% alcohol, dry at 130° C., and weigh as $KClO_4$.

($KClO_4 \times 0{\cdot}2822 = K$.)

Caution.—Alcoholic solutions of $HClO_4$ should not be heated over a flame, as dangerous explosions may occur.

RHODIUM

(Rh) Atomic Weight = 102·91

Metallurgical Occurrence

Small quantities associated with Pt in precious metal deposits, residues from platinum refining of the anode slime from electrolytic copper and nickel processes

Rhodium-platinum alloys for laboratory apparatus, furnace windings, thermocouples, magneto contacts, rayon spinnerets etc.

Rhodium plating for decorative, protective and reflection purposes (searchlight and other mirrors)

Source of Metal as Standard

Purified rhodium sponge 99·99% Rh is available, but rarely used as standards (Johnson Matthey & Co. Ltd., London).

Methods of Determination

GRAVIMETRIC

1. *Precipitation as metal by hydrazine hydrochloride from alkaline solution*
   (for medium-small amounts of the metal in the absence of Ir and Au. Most base metals should be absent).
2. *Precipitation as hydroxide by bromate hydrolysis*
   (for most alloys with precious or base metals—Ir and Pd interfere).
3. *Precipitation as metal by zinc or magnesium*
   (for alloys with certain base metals (those not precipitated by zinc or magnesium) but preferably fairly pure materials with Pd, Pt and Ru absent).

METHODS

1. Precipitation as metal by hydrazine hydrochloride

(Schoeller and Powell, loc. cit.)

The procedure is very similar to that already described for Pt (and for Ir) except that with Rh (and Ir) the chloride solution containing the metal must be not only neutralized with sodium carbonate but rendered decidedly alkaline before the boiling with excess 10% hydrazine hydrochloride until the precipitated metal coagulates. Filter, wash the precipitate with 1% HCl, ignite in a tared porcelain crucible, reduce in H_2 and finally cool in CO_2 (just as described under Platinum).

2. Precipitation as hydroxide by bromate hydrolysis

(Schoeller and Powell, loc. cit.)

Sodium bromate in the presence of caustic alkali, precipitates on boiling, the hydroxides of Pd, Rh and Ir from a neutral chloride solution containing these metals (Pt remains in solution).

The chloride solution of the metals is evaporated to remove most of the acid and after diluting to about 500 ml. (to contain up to 0·5 g Pt metals), is boiled with 20 ml. 10% sodium bromate solution followed by 10% $NaHCO_3$ additions until the dark green solution becomes cloudy. Exact neutrality is carried out using a drop of bromo-cresol purple (changes from yellow to blue when sufficient $NaHCO_3$ is added). Add another 10 ml. of sodium bromate solution, boil 5 minutes and correct for neutrality as before using $NaHCO_3$ solution, finally add another 10 ml. of sodium bromate solution, boil 15 minutes and correct neutrality as before.

Filter off the flocculent hydroxides (Rh is dark green) of Pd, Ir and Rh if all present on a sintered glass crucible, wash with hot 1% NaCl and return crucible and precipitate to the precipitating beaker, add 20 ml. conc. HCl and simmer until precipitate is dissolved, well wash crucible (under suction with HCl to clean porous bottom).

In the absence of Ir, the chloride solution of Rh may be evaporated, neutralized with Na_2CO_3 and reduced to metal by hydrazine hydrochloride as in Method 1.

In the presence of either or both Ir and Pd, the chloride solution is nearly neutralized and first Pd precipitated with dimethylglyoxime (see also under 'Palladium'). The excess of reagent in the filtrate is destroyed by evaporation with HNO_3 and H_2SO_4 until strongly fuming. Cool and dilute to give about 35% H_2SO_4 (by volume) bring to the boil and add an excess of titanous sulphate or chloride solution which will precipitate Rh (also Pt and Pd) in metallic form whereas Ir is only reduced to the iridous condition and stays in solution.

If Ir is in predominance, a double precipitation may be necessary.

3. **Precipitation as metal by zinc or magnesium** (Schoeller and Powell, loc. cit.)

This precipitation applies only to chloride or sulphate solutions where nitrates must be absent. To the dilute solution heated to 80° C., an excess of pure powdered zinc is added and Rh together with other precious and base metals is precipitated as the metal. Filter, wash with 2% HCl, ignite and reduce in H_2 (in a porcelain crucible). Digest the ignited precipitate with 10% HCl, again filter, wash, ignite and reduce as before.

SELENIUM

(Se) Atomic Weight = 78·96

Metallurgical Occurrence

Native selenium or more usually as selenides—associated mainly with Cu, Ag and Au (pyritic) ores
0·25–1% added to copper alloys to improve machinability
About 0·25% often added to 18/8 stainless steels for similar reasons
Selenious acid (10% solution) + NaCl (1%) baths for anti-corrosion treatment of Mg alloys (against sea water)
Selenium coatings on metal rectifiers for A.C.
Selenium used in light-sensitive cells, and as a catalyst in oil hydrogenation.

Source of Metal as Standard

Selenium metal = 99·95% pure (New Metals & Chemicals Ltd., W.C.2).

Methods of Determination

GRAVIMETRIC

1. *Precipitation as selenium by SO_2*
(applicable to most materials even in the presence of small amounts of Te).

2. *Precipitation of selenious acid on ferric hydroxide by means of ammonia, with subsequent solution in HCl and precipitation by SO_2*
(applicable to small quantities of Se particularly in the presence of much Cu. As and Sb may be co-precipitated).

VOLUMETRIC

3. *Precipitation as selenium by SO_2 followed by solution in nitric acid and titration with sodium thiosulphate in the presence of potassium iodide*
(applicable to most materials including stainless steels, but large amounts of tungsten may interfere).

METHODS

1. Precipitation as selenium by SO_2

This is very reliable and the basis of most methods whether gravimetric or volumetric. Few other metals are precipitated by this reagent (see below for removal of Au, etc.), whereas reduction to metal by the reducing agents hydrazine hydrochloride or stannous chloride is liable to give contamination, Cu from use of the former and tin from the latter. Hydroxylamine hydrochloride is said (Pigott) to be an efficient precipitant but conditions of precipitation (heating at 90° C. for 4 hours in 45% HCl solution—Schoeller and Powell) may lead to loss of the metal by volatilization of the mono-chloride. It is for this reason that evaporation of HCl solutions (even in the presence of HNO_3) must be conducted with care at as low a temperature as possible.

The solution of selenium is only possible in nitric acid or *aqua regia*, both of which yield selenious acid (H_2SeO_3). HCl attack on selenides (*e.g.* in irons and steels) may result in loss of selenium as gaseous hydrogen selenide (H_2Se) therefore the necessary presence of the oxidizing agent nitric acid.

With certain materials (some stainless steels) nitric acid or *aqua regia* may not entirely effect solution. In these instances it may be advisable to use perchloric acid as the solvent which leaves selenium undissolved in the residue (Pigott, loc. cit.; Marven and Schumb, *Ind. Eng. Chem. Anal. Edn.*, 1936. **8.** 109).

Solution of irons and plain carbon steels may also be effected by acidified copper ammonium chloride which leaves Se in the residue (see Pigott, loc. cit. and Silverman, *Ind. Eng. Chem. Anal. Edn.*, 1936. **8.** 132).

The precipitation of Se by SO_2 from HCl solutions of selenious acid gives a red precipitate at the precipitation temperature of 20° C. (according to Pigott, precipitation below 15° C. is incomplete and above 22° C. occluded impurities may be present with the Se). This form is not easily filtered but may be heated to about 70° C. which converts to the grey crystalline form of the metal which is easily filtered and is dried and weighed as such since ignition causes volatilization.

SO_2 reduction will also precipitate Te unless the HCl concentration exceeds about 35% when the Te remains in solution.

Distillation of Se as chloride ($SeCl_4$) in a stream of Cl gas serves as another useful method of separation from Te. The Se chloride may be collected in water and precipitated as usual by SO_2 as below.

If present as a selenide or other insoluble compound, the substance is digested with conc. HNO_3 or with HCl + HNO_3 and filtered. Containing not more than 0·2 g Se the filtrate is evaporated just to dryness with HCl on a water bath so that all HNO_3 is expelled. 150 ml. conc. HCl is added and the solution is diluted to 200–250 ml. then saturated with SO_2 gas, when the selenium is precipitated as a red amorphous powder. The liquid is then heated to boiling, whereupon the selenium assumes a denser black form. It is then filtered through a Gooch crucible (or collected on a weighed paper), washed with water, then with alcohol, dried at 105° C. and weighed as Se.

If tellurium is present, it will also be precipitated by SO_2 unless the solution is strongly acid with HCl (at least 50% by volume).

If the selenium be present as a selenate or as selenic acid H_2SeO_4, it must be reduced to the selenious condition by long boiling with HCl, after which it is precipitated by SO_2 as above.

(*a*) *Fusion with Alkaline Oxidizer and Subsequent Treatment with HCl and H_2S.*—Substances not completely decomposed by HNO_3 or by HCl + HNO_3 may be finely ground and 1 g mixed with 5 g Na_2O_2. The mixture, covered with a further quantity (1 g) of the flux, is fused in a nickel crucible. The melt is extracted with water. Se and Te go into solution as alkaline selenates and tellurates. In this form they are not precipitated by H_2S, but most of the interfering substances (Pb, Bi, Cu, etc.) may be removed by passing H_2S and filtering.

The filtrate is then boiled to decompose excess peroxide, strongly acidified with HCl and precipitated with SO_2 as in method above.

(*b*) *Separation from Copper, Bismuth and Antimony.*—When these metals are present they may be partly precipitated by SO_2, together with Se and Te. The impure precipitate is filtered off, dissolved in HNO_3 and evaporated to dryness. The residue is taken up with KOH solution (20%) and treated on a water-bath with ammonium persulphate in small quantities at a time, by which means selenates and tellurates are formed. The solution is then boiled to decompose excess of persulphate, acidified with H_2SO_4 and cooled. H_2S is then passed, to precipitate Cu, Bi and

Sb, and excess H_2S expelled by passing CO_2. (Se and Te are not precipitated by H_2S from selenate and tellurate solutions.) The precipitate is filtered off and the filtrate boiled, acidified with HCl and reduced with SO_2 as before.

(*c*) *Separation from Gold.*—The solution in HCl (free from HNO_3) is largely diluted and treated with oxalic acid, which precipitates the gold, leaving Se and Te in solution. After filtering, these may be precipitated by SO_2 as in Method 1.

2. Precipitation of selenious acid on ferric hydroxide by means of ammonia with subsequent solution in HCl and precipitation by SO_2 (Schoeller and Powell, loc. cit.)

2–20 g of copper alloy are dissolved in 75% HNO_3 or *aqua regia* and any insolubles are filtered off after dilution to 200 ml. with water. The filtrate is treated with about 0·5 g ferric nitrate (weight of Fe present should be at least 30 times weight of Se and Te present) and excess ammonia. Filter off ferric hydroxide and selenious acid, wash with water and dissolve in 50% HCl (do not heat above 70° C.). Pass SO_2 and finish as in Method 1 above.

3. Precipitation as Se by SO_2 followed by solution in nitric acid and titration with sodium thiosulphate in the presence of potassium iodide

The details of this method are given in the section on 'Steel Analysis' but the following points are relevant:

(1) With certain alloy steels, solution in *aqua regia* may prove slow whereas solution in perchloric acid (70%) may be more effective, especially as the latter reagent leaves Se undissolved. However, when tungsten is present this is also left as a precipitate with perchloric acid.

(2) Selenious acid, produced from solution of Se in nitric acid, reacts with the potassium iodide added, to liberate iodine and metallic selenium thus:

$$H_2SeO_3 + 4KI + 4HNO_3 = Se + 2I_2 + 4KNO_3 + 3H_2O.$$

The iodine is then titrated to a colourless end-point in the presence of starch solution (as indicator).

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI.$$

Under these conditions: 1 ml. N/10 $Na_2S_2O_3$ = 0·00198 g Se.

(3) According to some authorities (Pigott) the solution to which potassium iodide is added prior to titration should be diluted to about 400 ml. to prevent occlusion of iodine by the precipitated selenium.

SILICON

(Si) Atomic Weight = 28·06

Metallurgical Occurrence

Aluminium and its alloys
Magnesium and its alloys
Certain copper alloys (silicon bronzes, Everdur etc.)
Irons and steels
Ferro-alloys
Stellite
Slags
Ores
Clays
Refractories (containing SiO_2, silicates and possibly silicon carbide)

Source of Metal as Standard

Metallic silicon is available but never used as an analytical standard.

Methods of Determination

GRAVIMETRIC

1. *Solution in suitable solvent followed by dehydration of silicic acid to silica, ignition and final volatilization as tetrafluoride*
   (this is the standard method and applies to all types of materials both metallic and refractory and with high and low silicon content).

COLORIMETRIC

2. *Comparison of the colour produced by ammonium molybdate with that produced in standard solutions of known silicon content*
   (widely used for routine analysis of Al alloys with up to 14% Si).

METHODS

1. Solution in suitable solvent followed by dehydration and ignition of silica and final volatilization as tetra-fluoride

The choice of solvent is of course entirely dependent upon the material being analysed. In general, aqueous caustic solutions are used for Al and its alloys, nitric acid for Mg and its alloys and mixtures of nitric, HCl and H_2SO_4 for Cu-based alloys.

With steels, it depends on the alloying elements present, thus with plain C steels and cast irons use HCl alone, and for low alloy steels HCl and later HNO_3 should be adequate, whereas high Cr steels require dilute H_2SO_4 or perchloric acid attack and high W steels (e.g. high-speed steels) require the presence of phosphoric as well as sulphuric acid to keep the tungsten in solution as phospho-tungstic acid $H_3[P(W_3O_{10})_4]_n \cdot H_2O$. More refractory materials such as ores, slags, clays, refractories, etc., usually require fusion with alkali carbonates or alkaline oxidants (Na_2O_2) to obtain solution of silicon as alkali silicates which is then acidified and finally the silicic acid produced in all cases is dehydrated to silica usually by fuming with sulphuric acid (perchloric acid acts

similarly) or by baking; in the latter instance take care not to bake excessively or at too high a temperature (200° C. max.) in the presence of Cr steels otherwise chromic oxide may be formed which is difficult to redissolve, similarly basic Cr sulphate may form on fuming with H_2SO_4—this is also fairly insoluble.

Apart from the possibility of WO_3 co-precipitation with SiO_2 during dehydration (except when H_3PO_4 is present as above), Ta, Cb and to some extent V and B also give dehydrated oxides. In the case of Ta, Cb and V, the Si is determined by loss in weight after volatilization with HF in the presence of H_2SO_4 (or oxalic acid). When B is present this is removed after the first baking, by leaching in HCl and evaporating in the presence of 25 ml. methyl alcohol when volatile methyl borate is produced [$B(OCH_3)_3$].

In all cases when complex carbides may be present (Cr, V, etc.) these must be treated during HCl or H_2SO_4 solution with conc. HNO_3 to break up and oxidize such carbides.

Elemental silicon will only dissolve in caustic alkali solutions or HF + an oxidant (HNO_3), in the latter case there is first conversion to silica then to the tetra fluoride (SiF_4). In high Si/Al alloys (12–14% Si) it often happens that Si occurs both in the 'amorphous' and crystalline 'graphitic' states and in this case, normal mixed acid attack leaves 'graphitic' Si unaltered whereas the 'amorphous' variety forms silicic acid. At the later dehydration and ignition stages it is only the silicic acid portion which is converted into SiO_2. Alternatively if the initial attack is by fusion with caustic alkali and the resulting alkali silicate solution is 'fumed' with H_2SO_4, the whole of the Si is converted first to silicic acid and then to SiO_2 (during fuming).

If, however, initial acid attack has been used and the dehydrated and ignited residue (of SiO_2 + Si) is weighed, first treat with 5 ml. HF + 0·5 ml. H_2SO_4, fume to dryness, reignite and weigh—loss in weight was due to SiO_2 in the original residue. Next treat this residue with 5 ml. HF + 0·5 ml. HNO_3 and repeat the fuming and ignition and weigh—loss of weight in this case represents *Si* present in the original residue. Silicon in the form of silicides (of Fe, Mn, Ca, etc.) in ferrous materials easily dissolve in HCl or H_2SO_4 to give silicic acid H_2SiO_3 which on baking or fuming is dehydrated thus:

$$H_2SiO_3 = SiO_2 + H_2O.$$

The ignited SiO_2 residues may be weighed as SiO_2, but sinec this is so liable to contamination from the oxides of Fe, Cr, W, Ta, Cb and insoluble sulphates and chlorides of Pb, Ba, Ca, it is most advisable to volatilize the SiO_2 as the volatile tetra-fluoride

by treatment with HF and record Si (or SiO_2) by loss in weight after reignition.

$$4HF + SiO_2 = SiF_4 + 2H_2O.$$

The volatilization is usually done in the presence of sulphuric or oxalic acids which retains Fe, Ta, Zr as sulphates or oxides and prevents their possible volatilization as fluorides. (Specific methods for estimating Si in : irons and steels ; ferro-alloys ; Al and Mg alloys ; Cu based alloys ; slags ; clays and refractories will be found under the appropriate sections elsewhere in this book.) Below are some selected methods for Si estimation in complex ores. Method (A) should *not* be used where extreme accuracy is essential.

(A) In cases where the ore contains sulphides of the heavy metals or other substances capable of attacking platinum, a preliminary treatment is necessary. Sometimes roasting in an open dish to remove S and the bulk of the As is sufficient, but where Pb, Bi, Hg, etc., are present it is best to proceed as follows. Evaporate a weighed quantity (0·5–1·0 g) of the finely-ground ore in a porcelain dish to complete dryness, with HCl + HNO_3, using relatively more HNO_3 if much S is present. Heat for some time at 150° C. Take up with water, adding 1–2 g NH_4Cl if Pb is present. Boil, filter, wash with hot water and dilute HCl. The residue should be practically free from sulphides. (When heavy sulphides or reducible metals are absent this preliminary treatment is omitted.)

Dry, ignite, mix in a platinum crucible with a mixture of alkali carbonates. This is usually known as 'fusion mixture' and contains 6 parts Na_2CO_3 and 4 parts K_2CO_3. The quantity of 'fusion mixture' used should be about ten times the weight of the dry residue, a portion of it being reserved for a cover. If any sulphide is still present, add a little KNO_3. Heat slowly over a small bunsen flame, or at the mouth of a muffle until all violent action ceases and the crust on the surface shows signs of fusion at the edges. The temperature may now be gradually raised until finally, at a good red heat, the contents of the crucible are in tranquil fusion and there are no signs of lumps or effervescence. Cool and extract with hot water. The cake may sometimes be detached by suddenly chilling the crucible while still fairly hot, by partly immersing in water, or by allowing a drop of water to fall at the edge of the solidified melt inside the crucible, when the greater part of the contents may be at once turned out into a suitable dish. The crucible is then rinsed out with a little hot water or dilute HCl. (If barium is present HCl should not be used ; in this case the melt is dissolved in water alone, and filtered before proceeding further.)

Otherwise, add HCl in excess, and evaporate to dryness, finishing slowly (not above 150° C.).

To the dry residue add 5–10 ml. conc. HCl, allow to stand, after stirring, for about ten minutes, dilute, heat to boiling, settle, filter, wash with warm dilute HCl. If the residue is now quite white it may be ignited and weighed as SiO_2. ($SiO_2 \times 0{\cdot}4672 = Si$.)

If the residue is not perfectly white it should be fused, after weighing, with a further quantity of 'fusion mixture' and the treatment with HCl and evaporation repeated.

(B) *Exact Method for the Determination of Silica in Silicate Rocks, Ores and similar Material.* (Fusion with alkali carbonates and repeated evaporations with HCl.) (Treadwell and Hall, 4th Edn., 485–489 and 491–493 ; Low, loc. cit.)

The ore is treated as in the previous method and fused with Na_2CO_3 or with $Na_2CO_3 + K_2CO_3$ as there described. (A blank assay should be made on the reagents and any silica found deducted from the final result.)

Treat the extract of the melt with dilute HCl. Evaporate to dryness in a porcelain dish on the water-bath, stirring frequently until dry. Moisten with concentrated HCl. Let stand at least twenty minutes. Add water, heat to boiling, stir, settle, decant through a filter. Wash three or four times by decantation with hot water, then transfer residue to filter, wash free of chlorides. (Test a drop of filtrate with $AgNO_3$.) Remove any brown stain (due to Mn) that may appear on the paper by adding a little conc. HCl and washing with hot water. Finally, drain the residue by suction (by means of vacuum pump), dry and ignite as in previous method.

Evaporate the filtrate to dryness on a water-bath ; digest on the water-bath one to two hours ; moisten with HCl, allow to stand not more than fifteen minutes. Add hot water, filter on a small paper, dry and ignite.

For very exact results a third evaporation of the filtrate is necessary.

Ignite the filters with residues (separately or together) in a platinum crucible, finally for thirty minutes or more over a blast lamp and weigh as SiO_2.

(C) *Determination of Silica in Minerals containing Barium and (or) Fluorides* (Berzelius).—[Fusion with alkali carbonate, treatment of filtrate with ammonium carbonate and zinc oxide, extraction with HCl and ignition to SiO_2.]

Fuse with alkali carbonates as in either of above methods, extract thoroughly with hot water and filter off the insoluble residue [$BaCO_3$, etc. = (a)].

To the filtrate add about 4 g $(NH_4)_2CO_3$, heat to 40° C. for some time, and settle overnight. Most of the SiO_2 is precipitated. Filter [residue (b)], wash with water containing $(NH_4)_2CO_3$.

To the filtrate add 1–2 ml. of an ammoniacal solution of ZnO, boil off excess of NH_4OH and filter. The remaining SiO_2 is precipitated as a silicate of zinc, mixed with $Zn(OH)_2$. Wash with water, rinse into a dish, dissolve in HCl, extracting the filter paper with the same, evaporate on a water-bath, take up with dilute HCl, filter and wash [residue (c)].

Dissolve residue (a) in HCl, evaporate and separate SiO_2 in the same way. Add the residues (b) and (c) and ignite all together. Weigh as SiO_2.

Note: With material of this class, direct evaporation of the melt with HCl would result in loss of Si by volatilization as SiF_4.

2. Colorimetric method using ammonium molybdate (*Chemical Analysis of Al and its Alloys*, British Aluminium Company's Publication No. 405, 1947)

Attack 0·1 g of Al alloy with 10 ml. 10% NaOH in a covered Ni crucible (2 in. dia. × 1¾ in. deep). When reaction has ceased, boil down to a paste, cool, wash crucible sides and lid with water and boil gently for a minute. Cool and transfer crucible contents to a beaker containing 10 ml. 30% HNO_3 and warm until all $Al(OH)_3$ has dissolved. Cool, filter any insolubles through a No. 44 Whatman paper or a sintered glass crucible and dilute the filtrate to 90 ml. Add 10 ml. 10% ammonium molybdate solution, shake well and stand for 10 minutes until the full intensity of the greenish yellow silicomolybdic acid ($SiO_2 . 12MoO_3 . 2H_2O$) has developed.

Measure the extinction value with a Spekker absorptiometer (using filament lamp, 4 cm. cells and Chance's No. O.B.2 and Wratten No. 36 filters) which has been calibrated against standard samples whose Si content has been determined by Method 1.

Alternatively the comparison may be done visually, using Nessler glasses and standards, similarly treated.

SILVER

(Ag) Atomic Weight = 107·88

Metallurgical Occurrence

Native silver and silver minerals often associated with precious metal and base metal (Cu, Pb, Ni, Zn, As, Te) minerals

Silver alloys (with Au, Pd, Cu, Ni, Zn, Sn) for industrial, electrical, jewellery and dental (analgam) purposes

Special white metal bearing alloys

Source of Metal as Standard

Fine silver = 99·98% Ag (Johnson Matthey & Co. Ltd., London).

Methods of Determination

GRAVIMETRIC

1. *Fire assaying of silver ores and rich silver alloys* (bullion)
   (not usually applied to low silver base metal alloys).
2. *Precipitation as silver chloride*
   (for materials rich in silver with Pb and Hg absent).

VOLUMETRIC

3. *Nepholometric method using sodium chloride* (Gay-Lussac's method)
   (routine method for silver bearing base metal bullion—Pb and Hg absent)
4. *Titration with a soluble thiocyanate using a ferric salt as indicator* (Volhard's method)
   (standard method for most alloys but Ni, Co, Hg and Cu in large quantities may interfere).

METHODS

1. Fire assaying of silver ores and rich silver bullion

Silver is generally determined in ores and similar substances by the same methods as gold, using the fire assay and usually similar fluxes. In cases where silver is the only commercially important metal, however, smaller charges may be used, hence the scorification assay is more frequently employed for silver than for gold.

Scorification Assay.—The following is given as a typical charge which may be varied according to the nature of the ore :

Ore, 0·25 *A.T.* (7·29 *g*)

Grain lead	45 g
Borax	1 g

Scorification should be carried out at a lower temperature than for ordinary gold assays.

The slag from the scorification may be cleaned by adding (say) 0·1 g powdered anthracite or charcoal before pouring. For details of assay, see 'Gold'.

Crucible Assay.—The following may be taken as typical charges for the commoner classes of ores :

(1) For siliceous ores.
(2) For basic or oxidized ores.
(3) For pyritic or sulphide ores.

Ore, 0·5 *A. T. in each*	(1)	(2)	(3)
Red lead (g) ..	22–40	22–40	30–45
Sodium Carbonate (g)	22–40	15–30	15–22
Borax (g)	7–15	7–22	7–22
Charcoal (g) ..	1–1·5	1·5–3	nil[1]

The following flux is suitable for cleaning the slags from crucible

[1] One or two strips hoop iron.

fusions. It may be added at the finish of the fusion, a little before pouring:

Red lead	20 g
Sodium carbonate	5 g
Charcoal	1 g

Wet and Dry Assays (see also under 'Gold')

(*a*) Decompose 0·5–1 A.T. of the ore with HNO_3. Add dilute HCl, avoiding an excess. Warm, settle, filter when clear. When amount of silver is small, allow to stand overnight before filtering. Fuse or scorify, and cupel the resulting lead button.

(*b*) (For low-grade material.) Treat 3–4 A.T. with HCl in a large beaker. Boil till decomposed. Add HNO_3 (say 20 ml.). Boil off red fumes. Dilute to about 2 litres; pass in H_2S till thoroughly saturated. Filter and wash with hot water.

Dry the residue and roast off the sulphur. Add about 30 ml. HNO_3, boil and dilute to 100 ml. Add 1 ml. HCl (1 : 100). Stir and settle overnight. Filter, dry and roast the residue. Flux with red lead, 100 g; charcoal, 1 g (with a little sodium carbonate and borax if siliceous material, iron, etc., are present). Cupel the resulting lead button.

Bullion Assay.—The general principle is the same as for gold. Usually both metals are determined in the same assay.

The customary charge for cupellation is 0·5 g of bullion, with 8 g lead foil. The amount of lead is increased when much base metal (copper, zinc, etc.) is present.

After a preliminary assay, a 'proof' is prepared consisting of pure silver (slightly more than the final weight of the preliminary assay), and added metals, (slightly less than the loss of weight in cupellation shown by the preliminary assay). The added metal may be copper, zinc, etc., according to circumstances. Gold, if present, is also added in amount shown by the preliminary assay.

The final assay is made on 0·5 g of the bullion, simultaneously with a 'check' or 'proof' as above. The loss of silver occurring in the cupellation of the proof is added to the weight of silver found in the final assay of the bullion to give the correct silver assay.

The final assays are generally made in duplicate, in the same cross-row of the muffle, with the corresponding 'proof' between them. Beads or cornets containing much more than 3 parts silver to 1 of gold usually break to pieces in parting, and require special care for collecting the gold.

2. Precipitation as silver chloride

This is only applicable to very rich material—substances in

which silver is a principal or important constituent. The metal is obtained in nitric acid solution. Add dilute HCl in slight excess; heat and stir till clear. Decant liquid through a small filter. Wash by decantation with dilute HNO_3, then with water until free of acid. Dry carefully. Heat to very low redness, until the material begins to show signs of fusion. Cool and weigh as AgCl.

If a paper filter has been used, the precipitate is separated as much as possible from the paper; the latter is then ignited and the ash treated successively with HNO_3 and HCl to reconvert any reduced silver into chloride. The whole is then ignited and weighed as above.

(AgCl × 0·7526 = Ag.)

3. Precipitation with sodium chloride (Gay-Lussac's Method)

This is the method commonly employed in mints, and is applicable to silver bullion, where the amount of silver is already approximately known.

The following solutions are generally used:

(*a*) Standard salt solution, 5·4162 g NaCl per litre—1 ml. = 0·01 g Ag.

(*b*) Decimal salt solution, 100 ml. of solution (*a*) diluted to 1 litre—1 ml. = 0·001 g Ag.

(*c*) Standard silver solution, 1 g pure silver dissolved in dilute HNO_3 and diluted to 1 litre—1 ml. = 0·001 g Ag.

Standardization of Salt Solution.—Weigh out exactly slightly more than 1 g of pure silver. Dissolve in dilute HNO_3, in a (stoppered) fumes bottle. Blow out nitrous fume. Add, from a standard pipette, 100 ml. of solution (*a*). Shake until clear. (Special apparatus is designed for carrying out this operation simultaneously on a number of samples.) Run in solution (*b*) 1 ml. at a time, so as to form a layer above the liquid in the bottle, noting if there is a cloudiness at the junction of the two solutions. Shake until clear, and continue adding (*b*) until no cloudiness appears. The amount of (*b*) used, divided by 10, gives the amount of solution (*a*) which should have been added to the 100 ml. used, to give complete precipitation of the silver.

If there is no cloudiness, add a measured volume of solution (*c*) and then proceed as above, correcting for amount of solution (*c*) added.

Bullion Assay.—Take a quantity containing a little more silver than would be precipitated by 100 ml. of solution (*a*) and proceed exactly as in standardizing. The operation should, if possible, be done simultaneously with the standardization, as the volumes of solution used are affected by temperature.

Note: In routine working on a large number of samples, standards are made up corresponding very closely to the composition of the alloy being analysed. After the addition of 100 ml. of solution (*a*) and shaking to coagulate the silver chloride, 1 ml. of 'decimal' salt solution (*b*) is added to standards and assays and with experience one is able to judge by the depth and intensity of the 'cloud' produced how much extra of solution (*b*) is needed to precipitate all the silver.

4. Titration with a soluble thiocyanate using a ferric salt as indicator (Volhard's Method)

The silver is obtained in a nitric acid solution. Standard potassium or ammonium thiocyanate is run in from a burette until a permanent reddish-brown colour is produced with the indicator (ferric nitrate, ferric sulphate or ferric alum)—

$$AgNO_3 + KCNS = AgCNS + KNO_3$$
$$Fe_2(SO_4)_2 + 6KCNS = 2Fe(CNS)_3 + 3K_2SO_4$$
1 ml. N/10 KCNS = 0·010788 g Ag

The thiocyanate cannot be prepared of exact strength by weighing a known quantity of the salt, owing to its deliquescent nature, but it may be standardized on a known weight of pure silver, and adjusted by dilution to any required strength. A solution containing 9·7 g KCNS per litre will be approximately N/10.

The silver must be in nitric or sulphuric acid solution, and a little free HNO_3 should be present, but nitrous acid must be removed, as this itself produces a red colour with the thiocyanate. Mercury, nickel and cobalt interfere, and copper in large amount obscures the end-point. Mercury must be absent since this element reacts similarly to silver. Copper, nickel and cobalt only interfere by giving coloured solutions which, if intense, mask the colour of the end-point.

Indicator solution.—A saturated solution of ferric alum with sufficient nitric acid added to decolorize and prevent hydrolysis to ferric hydroxide.

SODIUM

(Na) Atomic Weight = 22·997

Metallurgical Occurrence

Rock salt, nitre, borax, cryolite etc. etc. (natural salts and minerals)
Present in the gangue minerals of other ores
Fireclays
Fluxes
Present in Mg, Al and Al/Si alloys
Coal and coke ash

Source of Metal as Standard

Metallic sodium is never used. 'Analar' sodium chloride is used in certain analytical procedures.

Methods of Estimation

GRAVIMETRIC

1. *Conversion to chloride or sulphate and determination of the acid radical* (applicable to all materials especially fluxes, sodium compounds and other non-metallic materials).
2. *Sodium sulphate method* (applicable to Al and Al/Si alloys).
3. *Distillation or vacuum distillation of sodium and its precipitation with zinc uranyl acetate* (most accurate method for Al and Mg alloys).
4. *Solution in amyl alcohol and precipitation with zinc uranyl acetate* (applicable to all light alloys).
5. *Precipitation with zinc uranyl acetate after precipitation of Al as chloride* (applicable to Al and Al alloys).

METHODS

1. Conversion to chloride or sulphate and determination of the acid radical

Sodium is nearly always estimated indirectly. The Na and K, freed from other metals and from NH_4, are converted into chlorides or sulphates, ignited and weighed. The chlorine or SO_4 is then determined in the whole, or an aliquot part, of the substance, and the amounts of K and Na found by calculation. Alternatively, the K may be precipitated as chloroplatinate, K_2PtCl_6, and calculated to KCl (or K_2SO_4 as the case may be). Deducting the amount of KCl or K_2SO_4 from the total of the mixed chlorides or sulphates, the remainder represents NaCl or Na_2SO_4.

Formulae for Calculation of Sodium from Mixed Chlorides, after titration of Chlorine.—Let p = percentage of chlorine in mixture of NaCl and KCl. Then

$$\text{Na} = 3{\cdot}004\text{p} - 142{\cdot}864\,; \quad \text{Na} \times 2{\cdot}5417 = \text{NaCl}$$

$$\text{NaCl} = \frac{\text{p} - 47{\cdot}559}{0{\cdot}13098} = 7{\cdot}6354\text{p} - 363{\cdot}1231$$

(For derivation of these formulae see under 'Potassium'.)

Formulae for Calculating Sodium from Mixed Sulphates, after determination of SO_4.—Let p = percentage of SO_4 in a mixture of Na_2SO_4 and K_2SO_4. Then, by a similar calculation,

$$\text{Na} = 2{\cdot}5915\text{p} - 142{\cdot}8575\,; \quad \text{Na} \times 3{\cdot}0883 = \text{Na}_2\text{SO}_4$$

$$\text{Na}_2\text{SO}_4 = 8{\cdot}0033\text{p} - 441{\cdot}1868$$

2. Sodium sulphate method (British Aluminium Company's Publication No. 405, 1947).

Digest 30 g in a weighed dish, with 250 ml. water and 10 ml. of

a saturated solution of $HgCl_2$; add 400 ml. of HNO_3 (70% by volume); evaporate to about 600 ml.; filter the crystals through a porcelain funnel. Collect filtrate in a smaller dish; wash with 70% HNO_3; evaporate to crystallize; filter the crystals on a platinum cone in a silica funnel; wash with 70% HNO_3; collect filtrate in a $3\frac{1}{4}$ in. quartz basin. Add 2 ml. conc. H_2SO_4. Heat to fumes. Cool; add 10 ml. conc. NH_4OH, stir, stand overnight, warm, filter through 1 in. diameter paper into a weighed platinum basin; wash with hot water. Add 0·5 ml. H_2SO_4, evaporate, ignite; add 2 ml. of saturated $(NH_4)_2CO_3$; dry, ignite, weigh (W_1). Digest with hot water and filter (filtrate F) through small paper. Transfer residue back to dish, ignite, weigh (W_2).

$W_1 - W_2 =$ impure Na_2SO_4.

Determine Al, Fe and Mg in filtrate F. Deduct from $W_1 - W_2$.

Difference $= Na_2SO_4$.

$Na_2SO_4 \times 0{\cdot}3243 = Na$.

Run blank on reagents and deduct any Na found.

3. **Distillation of sodium and its precipitation with zinc uranyl acetate** (British Aluminium Company, loc. cit.) (modified Scheuer method)

This distillation process is carried out on a lump sample weighing 5–50 g. For normal distillation, the specimen is heated to 900° C. in an iron boat contained in an iron tube closed at both ends and all contained in an electrically heated tube furnace. After 30 minutes heating at temperature, the iron tube and contents are allowed to cool, then the end caps of the tube are removed and the interior and boat thoroughly washed with water until no longer alkaline. To these washings, either add a few drops of Sofnol No. 2 indicator and titrate the sodium hydroxide present with N/100 HCl (1 ml. = 0·00023 g Na), or precipitate the sodium content as sodium zinc uranyl acetate.

Thus just acidify the filtrate with HNO_3, then neutralize with NH_4OH using methyl red as indicator. Filter off $Al(OH)_3$, wash with 1% NH_4OH. Add 25 ml. conc. HNO_3 to the filtrate and evaporate to dryness. Leach with 10 ml. hot water and evaporate once again to 1 ml. Cool to room temperature, add 10 ml. zinc uranyl acetate solution and allow to stand 20 minutes with occasional stirring. Filter through a tared sintered glass crucible (porosity 3) using only gentle suction. Wash precipitate thoroughly first with zinc uranyl acetate solution then with alcoholic wash solution and finally with 5 ml. dry ether. Dry at 100° C. for 30 minutes and weigh. Wash the crucible, under suction, with 25 ml. warm water to dissolve the precipitate, and again dry and weigh.

The difference between the two weighings represents the weight of sodium zinc uranyl acetate: ($NaZn[UO_2]_3[C_2H_3O_2]_9 . 6H_2O$) (sodium factor = 0·01495). A blank should be carried out on the reagents alone.

For vacuum distillation, the operation is conducted with a lump specimen in a graphite boat which is contained in a stoppered evacuated vitreosil tube. This tube and its contents is heated to 900° C. for one hour as before, but in this case the projecting end of the tube has a jet of cold water directed upon it from the commencement of heating—this is to condense the sodium as a metallic film on the inside of the tube. This film is dissolved in a little dilute HCl and the solution evaporated and baked 30 minutes to dehydrate any SiO_2. Take up in 10 ml. 10% HCl, filter off any SiO_2 (and graphite) evaporate filtrate to 1 ml., add 5 drops 50% acetic acid, cool to 20° C., add 10 ml. zinc uranyl acetate and complete the determination as detailed above.

Zinc Uranyl Acetate Reagent.

Solution A.—77 g uranyl acetate ($UO_2[C_2H_3O_2]_2 . 2H_2O$) is dissolved in 13·3 ml. glacial acetic acid and 410 ml. water.

Solution B.—231 g zinc acetate ($Zn[C_2H_3O_2]_2 . 3H_2O$) is dissolved in 6·6 ml. glacial acetic acid and 262 ml. water.

Heat solutions *A* and *B* to 70° C., mix and stir until clear. Stand 24 hours and filter before use.

Alcoholic Wash Solution.—95% alcohol saturated with ($NaZn[UO_2]_3[C_2H_3O_2]_9 6H_2O$).

Sodium zinc uranyl acetate is prepared by precipitating 0·1 g NaCl in 5 ml. water with 50 ml. zinc uranyl acetate (as described in the method above). The precipitate is washed with 95% ethyl alcohol and then shaken with 1 litre 95% ethyl alcohol, allowed to stand 24 hours and filtered prior to use.

4. Solution in amyl alcohol and precipitation with zinc uranyl acetate (British Aluminium Company, loc. cit.)

5 g alloy is contained in a 350 ml. conical flask connected to a reflux condenser. To the sample add 20 ml. amyl alcohol (A.R.) and 10 ml. 5% mercuric chloride solution to accelerate the reaction. Heat gently as the reaction may become vigorous. When most of the reaction has abated, add another 50 ml. amyl alcohol and boil for 10 minutes (under reflux condenser) to effect solution.

Disconnect the condenser and evaporate the excess alcohol (in a fume chamber). Cool, add 50 ml. hot water, mix and filter on a No. 41 Whatman paper. Evaporate the filtrate to dryness, leach with 10 ml. hot water, filter any insolubles, re-evaporate the filtrate

to 1 ml. and precipitate sodium zinc uranyl acetate as described in Method 3 above.

A blank should be carried out on the reagents alone.

5. Aluminium chloride precipitation followed by precipitation of sodium zinc uranyl acetate (British Aluminium Company, loc. cit.)

Dissolve 5 g alloy in 100 ml. 70% HCl ; when dissolved, cool in ice-water and saturate with a stream of dry HCl gas (made by adding conc. HCl to conc. H_2SO_4 and aspirating off the gas—these operations should be conducted in a fume chamber). Filter off the precipitate of $AlCl_3$ and wash with 50 ml. cold conc. HCl saturated with HCl gas. Evaporate the filtrate to dryness, take up in 50 ml. boiling water and oxidize any iron with a few drops of conc. HNO_3. Neutralize with ammonia and add 5 ml. 50% NH_4OH in excess. Dilute to 100 ml. and pass H_2S for 30 minutes, add 5 ml. 50% NH_4OH to maintain alkalinity, stopper the flask and allow to stand overnight. Filter, acidify with HCl adding 5 ml. excess and boil down solution to half its bulk to expel H_2S. Add 25 ml. conc. HNO_3 to destroy ammonium salts and evaporate just to dryness. Extract the residue with 10 ml. hot water, evaporate to 1 ml. and complete the precipitation of sodium zinc uranyl acetate as detailed in Method 3.

A blank should be carried out on the reagents alone.

SULPHUR

(S) Atomic Weight = 32·066

Metallurgical Occurrence

Sulphide and sulphate minerals
Slags
Sulphide and sulphate minerals in coal, coal ash, coke, coke ash
As metal sulphides in irons, steels and ferro-alloys ; copper and nickel alloys
Sulphides in ironstone and in non-ferrous mattes
As SO_2, SO_3 and H_2S etc. in fuel and furnace gases

Source of Metal as Standard

The element is never used but 'Analar' sulphuric acid is often useful.

Methods of Determination

GRAVIMETRIC

1. *Oxidation to sulphate and precipitation as barium sulphate* (applicable to all solid materials).

VOLUMETRIC

2. *Combustion in oxygen, absorption of sulphur oxides and titration with standard alkali* (rapid routine method for irons, steels and ferro-alloys).

3. *Evolution as H_2S, absorption in a suitable medium and titration of the sulphide with standard iodine solution*
(suitable for all solid materials except irons and steels rich in alloying elements).

Note: Sulphur-bearing fuel and furnace gases are usually estimated in standard gas analysis burettes such as the Orsatt apparatus. The principles involved being very similar to those used in Methods 2 and 3 above.

METHODS

1. Oxidation to sulphate and precipitation as barium sulphate

For ores and minerals not containing Pb or Ba, digest 0·5 g with 10 ml. conc. HNO_3, heating very gently at first. When most of the nitrous fumes are driven off, add $KClO_3$ in small quantities at a time, up to a total of about 0·3 g, keeping the mixture very gently boiling. When all action has ceased and the sulphides are apparently completely decomposed, boil carefully to complete dryness. (Instead of $KClO_3$, some writers recommend evaporating to dryness with HNO_3 + HCl, but this may involve some loss of sulphur in the case of minerals such as pyrites, thus: $2FeS_2 + 15O = Fe_2(SO_4)_3 + SO_3$).

Cool and add cautiously 5 ml. conc. HCl; heat gently till dissolved, adding more HCl if necessary. Boil to dryness, add more HCl and repeat the operation until nitrates and chlorates are completely decomposed.

Finally add 4–5 ml. HCl and dilute so that there are about 100 ml. water for each millimetre of free HCl. Heat to boiling. Filter off SiO_2, wash with hot 50% HCl. To the filtrate add 10% barium chloride solution drop by drop (best through a pipette) until it is in slight excess, and no further precipitate is produced. Allow to stand warm for 2–4 hours or preferably to cool down and stand overnight. Filter through a close-grained filter paper, decanting the clear liquid first and passing this through a second time. When transferring the precipitate to the paper, filter into another vessel, in case any of the $BaSO_4$ should run through, and if so return to the filter until the liquid passes clear. Finally wash about ten times, with cold 5% HCl then cold water, until the washings run off free from chlorides.

Drain and ignite the moist paper and precipitate together at a moderate red heat. The ignited precipitate should be quite white. Weigh as $BaSO_4$. ($BaSO_4 \times 0{\cdot}1374 = S$.)

For exact work, a blank determination should be made of the

sulphur in the reagents, using the same quantities of each as in the assay, and the amount found deducted in calculating the result. Modifications of method may be necessary for ores not readily decomposed by acid or those which contain Ba and/or Pb (see below).

Modification for Ores not readily decomposed by Acids. Preliminary Ignition with Alkali Carbonate and Zinc Oxide.—Ignite 0·5 g of the ore with 0·6 g Na_2CO_3 and 2·4 g ZnO in a platinum or porcelain crucible to bright redness for 20 minutes. Digest with water, boil, filter and wash with hot water. (Iron, etc., remains in the residue.) Neutralize filtrate to phenolphthalein with HCl. Add 4 ml. conc. HCl in excess. Dilute to 400 ml. Boil, precipitate with $BaCl_2$ and proceed as in above method.

In presence of Barium and/or Lead. Extraction with Ammonium Chloride, Fusion with Alkali Carbonate and Removal of Barium and/or Lead as Carbonate.—Proceed as above until HNO_3 is expelled and a solution in HCl obtained. Add only 30 ml. of water, then (if Pb is present) 5 g NH_4Cl. Filter, wash with hot water (Filtrate F). Ignite the residue, fuse with $Na_2CO_3 + K_2CO_3$, extract with hot water (Ba remains as $BaCO_3$ in the residue), filter, wash with hot water, acidify filtrate with HCl and add to (F). Cool, add $NH_4OH + (NH_4)_2CO_3$ in excess; boil, settle, filter off lead carbonate, wash with hot water. Acidify filtrate with HCl, adding 4 ml. in excess. Dilute as required, boil and precipitate with $BaCl_2$ as in above method.

In this method, the iron is precipitated and separated before precipitation of the sulphur.

Alternative Fusion Methods.—Many other fusion mixtures have been suggested for ores or other material not readily decomposed by acids alone. The following are the most important:

(*a*) 0·5 g ore, 21·4 g Na_2CO_3, 3·6 g $KClO_3$ (applicable in presence of much copper).

(*b*) 1 g ore, 1 g $KClO_3$, 2 g Na_2CO_3, 4–6 g MnO_2. Ignite in crucible lined with MgO. The mixture sinters at 800° to 900° without fusing. (W. G. Waring.)

(*c*) 0·5 g ore, 5 g Na_2O_2, 4 g Na_2CO_3 in nickel or iron crucible. (W. Hempel and others.)

[For high S materials, *e.g.* Cu matter or pyrites, use 0.3 g and fuse with 10–15 g Na_2O_2.]

In all cases the fused or sintered material is extracted with water, excess of oxidizer removed, solution neutralized with HCl, adjusted to suitable acidity and dilution, and precipitated by $BaCl_2$ as already described.

For ferrous alloys, oxidation of sulphides present to sulphates

is effected usually by an initial attack with HNO_3 + HCl in the presence of KNO_3 or $KClO_3$ to ensure complete oxidation of sulphides and decomposition of alloying carbides.

Final precipitation of $BaSO_4$ is best done with the assay solution and $BaCl_2$ solutions hot so that the final precipitate is coarsely crystalline and easily filtered. To ensure this and to minimize solubility in the HCl present, the acid concentration prior to $BaCl_2$ addition should not exceed 2–3% HCl (by volume). Furthermore, it is found that in the presence of large amounts of ferric iron, there is a slight solvent action on the $BaSO_4$ precipitate and the possibility of co-precipitation as $([BaFe]SO_4)_4$ (Pigott) which on ignition gives $BaSO_4$ and Fe_2O_3 with corresponding low results.

High Cr steels may give basic chromates on baking and this may in turn cause contamination of the $BaSO_4$ precipitate by co-precipitation of barium chromate.

To minimize these possibilities of Fe and Cr contamination, it is advisable to add zinc (dust or granulated) to the acid solution after baking and prior to dilution and precipitation, this will reduce ferric iron to the ferrous state and chromates to chromic salts.

Where the sulphur content of the material to be analysed is likely to be less than 0·02% it is advisable to add a known amount of sulphate (N/100 H_2SO_4 is convenient) prior to $BaSO_4$ precipitation to ensure complete precipitation and to obtain a workable precipitate. (For full details of method for ferrous materials see under 'Iron and Steel'.)

Notes:

(1) Sulphur in coal or coke is usually determined either by (*a*) *Eschka's Method* by fusion of 1 g samples with 3 g of a mixture of two parts by weight of light calcined MgO and one part of pure anhydrous sodium carbonate carried out in a silica or porcelain crucible at approximately 800° C. for 1–2 hours. Leach out the solidified melt with hot water, add 10 ml. saturated bromine water and 15–20 ml. conc. HCl. Boil out excess bromine, filter insolubles and wash with water. Neutralize the filtrate (200–250 ml.) with ammonia, just acidify with HCl (to give approximately 2% of total volume) and heat to boiling. Add a slight excess of a hot 10% or 20% $BaCl_2$ solution (10 ml. 10% $BaCl_2$ = 0·13 g S), stir vigorously, stand in the warm 2–4 hours or overnight, filter on a Whatman No. 42 paper washing with cold water until free from chlorides. Dry and ignite at 800–900° C. and weigh as $BaSO_4$ (S factor = × 0·1374).

A blank should be run on the reagents used.

or (*b*) *Bomb calorimeter method* (more accurate method)—here the washings of the interior of the bomb after combustion of the fuel in oxygen are collected, a slight excess of a sodium carbonate solution is added, the solution boiled down to about 10 ml., diluted to 50 ml. and filtered. Wash the precipitate with water and to the filtrate (100 ml.) add 2 ml. conc. HCl, heat to boiling, and add $BaCl_2$ solution to precipitate $BaSO_4$ exactly as described above. (For details see under section on 'Analysis of Coal and Coke'.)

(2) For sulphur determinations in coal or coke ash, digest 1–5 g in conc. HCl evaporate to dryness and bake. Take up in 2 ml. conc. HCl and hot water and filter off insolubles (mainly SiO_2) and wash with hot water. Adjust the HCl content of the filtrate to 2% (by volume) and precipitate $BaSO_4$ exactly as described above.

(3) The sulphur content of slags can usually be determined by mixed acid attack in the presence of an oxidizing agent in a similar manner to that described for steel (see section on 'Iron and Steels'.)

2. Combustion in oxygen, absorption of sulphur oxides and titration with standard alkali

The combustion furnace assembly is very similar to that used for carbon estimation in steels except that higher temperatures are necessary to evolve the whole of the sulphur as SO_2 and SO_3. Because of this, precious metal windings (Pt) for the tube furnace or 'silit' rod (or 'globars') heating is used to attain temperatures in the range 1250–1300° C. (for plain carbon and low alloy steels and irons) and 1350–1400° C. (high alloying content such as high-speed steels). The impervious combustion tube and boat should be unglazed and no bedding material (Al_2O_3 or MgO) should be mixed with the sample because of possible absorption of SO_2. With alloy steels it is advantageous to mix 0·5 g tin shot per 1 g sample to help penetration of the sample and thereby speed up the oxidation of the sulphides present.

In this respect, ferrous materials rich in Mo (more than 1%) may advantageously be mixed with about 0·5 g Co_3O_4 instead of tin shot. This reagent helps to promote oxidation and liberation of any sulphur held up as the fairly stable molybdenum sulphate (Pigott).

The combustion is complete in about 7–10 minutes with a fairly rapid stream of dried oxygen (1–3 litres/minute).

The sulphur oxide gases are usually absorbed directly into

50–100 ml. of either 0·5% H_2O_2 in which case H_2SO_4 is produced, or 0·05–0·1% neutral $AgNO_3$ solution in which case HNO_3 is generated.

In either case the acid produced is then titrated with standard alkali (N/100 or N/200 NaOH) which has been preferably standardized on a steel of known sulphur content.

The indicator used for the titration is methyl red (0·1% solution in 60 : 40 alcohol-water mixture). (For further details, see under section on 'Iron and Steel').

3. Evolution as H_2S, absorption in a suitable medium, and titration of the sulphide with standard iodine solution

The details of the assembly for this method are given in the section on 'Iron and Steels'. The principle involved is the attack on iron and manganese sulphides in irons and steels with hot 50% HCl to liberate sulphur as H_2S. With high Cr steels (e.g. stainless varieties) 25% H_2SO_4 is found to be a more suitable solvent. This method does not give easily reproducible results with the majority of alloy steels (W, Mo, Ti, Se, Te, etc., present) since these do not respond readily to the acid attack used.

With Mo in particular, sulphur is retained as the fairly inert sulphide which is not appreciably decomposed by the acid attack.

The H_2S evolved may be absorbed in a number of reagents, notably sodium hydroxide (20% solution); ammoniacal cadmium chloride solution (about 2% $CdCl_2$ in 10% NH_4OH) or zinc acetate solution (about 10% solution in 2% acetic acid containing 2% ammonium acetate) in each case producing the respective metal sulphides.

The absorbent solution is then acidified with HCl or H_2SO_4 to give 5–10% acidity and the H_2S generated in solution is titrated with standard iodine solution to a blue end-point using starch solution as indicator.

$$H_2S + I_2 = 2HI + S.$$

Alternatively add a measured excess of standard iodine solution (in the presence of starch) and titrate the excess with sodium thiosulphate solution (of similar strength) to the disappearance of the blue starch-iodide colour.

A convenient iodine solution is N/100 (1·27 g Iodine + 3 g KI/litre) when 1 ml. = 0·0001603 g S, but it is advisable to standardize on a steel of known sulphur content treated in a similar manner. (For further details see under section on 'Iron and Steel'.)

TANTALUM

(Ta) Atomic Weight = 180·88

Metallurgical Occurrence

Tantalite and columbite minerals (associated with Fe and Mn minerals)
Radio and electrical industry (as a 'getter' and in rectifier construction respectively)
Chemical plant
Rayon spinnerettes
Machine tool tips (as the sintered cemented carbide)
As an alternative to columbium for prevention of 'weld decay' in austenitic stainless steels

Source of Metal as Standard

Tantalum metal of 99·85% purity is available but never used as a chemical standard (New Metals & Chemicals Ltd., London, W.C.2).

Methods of Determination

GRAVIMETRIC

1. *Dehydration of tantalic acid to the pentoxide, with removal of silicon as the volatile fluoride*
   (for alloy steels free from Cb and W—the presence of Ti and Zr may be estimated and allowance made).
2. *Oxalo-tartrate-tannin separation of Ta from Cb in mixtures of their pentoxides* (produced by Methods [1] or [3])
   (applicable to materials containing Cb or W, but Ti absent).
3. *Precipitation as a complex with cupferron and ignition to* Ta_2O_5
   (not suitable for materials containing Cb, Ti, W or Zr).
4. *Precipitation as potassium fluo-tantalate and conversion to* Ta_2O_5
   (suitable for ores etc. with Cb and W present).

METHODS

Since the chemistry of Ta is so similar to that of Cb, the methods for the determination of Ta follow closely to those already outlined for columbium.

Method 2 below is probably the most reliable method of separating the two metals from their combined oxides which are produced from one of the remaining methods as conditions permit.

1. Dehydration of tantalic acid to the pentoxide with removal of Si as the volatile fluoride (See under 'Columbium', Method 1)

In the absence of Cb and W, the final precipitate will contain Ta_2O_5 (with TiO_2 and ZrO_2 if present). Ti and Zr are estimated in the precipitate as detailed under 'Columbium' and the corrected weight for Ta_2O_5 obtained (factor × 0·8193 = Ta). (See also 'Cb and Ta in Steels'.)

2. Oxalo-tartrate-tannin separation of Ta from Cb in mixtures of their pentoxides (See under 'Columbium', Method 2)

This has been dealt with adequately under 'Columbium'. The yellow complex of oxalo-tantalic acid with tannin is ignited to Ta_2O_5 (factor as above). (See also under 'Cb and Ta in Steels'.)

3. Precipitation as a complex with cupferron and ignition to Ta_2O_5 (See under 'Columbium', Method 3.)

The cupferron complex is brown and very similar in constitution to that produced with Cb—probably $(Ta_2[C_6H_5N_2O_2]_5)$. On ignition the pentoxide is produced. (See also 'Cb and Ta in Steels'.)

4. Precipitation as potassium fluotantalate and conversion to Ta_2O_5

As described under 'Columbium' (Method 4) the fusion of Ta_2O_5 (and Cb_2O_5) with potassium acid fluoride and extraction of the melt with dilute HF gives potassium fluo-tantalate (K_2TaF_7) which on boiling is converted to potassium tantalum oxy-fluoride ($K_4Ta_4O_5F_{14}$). When filtered and treated with conc. H_2SO_4 to expel HF and finally diluted with a large excess of water and boiled, hydrolysis occurs and tantalic acid is precipitated. The constitution of tantalic acid is uncertain but it is best considered as a hydrated oxide which on ignition yields Ta_2O_5. (Cb is far less easily hydrolysed on diluting and boiling the sulphuric acid solution and therefore tantalic acid is precipitated in a fairly pure state.)

Note: Most tantaliferous minerals do not respond to acid attack (except in the presence of HF) and thus fusions are usually performed. NaOH or KOH fusions in Ni or Ag crucibles give on extraction with water a clear solution of potassium or sodium tantalate—$7Na_2O \cdot 5Ta_2O_5 \cdot 24H_2O$ (Pigott) from which dilute H_2SO_4 precipitates the hydrated oxide ('tantalic acid').

Potassium pyrosulphate fusions are said to produce basic tantalum sulphate which on extraction with water hydrolyses to tantalic acid (this is assisted by the small addition of NH_4OH).

TELLURIUM

(Te) Atomic Weight = 127·61

Metallurgical Occurrence

Native tellurium and as tellurides associated with Cu, Ag and Au ores
As with Se, added to steels and copper to impart free machining properties
0·05% Te added to Pb refines grain size and improves mechanical properties (used for cable sheathing, chemical plant and battery plates).

0·1% Te added to Sn base bearing alloys to increase strength
0·05–0·1% Te added to cast irons for inhibiting graphitization thereby giving greater depth of chill (e.g. for rolls, car wheels etc.)

Source of Metal as Standard

Tellurium metal = 99·9% + Te (New Metals & Chemical Ltd., W.C.2).

Methods of Determination

GRAVIMETRIC

1. *Precipitation as Te by SO_2 and hydrazine hydrochloride*
   (applicable to all materials even with Se present).
2. *Precipitation as the dioxide*
   (general application even in presence of Se [preferably small amounts of Se]).

VOLUMETRIC

3. *Oxidation to telluric acid by potassium dichromate*
   (general application, Se does not interfere, but metals which are also oxidized or react with $K_2Cr_2O_7$ should be absent).

METHODS

The similarity in chemical behaviour to that of Se is most marked and in general both metals will be present in the material being tested. The methods below are for separating such combinations, but reference should also be made to the section on 'Selenium'.

1. Precipitation as Te by SO_2 and hydrazine hydrochloride (Schoeller and Powell, loc. cit.)

As with Se, SO_2 precipitates Te from HCl solution of tellurous acid but only if the HCl concentration is below 25% (by volume). Thus precipitate Se first from strong HCl solution (80%) of the mixed metal acids (in the -ous condition), filter and wash with water, alcohol and ether. Te in the filtrate is less easily precipitated by SO_2 even on dilution of the acid concentration and therefore a combination of SO_2 with hydrazine hydrochloride should be used.

Dilute the filtrate to give 25% HCl, boil and add 15 ml. of saturated SO_2 solution and 10 ml. 15% solution of hydrazine hydrochloride and finally a further 25 ml. of the SO_2 solution. Boil 5–10 minutes when all the Te is precipitated as the metal (black). Filter on a tared filter, wash with water until acid free, then with alcohol. Dry at 105° C. and weigh as Te.

Note: The initial concentration of (Se + Te) prior to precipitation should not exceed 0·25 g/100 ml. solution.

2. Precipitation as tellurium dioxide (Schoeller and Powell, loc. cit.)

The slightly acid solution of the chlorides of metals present (for Te and Se this is achieved by HNO_3 attack on the metals, followed

by careful water-bath evaporation to dryness and solution of the residue in the minimum HCl) is diluted to 200 ml. with hot water, made slightly ammoniacal and then faintly acid with acetic acid. On boiling TeO_2 is precipitated (white) but Se remains in solution. Cool, filter on a tared filter, wash with warm water and dry at 105° C. Weigh as TeO_2 (factor × 0·80 = Te).

3. Oxidation to telluric acid by potassium dichromate (Lenher and Wakefield, *Jnl. Amer. Chem. Soc.*, 1923. **45**. 1423 ; Schoeller and Powell, loc. cit.)

The solution of tellurous acid in HCl (e.g. from initial HNO_3 attack or filtrate from Method 1 after Se precipitation) is diluted to 200 ml. to give about 8% HCl (by volume). To the cold solution add a measured excess of N/10 $K_2Cr_2O_7$, stand half an hour, then add a measured excess of N/10 ferrous ammonium sulphate and titrate the excess ferrous salt with N/10 $K_2Cr_2O_7$ using diphenylamine or Na diphenylamine sulphonate (3 drops) internal indicator in the presence of $H_2SO_4 + H_3PO_4$ (see under 'Iron').

The total $K_2Cr_2O_7$ solution used minus the volume of ferrous solution added gives the amount of $K_2Cr_2O_7$ used to oxidize the tellurous acid thus :

$$2CrO_3 + 3TeO_2 = Cr_2O_3 + 3TeO_3$$

1 ml. N/10 $K_2Cr_2O_7$ = 0·00638 g Te.

THALLIUM

(Tl) Atomic Weight = 204·39

Metallurgical Occurrence

Minerals
Flue dust from pyrites burners
Thallium-lead special electrical fuses
Silver-thallium tarnish resisting alloys
Thallium-tin-lead alloys—anti-corrosive tank linings

Source of Metal as Standards

Thallium metal = 99·99% pure (New Metals & Chemicals Ltd., W.C.2), (Johnson, Matthey & Co. Ltd.).)

Methods of Determination

GRAVIMETRIC

1. *Precipitation from alkaline solution as thallous chromate*
   (applicable in the absence of Zn, Ni, Co, Cd, Pb, Mn, Bi, Cu, Ag).
2. *Separation as sulphate and precipitation as thallous iodide*
   (Pb, Hg and Group II metals are removed in the process).
3. *Precipitation as a thionalide complex*
   (Hg, Bi and Pb would interfere unless precautions are taken).

METHODS

1. Precipitation from alkaline solution as thallous chromate

The metal is obtained in a neutral or faintly ammoniacal solution, and precipitated by addition of K_2CrO_4:

$$2TlCl + K_2CrO_4 = Tl_2CrO_4 + 2KCl.$$

The precipitate is washed with 1% NH_4OH containing 1% K_2CrO_4; in some cases, as when Zn, Ni, Co or Cd are present, the precipitate should be redissolved in HCl and re-precipitated by NH_4OH, finally weighing as Tl_2CrO_4 after washing with 50% alcohol and drying at 120° C.

Other metals, such as Pb, Mn and Bi are separated as phosphates before precipitation of the thallium. Cu and Ag may be kept in solution by adding KCN to the ammoniacal solution. Sn is separated by hydrolysis with NH_4NO_3 and CH_3COOH.

$$Tl_2CrO_4 \times 0{\cdot}7789 = Tl.$$

2. Separation as sulphate and precipitation as thallous iodide

Dissolve the ore in *aqua regia*, add conc. H_2SO_4 and evaporate to fumes. Dilute and pass H_2S to remove metals of second group; filter, wash, boil off excess H_2S. Nearly neutralize the solution with Na_2CO_3 and add an excess of KI. Thallium is precipitated as the yellow thallous iodide, thus:

$$Tl_2SO_4 + 2KI = 2TlI + K_2SO_4.$$

Collect on a weighed filter; wash with cold water or (better) dilute KI, finally with alcohol; dry at 100° to 150° C. and weigh as TlI.

$$TlI \times 0{\cdot}6169 = Tl.$$

Metals forming insoluble iodides (Pb, Cu, Hg, etc.), in weak acid solution must be absent.

3. Precipitation as a thionalide complex (Berg and Fahrenkamp *Zeit. Anal. Chem.*, 1937. **109.** 305; Schoeller and Powell, loc. cit.)

Thionalide (thioglycollic β-naphthylamide) is said to be specific for thallium under the conditions quoted below.

100 ml. of the faintly acid solution of the metals is treated in succession with 25 ml. 20% sodium tartrate solution; 2N NaOH solution until just alkaline to phenolphthalein; 20% KCN solution until the solution contains 5% KCN and more NaOH until the solution is 2N in alkalinity. Thallium is then precipitated by adding a solution of 0·5 g thionalide in 10 ml. acetone for each 0·1

g thallium present, boil the solution and cool. The precipitate $C_{10}H_7NH \cdot CO \cdot CH_2 \cdot S \cdot Tl$ is collected on a tared sintered glass crucible, washed with cold water and then acetone, dried at 100° C. and weighed as the complex, which contains 48·6% Tl.

In the presence of Hg, Pb and Bi, 10% more precipitant is added followed by sufficient acetone to give at least 30% acetone (by volume). This treatment keeps the thionalide compounds of these metals in solution.

THORIUM

(Th) Atomic Weight = 232·12

Metallurgical Occurrence

Minerals (radioactive types often with U, Zr and Ce present)
Lamp filaments (ThO_2)
Special sparking-plug alloys

Source of Metal as Standard

Thorium metal is available 98·5% pure but thorium nitrate is more useful as an analytical standard if necessary.

Methods of Determination

GRAVIMETRIC

1. *Precipitation as oxalate and ignition to dioxide*
   (this is the standard method and is of general application. Previous separation of Ti, Zr and rare earths is often necessary since these interfere. Separation is effected by one of the following methods (A), (B) or (C).
   (A) *Iodate method*
   (B) *Thiosulphate Method*
   (C) *Hexamine Method*
   } initial methods of separation prior to oxalate precipitation.
2. *Hydrogen peroxide method*
   (alternative method to (1) but less accurate. Suitable for minerals).

METHODS OF SEPARATION

(A) Iodate method (Schoeller and Powell, loc. cit.)

Obtain Th as a nitrate solution (by treatment with HNO_3 or *aqua regia* and repeated evaporation with HNO_3) in which H_2SO_4 and H_3PO_4 may be permitted. To 100 ml. $Th(NO_3)_4$ solution add 50 ml. conc. HNO_3 followed by 100 ml. 15% KIO_3 in 50% HNO_3. Stir, stand half an hour and filter the white iodate precipitate ($Th[IO_3]_4$) washing thoroughly with 1% KIO_3 in 10% HNO_3. Dissolve precipitate in 30 ml. hot conc. HNO_3 and reprecipitate with 4 g KIO_3 in 50 ml. 50% HNO_3 when cool. Dilute with 100 ml. water and filter. Wash as before. Dissolve in HCl + H_2SO_3 (this solution will contain all the Th and any Ti and Zr if present), boil with slight excess of NH_4OH, filter off hydroxides of Th (+ Ti and Zr), wash with water, dissolve in 10 ml. conc. HCl and

reserve this chloride solution ($ThCl_4$) for the oxalate precipitation (all rare earths now absent and separation from metals of the ammonia group (+ Ti and Zr) is effected by the oxalate precipitation (see below)).

(B) Thiosulphate method (Schoeller and Powell, loc. cit.)

The chloride solution of Th (from *aqua regia* attack) containing not more than 0·25 g Th, is evaporated to dryness on a water-bath. Moisten the cake with water, evaporate again and then dissolve the cake in 200 ml. hot water. Cool, and when cold add 5 g $Na_2S_2O_3$ and heat with stirring to 85° C. Stand at 70° C. for half an hour for the hydroxide precipitate to settle and filter on a Whatman No. 41 filter. Wash with warm water and redissolve in 5 ml. conc. HCl by boiling. Filter off any S (and small amounts of Group II metals—if these preponderate, remove initially). Th in the filtrate is re-precipitated with 3 g $Na_2S_2O_3$. Filter, wash and ignite to ThO_2. ($ThCl_4 + 2Na_2S_2O_3 = Th(S_2O_3)_2 + 4NaCl$).

This precipitate may be further purified by fusion with potassium bisulphate in a silver crucible, leach with hot water and re-precipitate the hydroxide of Th with NaOH solution. This final precipitate is dissolved in 5 ml. conc. HCl as before and reserved for the oxalate precipitation.

(C) Hexamine method (Ismail and Harwood, *Analyst*, 1937. **62.** 185; Schoeller and Powell, loc. cit.)

This reagent (hexamethylenetetramine) precipitates $Th(OH)_4$ completely at a pH about 6·5 and the rare earths do not interfere. Ti and Zr, however, will co-precipitate and must be removed by a subsequent oxalate precipitation for the Th. The Th is obtained as a chloride solution and is treated with 10% NH_4OH to produce a *faint* turbidity. Clear with a few drops of 50% HCl, dilute to 200 ml., add 10 g NH_4Cl and heat to 80° C. Add slowly a 2% solution of hexamine until no further $Th(OH)_4$ precipitates. Filter, wash with 5% NH_4Cl solution and redissolve in 5 ml. conc. HCl, neutralize and reprecipitate as above. The final hydroxide precipitate is dissolved in 5 ml. conc. HCl and the Th precipitated as oxalate (see below).

METHODS OF DETERMINATION

1. Precipitation as oxalate and ignition to dioxide

The $ThCl_4$ solution from methods (A), (B) or (C) above is nearly neutralized with NH_4OH (do *not* produce a permanent precipitate). Dilute to 100 ml., heat to boiling and add a hot 4% solution

of ammonium oxalate (10–50 ml.). To the resulting clear solution add drops of 50% HCl with stirring to produce a permanent white precipitate and complete by adding a further 10 ml. conc. HCl. Stand overnight, then filter the crystalline precipitate of thorium oxalate ($Th[C_2O_4]_2 . 6H_2O$), wash with 2% oxalic acid and ignite to ThO_2, which if pure, should be white when hot and cold.

(Factor × 0·8789 = Th.)

2. Hydrogen peroxide method (Schoeller and Powell, loc. cit.)

Thorium as a nitrate solution free from chlorides and sulphates is evaporated to dryness on a water bath, the cake moistened with water and re-evaporated. Leach with hot water and to this nearly neutral nitrate solution add 100 ml. 10% ammonium nitrate solution, heat to 70° C. and add 3% H_2O_2 solution until no further white gelatinous precipitate of the peroxide is produced. Filter on a Whatman No. 41 filter and wash with 2% ammonium nitrate solution. Dissolve in minimum conc. HNO_3 and boil to decompose the peroxide. Evaporate to dryness and repeat the precipitation. Finally ignite and weigh as ThO_2.

(Factor × 0·8789 = Th.)

Note: The rare earths remain in the filtrate and may be precipitated by NH_4OH.

TIN

(Sn) Atomic Weight = 118·7

Metallurgical Occurrence

Tin minerals (cassiterite [SnO_2] etc.) often associated with W compounds
Tin base bearing alloys and type metals
Solders
Brasses, bronzes, gunmetal
Aluminium alloys
Zinc diecasting alloys
Steels—tinplate
Tinned copper wire
Tinfoil in the food industry

Source of Metal as Standards

'Chempur' tin = 99·993% pure (Capper Pass Ltd., Bristol).

Methods of Determination

GRAVIMETRIC

1. *Precipitation as metastannic acid and ignition to dioxide*
(mainly applicable to materials of less than 5% tin content [but often used up to 20% in bronzes], with As, Sb and P absent; with P present [phosphor bronzes] a modified treatment may be practised).

VOLUMETRIC

2. *Reduction to stannous chloride and titration with iodine*
(standard method for high tin content, applicable to ores, babbitts, solders, bronzes etc.—Cu, Ti, Mo, V and Cb interfere and must be removed).

DRY ASSAYING

3. *Fusion with KCN and weighing as metallic tin*
(applicable only to rich tin oxide concentrates. Other base metals present may also be reduced and enter the tin bead).

METHODS

1. Precipitation as metastannic acid and ignition to dioxide

Dissolve 2–10 g of the brass or bronze in 15–40 ml. 75% HNO_3. Cu, Zn and traces of Pb and Fe go into solution as nitrates leaving tin (As, Sb) as meta-acids and P (as tin phosphate) and W (as WO_3).

Evaporate the solution to a paste (not to dryness), dilute to 100 ml. with hot water and digest at 70° C. for half an hour. Filter through a Whatman No. 40 paper with a little filter pulp, wash the white precipitate (grey if Sb is present and yellow if W is present) with hot 5% HNO_3 and hot water until washings are Cu free.

Ignite at 700–800° C. and weigh as SnO_2 (factor × 0·7880 = Sn).

With brasses and bronzes the arsenic and antimony contents can usually be ignored as can P below 0·05% (present from deoxidation with phosphor-copper or phosphor-tin) but with P contents up to 0·25% the weight of SnO_2 must be reduced by the P_2O_5 equivalent of the P content of the material which has been determined on a separate sample by the volumetric or lead molybdate methods (see under 'Phosphorus'). With P contents above 0·25% or in the presence of more than 0·1% Sb, the alternative methods below should be used.

The essential reactions are :

$$Sn + 4HNO_3 = H_2SnO_3 + H_2O + 4NO_2$$
$$5H_2SnO_3 = H_{10}Sn_5O_{15}$$
$$H_{10}Sn_5O_{15} = \text{on ignition } 5SnO_2 + 5H_2O$$

With P present but Sb absent, treat the washed impure metastannic precipitate (prior to ignition) with 50 ml. yellow ammonium sulphide in a beaker and warm until dissolved (P_2O_5 remains insoluble). Filter, wash with 2% ammonium sulphide and to the filtrate and washings add 50% acetic acid until *just* acid. On warming, stannic sulphide and sulphur are precipitated. Filter, wash with 2% ammonium acetate just acidified with acetic acid and saturated with H_2S. Ignite the precipitate gently at first to volatilize sulphur without burning and finally heat to 700–800° C. and weigh as SnO_2.

With Sb present, dissolve the sample in *aqua regia*, carefully

evaporate to half volume, add 100 ml. water, 10 g tartaric acid and a slight excess of 30% NaOH solution. Warm to 80° C. and add a slight excess of Na_2S solution to precipitate the sulphides of Cu, Pb, Fe, Zn, etc., but Sn, Sb (and As) stay in solution. Filter and wash with 2% Na_2S. HCl is added to the filtrate until 10% acidity is reached and H_2S passed into the hot solution for half an hour. The sulphides of Sn, Sb (and As) are precipitated, washed with 2% ammonium nitrate solution and redissolved in 50% HCl (with a few crystals of $KClO_3$ if necessary). To the clear solution add 3 g tartaric acid, neutralize with ammonia, add 15 g oxalic acid and pass H_2S through the hot solution diluted to 250 ml. Antimony sulphide is precipitated but tin remains in solution probably as a complex oxalate-tartrate. Filter off antimony sulphide and boil the filtrate to expel H_2S. Neutralize the oxalic acid present with NH_4OH and just acidify with acetic acid. On passing H_2S through the warm solution, SnS_2 is precipitated. Treat the precipitate after filtering with minimum conc. HNO_3, heat to dryness and ignite at 800° C. Weigh as SnO_2.

Notes:

(*a*) The antimony sulphide may be similarly treated with HNO_3 and ignited to Sb_2O_4. (Factor × 0·7919 = Sb.)

(*b*) If As is present, it may be removed by digesting the sulphides of Sn, Sb and As which have been precipitated from 10% HCl solution (as above) in hot 10% ammonium carbonate solution. As sulphide dissolves leaving Sn and Sb sulphides to be treated as described above.

2. Reduction to stannous chloride and titration with iodine (Pearce-Low method and modifications)

Tin ores are usually attacked by an alkali fusion carried out in a Ni or Fe crucible. With non-pyritic cassiterites 0·25–2 g ore are fused with 3–10 g NaOH with or without 0·25 g powdered charcoal, but with the presence of usual proportion of sulphides, Na_2O_2 is used instead of NaOH + C (and this is the more general procedure). With highly pyritic ores, a preliminary roast is useful and follow with NaOH fusion. The fusion is usually complete after 15–20 minutes at about 600–800° C. The cooled melt is leached with water then acidified with HCl to give 25–40% HCl (by volume).

For alloys, attack white metal bearing alloys (1–2 g for low Sn contents, e.g. Pb base bearings, and 0·2–0·3 g for tin base babbitts) with either conc. H_2SO_4 or conc. HCl (+ $KClO_3$ or bromine water). With H_2SO_4 attack, the Sb may be estimated first (by $KMnO_4$ titration—see under 'Antimony') but in this case, HCl

must be added later to give about 30% HCl (by volume) before reduction of tin is started.

Direct volumetric tin estimation is not so common with Cu-based alloys and with high tin bronzes, the impure metastannic acid is precipitated as in Method 1, washed, dissolved in 15–20 ml. conc. H_2SO_4 with warming, diluted and HCl added to give 30% HCl as above.

The stannic chloride solution so produced is next reduced to the stannous condition by one of several reagents :

(*a*) Swedish iron nails (5–10 g).

(*b*) Powdered antimony (2 g of 100 mesh).

(*c*) Nickel coil (sheet $\frac{1}{32}$ in. × 4 in. × 2 in. rolled into a spiral about $\frac{3}{4}$ in. diameter supported on a glass rod with a bend or knob at lower end).

(*d*) Aluminium (2 g of $\frac{1}{64}$ in. Al sheet).

With (*a*) or (*b*) the iron or antimony is added to the stannic solution and simmered for a half to three-quarters of an hour (for about 0·3 g Sn).

With nickel coils (most usual method) the coil on the glass rod is supported vertically in and covered by the stannic solution by being carried in a two-holed cork fitted in the neck of the flask. It is advisable to activate the coils before use by 'etching' the surface (boil coils 10 minutes in 10% $FeCl_3$ solution acidified with HCl, wash and then use for reducing the stannic chloride solution).

There is no indication of complete reduction when using iron, antimony and nickel, but simmering for a half to three-quarters of an hour should be adequate for 0·2–0·4 g Sn. The use of iron nails is often preferred to nickel since the resulting solution is less intensely coloured.

As, Sb, Bi and Cu may be precipitated during reduction but they do not interfere during titration in cold solutions. The iron nails and nickel coil are washed (with cold boiled water, i.e. O_2 free) and removed from the flask before titration, but the powdered antimony may remain—it does not appear to reduce tin in cold solutions.

In all methods of reduction it is advisable to have an atmosphere of CO_2 in the flask (from a cylinder or Kipp via tubes in the cork of the flask), this atmosphere being maintained during titration by the same manner (use a three-holed cork) or by introduction of pieces of marble into the stannous chloride solution.

In the case of Al reduction (Pugh, *Analyst*, 1931), the reduction proceeds in the cold to the state of spongy tin (also Sb, Cu, As). In this case a 750 ml. conical flask carrying a three-holed cork is essential for leading in and out a stream of CO_2 during and after reduction, for adding 50 ml. conc. HCl from a thistle funnel

permanently fitted through one hole of the cork and for subsequent titration.

When the 2 g Al strip added to the stannic solution has precipitated all the tin (with CO_2 passing through the flask) add 50 ml. conc. HCl via the thistle funnel in the cork and warm to effect solution of residual Al and spongy Sn, any Cu, Sb and Bi stays as a black sludge and As is evolved as arsine. When solution is complete, cool the flask, maintaining a CO_2 atmosphere, and titrate when quite cold with iodine or potassium iodate solution as with all other methods of reduction. The CO_2 supply is not disconnected until the end of the titration.

This method gives very accurate reproducible results on very tin-rich materials (tin base bearings, tinfoil, etc.).

During reduction by any of the methods quoted, the solution should be pale green (Fe and Ni) or almost colourless (Sb and Al); should the solution turn blue-violet or brown, Ti, Cb, W or Mo are present in which case the determination is useless since these metals will be reoxidized by iodine or giving coloured solutions will mask the end point, therefore in this case, repeat as follows:

With a fresh sample of ore (0·25–2 g) fuse with 5–8 g potassium bisulphate in a silica crucible until no further dark particles are seen, only pale brown SnO_2 and colourless SiO_2. Cool, leach with 100 ml. 5% sulphuric acid solution by gentle boiling (SnO_2 and SiO_2 remain undissolved). Pass H_2S into the solution at 50° C. to precipitate any traces of Sn in solution, filter, wash with hot water (if W is suspected, wash the precipitate with 50% NH_4OH which dissolves WO_3 giving soluble ammonium tungstate. Wash with 2% NH_4OH), burn off the filter paper and fuse the residue with 5–8 g Na_2O_2 as usual in a nickel or iron crucible.

Titration of all reduced solutions is carried out by solutions of iodine, potassium iodate or potassium iodide-iodate in the presence of starch as indicator and with an atmosphere of CO_2 to prevent atmospheric oxidation of the stannous chloride solution. The end-point is when the first drop excess of the iodine solution gives a permanent blue coloration with the starch.

Iodate solutions are often preferred due to their relative stability during storage.

Essential reactions are:

$$Na_2O_2 + SnO_2 = Na_2SnO_3 + O$$

$$Na_2SnO_3 + 6HCl = SnCl_4 + 2NaCl + 3H_2O$$

$$SnCl_4 + Ni = SnCl_2 + NiCl_2 \text{ (similarly with Fe, Sb and Al}$$

$$SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI$$

Convenient iodine solutions to use are :

21 g iodine + 40 g KI/litre : 1 ml. = 0·01 g Sn (approx.) or a weaker solution :

6·35 g iodine + 13 g KI/litre : 1 ml. = 0·003 g Sn (approx).

Because of the instability of iodine solutions on keeping, always standardize before use.

STANDARDIZATION

(*a*) *On Metallic Tin.*—Dissolve 0·1–0·2 g of pure tin in conc HCl with addition from time to time of small quantities of $KClO_3$. When all has dissolved, boil off excess of chlorine, dilute with 25 ml. conc. HCl and 75 ml. water, add iron nails or nickel coil and proceed as in the assay.

(*b*) As pure tin dissolves slowly in HCl, even with addition of $KClO_3$, it is sometimes preferable to standardize indirectly on sodium arsenite. Dissolve 0·2–0·3 g pure As_2O_3 by warming gently with dilute NaOH. Add a few drops of phenolphthalein, acidify slightly with HCl, cool to room temperature, add 3–4 g of $NaHCO_3$ and a little neutral starch solution ; titrate with iodine to a permanent blue, disregarding a reddish purple discoloration which may occur before the finish. The reaction is :

$$Na_3AsO_3 + I_2 + H_2O \rightleftharpoons Na_3AsO_4 + 2HI.$$

To prevent the reverse of the reaction, the liberated HI must be neutralized. NaOH or Na_2CO_3 cannot be used as they react with iodine but sodium bicarbonate is used and reacts thus :

$$2NaHCO_3 + 2HI = 2NaI + 2CO_2 + 2H_2O.$$

From these reactions it is evident that $As_2O_3 = 4I = 2Sn$; or 197·92 parts As_2O_3 are equivalent to 237·4 parts Sn ; or 1 g As_2O_3 = 1·1995 g Sn. (For methods for specific alloys see also under 'Tin in Al Alloys', 'Tin in Steel', etc.)

3. Fusion with KCN and weighing as metallic tin

This method gives fairly accurate results with moderately rich ores free from large quantities of other metals. It is generally applied to concentrates obtained by vanning or other mechanical process, on ore which has previously been crushed, not too finely, and the heavier portion separated by this means, taking advantage of the high specific gravity of cassiterite (the native oxide, SnO_2).

10–20 g of the ore or concentrate is taken, after grinding to 80-mesh. If sulphides of iron, or other interfering substances are present, it is treated with HCl and HNO_3, boiled, diluted and filtered. If tungsten is present, this residue is further treated with alternate washes of ammonia and boiling water till free from chloride

and tungsten. The washed residue is then dried, roasted and (roughly) weighed.

It is then mixed with an equal weight of commercial KCN, charged into a small clay crucible, and an equal weight of KCN placed on top as a cover. Sometimes 2–3 g of charcoal is also added. Heat to redness till thoroughly fused (this takes usually about 20 minutes) and keep molten three to six minutes. Tap the crucible to cause any detached particles to settle, and pour carefully into an iron mould.

When cool, detach the slag with a hammer, wash the button in water, collecting any detached prills of metal, dry and weigh as metallic tin.

TITANIUM

(Ti) Atomic Weight = 47·9

Metallurgical Occurrence

Minerals (ilmenite [titaniferous iron ore], rutile [TiO_2] etc.)
Al alloys (as a grain refiner)
Steels (in austenitic stainless steels as a weld-decay preventive and for removal of oxygen, nitrogen and sulphur in steels generally, also added to high-speed steels to replace some vanadium)
Ferro-titanium (for adding to steel and use in welding rods, rutile also used in coatings for welding rods)
In the alloy 'Konel' (Fe, Ni, Co, Ti) used for certain valve filaments
Special age-hardenable Cu based alloys
Small quantities found in Bauxite, clays, iron ores etc.
Sintered carbides

Source of Metal as Standard

Titanium metal = 99·5% pure is obtainable but rarely used as an analytical standard. Instead either 'Analar' grade titanium dioxide is used (for converting to titanium sulphate) or 'Analar' grade potassium titanium oxalate.

Methods of Determination

GRAVIMETRIC

1. *Precipitation by cupferron and ignition to dioxide*
   (useful for Al alloys since large amounts of Al do not interfere. Cu, Fe, V, U, Cb, Ta, Zr, Si, Pb, W, Ag, Hg interfere and must be previously removed. Cr, Co, Ni, Zn, Mn, P, Mg, Ca and Ba do not interfere. Suitable for all but small quantities of Ti).
2. *Hydrolysis precipitation of hydrated dioxide ('metatitanic acid') from acetic acid solution or by sodium thiosulphate*
   (Fe, W, Si, Mo, Cu, Al, Zr, U, Sn and Al interfere but may be prevented by separations subsequent or prior to hydrolysis—of general application).

COLORIMETRIC

3. *Comparison of the yellow colour produced by H_2O_2 with that produced in standards*
   (most common method for the estimation of small amounts of Ti such as that found in steels, iron ores, clays, aluminium, bauxite etc. The essential features are removal of those elements [V, Mo, Ce, Cr] which give

coloured solutions with H_2O_2 [red-brown, yellow, orange and violet respectively] and of those whose normal salts are coloured [Fe, Ni, Co and Cu]—most accurate when not more than 0·003 g Ti is present).

METHODS

1. **Cupferron precipitation** (Low, Weinig and Schoder, loc. cit., 1947. 245; Pigott, loc. cit.; British Aluminium Company's Publication No. 405, 1947. 144)

This reagent is made use of in steels and Al alloys for precipitation of Ti in the presence of ferrous Fe, Al, Cr, Mo, U (sexivalent), the latter group remaining in solution. Cu, Zr, V, Ta and ferric iron co-precipitate with Ti and must be eliminated. V (also W, Mo and Cr) is removed after fusion of the complex with Na_2CO_3 when Ti remains insoluble as a sodium titanate and after re-precipitation with cupferron and washing with NH_4OH, Cu is dissolved as a cuprammine.

Zr and Fe may be separated by a tannin precipitation from dilute mineral acid solution (see under 'Zirconium').

Ta (and Cb) are best removed (with Si and W) at the initial acid attack, by dehydration to the insoluble form (tantalic and columbic acid, SiO_2, WO_3) by baking or by using perchloric acid (see under 'Columbium').

In steels, etc., where the above interfering elements are absent (Al, Cr and Mo may be present), the cupferron precipitation may be performed directly, and the estimation finished gravimetrically by igniting the complex to TiO_2 or more usually colorimetrically after fusion with potassium bisulphate and treatment with H_2O_2. (See Method 3.)

Methods employing cupferron for estimating Ti in Al alloys and ores are given below.

(*a*) *Al Alloys* (British Aluminium Company's method).—1 g alloy is attacked with 30 ml. 20% NaOH solution, when dissolved dilute to 250 ml., boil, filter and wash with hot 1% NaOH.

Dissolve residue in hot 50% HCl, boil to low bulk, dilute to 300 ml., add 5 g tartaric acid, make nearly neutral with NH_4OH and pass H_2S for 10 minutes. Filter off CuS, etc., make the filtrate alkaline with 20 ml. NH_4OH and pass H_2S for 20 minutes. Filter off Fe, Ni, Co, Zn, Mn sulphides and wash with 10% NH_4OH saturated with H_2S. Add 40 ml. 50% H_2SO_4 to the filtrate and boil out H_2S. Filter off S, dilute filtrate to 300 ml., cool in ice water and precipitate Ti with a large excess of 6% solution of cupferron (10 × weight of Ti present) added dropwise with constant stirring. Allow to stand cold for 2 hours and filter off the bright yellow complex. Wash with 20% HCl. Dry, ignite the

filter and precipitate first at low temperature, then at 850° C. Cool and weigh as TiO_2 (factor × 0·5995 = Ti).

(*b*) *Ores* (Low, Weinig and Schoder, loc. cit.).—Any Cb, Ta or Zr present will be co-precipitated with Ti and require eventual separation. In the presence of appreciable SiO_2, W, P or V, the ore (0·25–0·5 g) must first be fused in a Pt crucible with 5 g Na_2CO_3 + 1 g $NaNO_3$ to give a clear melt, cool and leach out with 10% NaOH solution. SiO_2, W, P and V are now converted to soluble salts but Cb, Ta, Zr and Ti (as sodium titanate) remain insoluble and are filtered off. Dissolve precipitate in a little HCl and dilute to 50 ml. Boil off CO_2 and precipitate Ti, etc. (with any Fe, Al and Cr), with NH_4OH in slight excess. Filter and wash with hot 2% ammonium nitrate solution.

(If proportion of SiO_2, W, P and V had been small, this stage may be omitted and the ore fused directly as below.)

Fuse the ammonium precipitate with 2–5 g potassium bisulphate. Cool, leach with hot 5% H_2SO_4 containing 10 g tartaric acid. Pass H_2S into the warm solution until all Fe is reduced and any Group II metals precipitated (filter off), if no precipitate, make ammoniacal and filter off precipitate of Fe and Group IV metals; wash with 5% ammonium sulphide. Acidify with H_2SO_4 to give 20% acid concentration and boil the filtrate until all H_2S is removed, cool to 60° C., add $KMnO_4$ solution to oxidize Ti, etc. (a faint pink flush only is required), dilute to 200 ml. and cool in ice.

Precipitate Ti, etc., with cupferron as previously described and ignite to TiO_2 and weigh. If the precipitate is contaminated with iron and/or Cb, Ta and Zr are suspected, fuse the TiO_2 precipitate in a silica crucible with potassium bisulphate, leach with 1% tannin in 5% H_2SO_4, warm to dissolve the melt then cool to room temperature. Filter off Cb and Ta complexes washing with 5% H_2SO_4. Add 10 ml. conc. H_2SO_4 to the filtrate and boil down until solution darkens and foams. Add conc. HNO_3 to destroy carbon and fume strongly. Cool, add 100 ml. cold water and a slight excess of H_2O_2 (over that required to oxidize Ti).

Add 1 g ammonium phosphate and allow to stand 2 hours in the warm. Filter off zirconium phosphate, dry and ignite to the pyrophosphate ($Zr_2P_2O_7$) which contains 46·3% ZrO_2. Ignite the earth acid complexes to Ta_2O_5 and Cb_2O_5 and obtain weight of TiO_2 by difference.

The reaction for the cupferron precipitation of Ti is as follows:

$$4C_6H_5N(NO) \cdot ONH_4 + Ti(SO_4)_2 = (C_6H_5N[NO]O)_4Ti + 2(NH_4)_2SO_4$$

(yellow precipitate)

2. Hydrolysis precipitation of metatitanic acid from acetic acid solution or by sodium thiosulphate

$Ti(SO_4)_2$ in weak acid solution, hydrolyses on boiling to give metatitanic acid (H_2TiO_3) especially in the presence of acetic acid and ammonium acetate. This reaction is inhibited by the presence of citric, tartaric and oxalic acids.

Fuse 10 g $KHSO_4$ in a platinum, porcelain or silica crucible, heating till water is expelled and the bisulphate converted to pyrosulphate: $2KHSO_4 = K_2S_2O_7 + H_2O$.

Add, gradually, 1 g of the finely powdered ore and continue heating until completely fused. Cool, extract the melt with cold water. Add 50 ml. of strong SO_2 water (or pass in a current of SO_2 gas). Stir, settle, filter, wash with cold water. The Ti is partly in the residue A and partly in the filtrate B.

Residue A (may also contain SiO_2, Sn, W, Ta, Nb and Cr).—Dry, ignite, treat with HF + H_2SO_4 in a platinum dish; evaporate to dryness, weigh and repeat treatment with HF till constant weight, showing that SiO_2 is expelled. Fuse residue with Na_2CO_3, dissolve melt in H_2SO_4, filter and add filtrate to B.

Filtrate B (contains Fe, Al, Zr and bulk of Ti).—It should be colourless and smelling strongly of SO_2. Add one-sixth of its volume of acetic acid and 20 g sodium acetate. Boil, settle, filter, wash with hot acetic acid (1 : 5), then with hot water. Ignite residue and weigh as impure TiO_2.

This residue may still contain some Fe_2O_3 and Al_2O_3. Fuse with Na_2CO_3, extract with hot water, filter, wash; dry the residue, fuse again with Na_2CO_3. Extract the cold melt with dilute H_2SO_4 and repeat precipitation with SO_2 and sodium acetate as under B. Filter, wash, ignite, weigh as TiO_2.

$TiO_2 \times 0{\cdot}5995 = Ti$.

Hydrolysis by means of sodium thiosulphate (see under 'Zirconium' and 'Ferrotitanium') gives separation from iron, but any Mo or Cu is co-precipitated as sulphides and Al and Zr as hydroxides together with U and Sn.

Appreciable Cu should be removed previously with H_2S from acid solution, U and Zr should be removed by the tannin separation (Ti is precipitated, see under 'Uranium'), Al should be separated by cupferron treatment as in Method 1.

The final ignited precipitate of TiO_2 may be fused with Na_2CO_3 to remove Mo, Cr, Al, V, P and U.

3. Comparison of the yellow colour produced by H_2O_2 and titanium sulphate with that produced in standards

The procedure for obtaining Ti in solution as sulphate depends

entirely on the nature of the material analysed and whether interfering metals are present (as quoted under 'Methods of Determination' [3]).

With minerals, rutile usually responds to a potassium bisulphate fusion which gives on extraction with 10% H_2SO_4, the titanium directly as sulphate. Ilmenite may be similarly treated but some react more favourably to a sodium peroxide fusion. This latter is advantageous since iron is left as insoluble Fe_2O_3 whereas titanium passes into solution as sodium pertitanate which may be acidified with H_2SO_4 as before.

For Ti-rich materials either take a small sample (0·1 g) or a normal sample (0·5 g) and take an aliquot portion of the titanium sulphate solution (to contain up to 0·005 g Ti) for colorimetric comparison.

The normal colour of ferric salts would interfere (after a $KHSO_4$ fusion) but may be removed by treatment with H_3PO_4 (see below in 'Treatment of Steels').

For irons and steels, in the absence of V, W, Mo, Ce, Cr, Ni, Co and Cu, direct solution of 1 g steel in 50 ml. 12% H_2SO_4 with addition of a few drops of HNO_3 to oxidize iron and filtering off SiO_2, gives Ti ready for estimation by treating the cold Ti $(SO_4)_2$ solution with a known volume of conc. H_3PO_4 until the colour due to ferric salts has been discharged, transfer to Nessler glasses, add 5 ml. 20 volume H_2O_2 (or 6% solution of H_2O_2) and compare the yellow colour of pertitanic acid sulphate produced with that of a standard steel (free from interfering elements) either of known Ti content or Ti free, in which case standard titanium solution is added to the Nessler glasses until the colours match.

It is essential that assays and standards be treated identically, especially with respect to volume of H_2O_2 and H_3PO_4 added, since an excess of either tends to bleach the colour.

As a check for the presence (or absence) of V, treat the yellow solution (after estimation) with a few drops of HF. This will bleach the Ti colour but the red-brown coloration due to V is unaltered.

The main reaction is :

$$Ti(SO_4)_2 + H_2O_2 = H_2TiO_2(SO_4)_2$$
(yellow solution)

Standard titanium sulphate solution may be prepared by one of the following methods :

(*a*) Dissolve 0·737 g (pure) potassium titanium oxalate $(K_2TiO[C_2O_4]_2 \cdot 2H_2O)$ in 30 ml. water, add 10 ml. conc. H_2SO_4, evaporate just to fumes, cool and dilute to 1 litre with 5% H_2SO_4.

1 ml. = 0·0001 g Ti.

The solution may be exactly standardized by treating a cold 50 ml. portion and precipitating Ti *either* by cupferron (6% solution) and igniting to TiO_2 (factor × 0·5995 = Ti) *or* by precipitation of Ti with excess NH_4OH in the presence of 5 g NH_4Cl. Again ignite the hydroxide to TiO_2, or

(*b*) Fuse 0·1 g pure TiO_2 in a silica crucible with 5 g $KHSO_4$ using a lid. Take care that no loss occurs from spattering. Dissolve the cooled melt in 10% H_2SO_4 and dilute to 1 litre with the diluted acid, then 1 ml. = 0·0001 g TiO_2 or 1 ml. = 0·00006 g Ti.

Modifications for small amounts (up to 0·5% each) of Ni, Cr, Cu, Mo.—The effect of these coloured solutions on the Ti yellow may be overcome by adding the equivalent as metal sulphates or ammonium molybdate to the standard prior to adding H_2O_2. Match the colours as before.

For steels having appreciable content of Al, Cr, Mo, Cu, V, with W, Ni, Co, Mn, P and Be also present, the procedure is to precipitate Ti free from Fe, Al, Cr, Mo, Ni, P, Be, Mn, and Co with cupferron from cold 10% H_2SO_4 solution of the steel. Ignite the complex to impure TiO_2 and fuse in Pt with 5 g Na_2CO_3 and 1 g $NaNO_3$. On extracting with water, W and V are in solution leaving Ti as sodium titanate (and Cu if present). Fuse with $KHSO_4$ and leach with 10% H_2SO_4 then if Cu is present (blue solution) precipitate Ti with cupferron once again, filter and wash thoroughly with 100 ml. 50% NH_4OH which dissolves out Cu and converts Ti to the insoluble hydroxide. Wash with cold water, ignite in Pt and either weigh as TiO_2 or more usually, fuse with $KHSO_4$, extract with 10% H_2SO_4 and finish colorimetrically. (See also specific methods under 'Steels and Ferro-titanium'.)

TUNGSTEN

(W) Atomic Weight = 183·92

Metallurgical Occurrence

Minerals (wolframite, scheelite)
Special alloy steels (including high speed steel)
Sintered carbides
Ferro-tungsten
Stellite (Co, Cr, W, Fe, Si, C alloy)

Source of Metal as Standard

Tungsten powder = 99% + pure is available (Murex Ltd., Rainham) but either standard tungsten steels or alkali tungstates (Na or Ca) are more useful for standards. With most analyses, gravimetric determinations are usual, which do not need metal standards.

Methods of Determination

GRAVIMETRIC

1. *Precipitation as tungstic acid from oxidized HCl solution and ignition to WO_3*
   (of general application. Method of initial solution varies with material being analysed. The WO_3 precipitate may contain oxides of Si, Sn, Fe, Cr, Mo, V, P, Ti, Cb, Ta, Zr which must be separated and WO_3 corrected for their weights. NOT suitable for less than 1–2% W owing to incomplete precipitation).
2. *Precipitation as a complex by cinchonine hydrochloride and ignition to WO_3*
   (of general application for materials containing less than 2% W. Same contamination of precipitate possible as with Method [1]).
3. *Precipitation as mercurous tungstate and ignition to WO_3*
   (applicable to ores, slags and alloys of medium-low tungsten content. Cr, Mo and V may contaminate the precipitate).

METHODS

1. Precipitation as tungstic acid from oxidized HCl solution and ignition to WO_3 (Applicable to wolframite and similar ores in which tungsten is associated with tin)

Fuse 0·5 g of the ore with 2–3 g each of Na_2CO_3 and K_2CO_3 for half to three-quarters of an hour in a platinum crucible; extract with boiling water; filter. (W is in solution as Na_2WO_4.) Dissolve the residue in HCl, filter, wash, dry, re-fuse residue with $Na_2CO_3 + K_2CO_3$; dissolve in water and filter as before, adding the solution to previous filtrate. To united filtrates add HNO_3 in excess. Evaporate to dryness several times with HNO_3 to expel HCl. Dry at 120° C. Take up with conc. HNO_3; allow to stand 15–20 minutes; add some hot 5% NH_4NO_3, filter and wash with hot dilute NH_4NO_3 and HNO_3 to remove soluble salts. (W remains as WO_3 in the residue, with SiO_2 and SnO_2.) Dry, moisten the paper with NH_4NO_3 and ignite. Weigh as $WO_3 + SnO_2 + SiO_2$. Evaporate in platinum crucible with $HF + H_2SO_4$, and weigh as $WO_3 + SnO_2$. Mix residue with NH_4Cl and again ignite, placing the crucible inside a larger covered one. Sn is volatilized as $SnCl_4$: $SnO_2 + 4NH_4Cl = SnCl_4 + 2H_2O + 4NH_3$. Repeat ignition with NH_4Cl till constant weight is obtained. Weigh as WO_3: $WO_3 \times 0{\cdot}7931 = W$. Do not ignite tungstic acid precipitates above 850° C. otherwise volatilization of WO_3 occurs.

With steels, initial solution is usually effected by conc. HCl to which the minimum conc. HNO_3 is added to complete oxidation of carbides, iron and tungsten and on evaporation and baking, SiO_2 and certain metal oxides, are likely to contaminate the precipitated WO_3.

In general the following chemical reactions are made use of in the removal of these impurities:

SiO_2 removed by $H_2SO_4 + HF$ treatment on the WO_3 precipitate.

Oxides of Cr, Mo, V and W are removed by Na_2CO_3 fusion on the WO_3 precipitate which dissolves these, but Ti and Fe remain as titanate and ferric oxide respectively as also does ZrO_2. With ZrO_2 there may be slight attack by Na_2CO_3 giving sodium zirconate in which case treat filtrate with NH_4OH and boil to precipitate $Zr(OH)_2$. Cb and Ta precipitate as their respective acids on leaching the Na_2CO_3 melt with water, an excess of NH_4OH helps.

The main reactions are :

Tungstic acid (H_2WO_4) from HCl + HNO_3 attack on the steel :

$$\text{on ignition } H_2WO_4 = WO_3 + H_2O$$

Treatment of the ignited precipitate with H_2SO_4 + HF :

$$4HF + SiO_2 = SiF_4 + 2H_2O$$
$$WO_3 + 4HF = WOF_4 + 2H_2O = WO_3 + 4HF \quad \text{(on re-ignition)}$$

After Na_2CO_3 fusion of the precipitate :

$$WO_3 + Na_2CO_3 = Na_2WO_4 \text{ (soluble)} + CO_2$$
$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 = 4Na_2CrO_4 \text{ (soluble)} + 4CO_2 \quad \text{(sluggish)}$$
$$V_2O_5 + Na_2CO_3 = 2NaVO_3 \text{ (soluble)} + CO_2$$
$$TiO_2 + Na_2CO_3 = Na_2TiO_3 + CO_2$$

on boiling

$$9Na_2TiO_3 + 6H_2O = Na_2O \cdot 9TiO_2 \cdot 5H_2O \text{ (insoluble)} + 2NaOH.$$

(Specific methods for steels, tungsten carbide, ferrotungsten, etc., see under their respective headings.)

2. Precipitation as a complex by cinchonine hydrochloride and ignition to WO_3

In the previous method where WO_3 is produced by dehydration of tungstic acid (on baking or evaporation) produced from HCl — HNO_3 attack, this is liable to give low results in materials of small tungsten content due to incomplete separation of tungstic oxide.

The use of cinchonine hydrochloride ($C_{19}H_{22}N_2O \cdot HCl \cdot 2H_2O$) in weak acid solutions of tungstates provides a carrier for the small quantity of tungsten by forming a fairly voluminous precipitate of insoluble hydrotungstates of indefinite composition which yield WO_3 on ignition.

Again for complete precipitation, several hours (preferably overnight) standing is necessary and the ignited precipitate is liable to contamination as in Method 1.

Fuse ore with $KHSO_4$ which leaves WO_3 unaltered. Leach out with NH_4OH. If Na_2CO_3 is used for the fusion as in Method 1 the tungsten is obtained as $NaWO_4$, acidify with HCl and make

slightly alkaline with NH_4OH. Boil off excess NH_4OH. Add HCl until acid, then add 3 ml. conc. HCl in excess (neglecting any precipitate of WO_3). Dilute to 100 ml. Add 10 ml. of the 10% cinchonine solution described below to the hot liquid. Stir and settle until clear. Filter; wash with dilute cinchonine solution (see below), finally with a little cold water. Dry, ignite and weigh as WO_3.

Avoid using large amounts of ammonium salts or alkali chlorides.

Cinchonine Hydrochloride.—100 g cinchonine, dissolved in HCl (1 : 2) and made up to 1 litre with HCl (1 : 2).

Wash Solution.—30 ml. of the above, with 30 ml. HCl made up with water to 1 litre.

This method was tested by the authors and found to give satisfactory results, which agreed with those obtained by the mercurous nitrate precipitation—Method 3. (For low W steels see under Steel'.)

3. Precipitation as mercurous tungstate and ignition to WO_3 (Applicable to wolframite, scheelite and other ores; also to many alloys not easily soluble in acids or attacked by alkaline fluxes.)

Add 0·5–1 g of the finely-ground ore or coarsely-powdered alloy to previously fused $KHSO_4$ (i.e. $K_2S_2O_7$) in a platinum dish. (Silica may be used.) Fuse until completely melted; extract with boiling water, adding a little H_2SO_4. Filter and wash. (W is in residue; Fe, etc., in solution.) Extract the residue with NH_4OH or $(NH_4)_2CO_3$; dilute to 200 ml.; acidify slightly with HNO_3. Add 20 ml. of a saturated solution of mercurous nitrate and a few drops of NH_4OH. The liquid must not be made alkaline. Stir; a precipitate, first yellow, then black, is formed, consisting of mercurous tungstate, Hg_2WO_4, mixed with mercuric amino-tungstate and mercury. The reaction is partly as follows:

$$(NH_4)_2WO_4 + Hg_2(NO_3)_2 = Hg_2WO_4 + 2NH_4NO_3$$

Stir, warm, settle, filter and wash with dilute mercurous nitrate. Ignite carefully until Hg is expelled, then at moderate red heat. Cool in a desiccator and weigh as WO_3.

URANIUM

(U) Atomic Weight = 238·07

Metallurgical Occurrence

Minerals (pitch blende—associated with V, Pb, Ag, Co and Sn ores, with Th, Zr and rare earths often present)
Salts used for their fluorescence
Certain special steels (as a substitute for tungsten)

Methods of Determination

GRAVIMETRIC

1. *Precipitation as a complex by cupferron and ignition to U_3O_8*
   (for small quantities of U in steels, ores etc., in the presence of Mo, Cr, Al, V, Zr, Fe, Cu, Ti, Ce, Sn, Mn and P).
2. *Precipitation as uranyl ammonium phosphate and ignition to the pyrophosphate*
   (Al and Cr may interfere but [ferrous] Fe, Mn, Ni, Co, Zn, V do not).

VOLUMETRIC

3. *Precipitation of uranyl ammonium phosphate, reduction with zinc and H_2SO_4 and quantitative reoxidation with standard permanganate solution*
   (of general application [especially ores] in the presence of Fe, Cr, Al, V Ti etc.).

SEPARATIONS

Uranium is either weighed as U_3O_8 from ignition of the cupferron complex (also of the tannin complex or NH_4OH precipitate) or weighed as uranyl pyrophosphate from ignition of uranyl ammonium phosphate. This latter method gives the initial separation from Fe, Mo, V, Ti, Cr, which is so necessary in the volumetric method.

Pb is best separated as $PbSO_4$ by fuming with H_2SO_4.

Group II metals may be removed by H_2S from acid solution, as uranyl sulphide (UO_2S) is not precipitated; but may be occluded in bulky group precipitates ; therefore advisable to re-precipitate in the presence of tartaric acid (helps prevent co-precipitation or occlusion of U).

Group III metals are precipitated by $NH_4OH + (NH_4)_2CO_3$ whereas soluble uranyl ammonium carbonate is produced. ($UO_2CO_3 \cdot 2[NH_4]_2CO_3$). Group IV metals are precipitated by alkali sulphides in the presence of alkali carbonates or tartrates whereas (brown) uranyl sulphide (UO_2S) is not.

U may be separated from Fe, V, Ti and Zr, etc., by the precipitation of this group with cupferron from mineral acid solution, after oxidation of U to the hexavalent condition by $KMnO_4$ in which state it is unaffected by the organic precipitant.

Separation of U from Ti, Cb and Ta is effected by the use of tannin whereby the complex precipitated contains the above rare earth group and the filtrate contains U (and any Zr, Be and Al if present) since the dark brown uranium-tannin complex is only precipitated from neutral tartrate or ammoniacal oxalate or acetate solution and not from weak mineral acid solution.

A brief outline of the ammonia precipitation and tannin precipitation methods are given below, but these are less reliable than Methods 1–3 and mainly suitable to fairly pure solutions of the metal.

(A) Ammonia precipitation and ignition to U_3O_8 (Schoeller and Powell, loc. cit.)

Acid sulphate, nitrate or chloride solution, free from those elements precipitated by NH_4OH, is treated with NH_4NO_3 and NH_4OH and heated to boiling. The yellow precipitate of ammonium diuranate ($[NH_4]_2U_2O_7$) is mixed with filter pulp, allowed to settle, filtered and washed with hot 2% ammonium nitrate solution. Ignite to 900° C. in a tared porcelain crucible, cool and weigh the dark green U_3O_8.

Test the residue for SiO_2 and V by dissolving in minimum of conc. HNO_3, evaporate to dryness, bake, take up with 10% H_2SO_4 and filter off any SiO_2. Ignite and weigh and deduct from weight of U_3O_8.

The filtrate may be tested for V by adding a few ml. H_2O_2 which gives a brownish-red coloration due, it is thought, to a peroxidized-sulphate of V. The V value (compared with standards) is converted to V_2O_5 and deducted from the weight of U_3O_8 found.

($U_3O_8 \times 0{\cdot}848 = U$.)

(B) Tannin precipitation and ignition to U_3O_8 (Schoeller and Powell, loc. cit.)

This precipitation is effective in weak acetic acid, ammonium tartrate or ammonium oxalate solutions but *not* from mineral acids or strong acetic acid solution due to the solubility of the complex in these media.

The nearly neutral solution containing U is treated with 5 g NH_4Cl and an excess of tannin solution (1%) — (5 × weight of U present). Add ammoniacal 10% ammonium acetate until no further precipitation, stir in filter pulp, allow to settle and filter. Wash with 2% ammonium acetate solution and ignite to U_3O_8. Test purity of residue as above.

METHODS

1. Precipitation as a complex by cupferron and ignition to U_3O_8 (Low, Weinig and Schoder; Pigott, etc.)

0·5–1 g ore is fused with 5 g Na_2CO_3 + 1 g KNO_3 or attacked with 10 ml. conc. HCl + 5 ml. conc. HNO_3—this latter (or 15% H_2SO_4) being also a suitable solvent for steels.

Extract the fused melt with water, boil and filter (the ignited precipitate should be re-fused, extracted as before and the filtrates combined)—this step removes Fe, Cu, Ti, Zr, Sn, Ce as insoluble oxides, hydroxides or carbonates.

If an *aqua regia* attack is used, evaporate to dryness, take up with 5 ml. conc. HCl + 10 ml. water, dilute to 50 ml., warm and pass H_2S (precipitate Group II). Boil out H_2S from the filtrate, add 10 ml. 20 volumes H_2O_2 followed by solid Na_2CO_3 to neutralize all acid and give 2 g excess, boil out CO_2 and filter off insoluble compounds as before. Neutralize with 50% H_2SO_4 and add 20 ml. excess, boil down to 100 ml. and add just sufficient $KMnO_4$ to oxidize U to the hexavalent state (pink tinge). Follow with 5 ml. 20 volumes H_2O_2 to decolorize excess $KMnO_4$ (and reduce Cr to the trivalent state if present).

With steels, either the solution from the initial H_2SO_4 attack is diluted to give 6–8% H_2SO_4, or with *aqua regia*, fume with H_2SO_4 and dilute (remove SiO_2, etc.).

To the ice-cold weak H_2SO_4 acid solution (in all cases) add slowly a 6% aqueous solution of cupferron until a white momentary precipitate shows excess of the reagent. Add filter pulp, stir and filter, washing with cold 1% H_2SO_4 (containing a few drops of cupferron)—V is in the precipitate (brown), Mo, Cr, Al and U remain in the filtrate which is evaporated with conc. HNO_3 until all carbon is removed and finally fume with H_2SO_4, cool, dilute to give 5–8% H_2SO_4, warm and add 5–10 g granulated Zn, allow to stand until dissolved, filter through pulp, washing with cold water.

To the cold filtrate add 20–75 ml. cupferron solution until excess reagent is present. Filter, wash 1% H_2SO_4 (containing a few drops of cupferron), dry and ignite first at low temperature then at 900–1000° C., cool and weigh as U_3O_8.

$(U_3O_8 \times 0{\cdot}848 = U.)$

Reactions involved are :

Removal of V.

$$VOCl_2 + 4(C_6H_5N \,.\, NO \,.\, ONH_4) + H_2SO_4 = V(C_6H_5N_2O_2)_4 + (NH_4)_2SO_4 + H_2O + 2NH_4Cl$$

and

$$2H_3VO_4 + 10(C_6H_5N \,.\, NO \,.\, ONH_4) + 5H_2SO_4 = 2V(C_6H_5N_2O_2)_5 + 5(NH_4)_2SO_4 + 8H_2O.$$

Reduction of U.

$$UO_2SO_4 + Zn + 2H_2SO_4 = U(SO_4)_2 + ZnSO_4 + 2H_2O.$$

Precipitation of U.

$$U(SO_4)_2 + 4(C_6H_5N \,.\, NO \,.\, ONH_4) = U(C_6H_5N_2O_2)_4 + 2(NH_4)_2SO_4.$$

2. Precipitation as uranyl ammonium phosphate and ignition to the pyrophosphate (See also Low, Weinig and Schoder, loc. cit.)

0·5–1 g of the ore is evaporated with HNO_3 or with HCl + HNO_3 to dryness. Take up with dilute HCl. Dilute, pass H_2S, filter, boil off excess H_2S, add $KClO_3$ or 5 ml. 20 volumes H_2O_2 and boil (to convert Fe″ into Fe‴). Add a little $(NH_4)_2HPO_4$, nearly neutralize with NH_4OH and pour this solution into a solution of about 5 g Na_2CO_3 in 50 ml. water. Boil, add NH_4Cl equal in weight to the Na_2CO_3 used. Stand and settle. Filter and wash with dilute $(NH_4)_2CO_3$. (The residue contains Fe, V, etc., the filtrate contains the U.) Boil, add excess of HNO_3; boil off CO_2 and add 2–5 g of microcosmic salt ($Na.NH_4.H.PO_4$), then add NH_4OH until a precipitate appears, and HNO_3 until this just dissolves. To the boiling solution add 10 g $Na_2S_2O_3 . 5H_2O$, acidify strongly with acetic acid, boil 5 minutes, add 5 ml. ammonium acetate 20% solution, boil, settle, filter the greenish-yellow precipitate of uranyl ammonium phosphate ($UO_2NH_4PO_4$) often contaminated with S, and wash with hot water. Dry, ignite, cool; moisten the residue with HNO_3 and evaporate slowly to complete dryness. Ignite at low redness and weigh as $(UO_2)_2P_2O_7$.

$(UO_2)_2P_2O_7 \times 0{\cdot}6668 = U.$

3. Precipitation of uranyl ammonium phosphate, reduction with zinc and sulphuric acid and quantitative reoxidation with standard permanganate solution

In the presence of Fe, Cr, V and Ti which are reducible by zinc and H_2SO_4, separate U as in Method 2 above and precipitate as uranyl ammonium phosphate which is converted to uranyl sulphate by solution in minimum hot 25% H_2SO_4. Alternatively U_3O_8 from a cupferron separation may be dissolved in conc. HNO_3 and fumed with H_2SO_4—nitrates must be absent. Adjust the volume (50–75 ml.) to give an acidity of 5% H_2SO_4 and not more than 1% U present and treat with a few drops of N/10 $KMnO_4$ to a permanent pink tint (to oxidize organic matter), cool solution to 20° C. and either pass through a Jones reductor containing 20 mesh amalgamated zinc (2% Hg), or with the acidity adjusted to 15% H_2SO_4, treat with 5–10 g of granulated zinc or strip Al and allow to react for half an hour. Filter off any unconsumed reducing agent (glass wool or asbestos) and titrate the green uranous sulphate solution with N/10 or N/20 $KMnO_4$ to a pink tinge.

The essential reactions are:

$$UO_2SO_4 + 2H_2SO_4 + Zn = U(SO_4)_2 + ZnSO_4 + 2H_2O$$

$$5U(SO_4)_2 + 2KMnO_4 + 2H_2O = 5UO_2SO_4 + 2KHSO_4 + 2MnSO_4 + H_2SO_4$$

1 ml. N/10 $KMnO_4$ = 0·01191 g U.

If the permanganate is standardized on ferrous ammonium sulphate, the Fe to U factor = 2·1320; with sodium oxalate, $Na_2C_2O_4$ to U factor = 1·7766.

VANADIUM

(V) Atomic Weight = 50·95

Metallurgical Occurrence

Minerals (vanadates associated with U, Pb, Fe, Mo etc.)
Steels (including high-speed steel) and ferrovanadium
Blast furnace slags
V_2O_5 catalyst in the chemical industry

Source of Metal as Standards

Pure vanadium metal is available = 99% + V (Blackwell's Ltd., Liverpool), (Everitt & Co. Ltd., Liverpool) but more usual to use 'Analar' purity ammonium meta vanadate or standard steels of known V content.

Methods of Determination

GRAVIMETRIC

1. *Fusion with alkaline oxidizing fluxes followed by precipitation (a) as mercurous vanadate and ignite to V_2O_5, or (b) as lead vanadate and convert to V_2O_5*
   (gravimetric methods still find limited application for ore analysis but in the main they have been superseded by volumetric methods (Method 2) which are of general application).

VOLUMETRIC

2. *Measured reduction of vanadic salts to the vanadyl state followed by quantitative reoxidation using standard $KMnO_4$ solution*
   (applicable to all materials. Cr, Co and Ni do not interfere chemically [but give coloured solutions]. Mo, U, As, B, Ce, Mn, Ti, Ta, Cb and Zr do not interfere, but W, Se and Te must be removed).

COLORIMETRIC

3. *Comparison of the brown coloration produced with H_2O_2 with that produced with standards of known vanadium content*
   (large amounts of Cu, Cr, Ni, Co, Mo and Ce [which give coloured solutions] may interfere, as will Ti [for similar reasons] but Ti interference may be overcome. W should be removed as in Method 2).

METHODS

1a. Fusion with alkaline oxidizing fluxes followed by precipitation as mercurous vanadate and ignite to V_2O_5

Fuse 5 g of the finely-ground ore with 20 g Na_2CO_3 and 3 g KNO_3. Extract with water, adding alcohol if a green colour shows presence of Mn. Nearly neutralize with HNO_3, evaporate nearly to dryness, take up in water and filter. (Residue contains Al and most of the SiO_2.)

To the cold slightly alkaline solution add an almost neutral solution of $HgNO_3$ as long as a grey precipitate forms. If precipitate

is very bulky, partly dissolve in HNO_3 and add a little more $HgNO_3$. Boil, filter, wash with water containing NH_4NO_3, dry, ignite at low temperature in a fume cupboard. Weigh as V_2O_5 (impure).

($V_2O_5 \times 0{\cdot}5602 = V$.)

If Cr, Mo, W, As or P are present, they may exist in the ignited precipitate. These may be separated by dissolving in nitric acid, nearly neutralizing with NH_4OH and pouring into a 10% solution of Na_2CO_3. Heat to boiling, add NH_4Cl equal to weight of Na_2CO_3 used. Stir and settle thoroughly. The V is precipitated as ammonium meta vanadate, leaving the other elements in solution. Filter and wash with water containing a little $(NH_4)_2CO_3$.

Dissolve the precipitate in HNO_3, neutralize with NH_4OH and precipitate again with $HgNO_3$. Boil, filter, wash with dilute NH_4NO_3, dry, ignite and weigh as V_2O_5.

Note: Sodium peroxide may be used instead of KNO_3 in the preliminary fusion. When little silica is present, the fusion may be made with Na_2O_2 alone.

(See also under 'Vanadium in Steels'.)

1b. Fusion with alkaline oxidizing fluxes followed by precipitation as lead vanadate and convert to V_2O_5

Weigh out 0·25–1 g of the ore. Fuse with 6 parts Na_2CO_3 + 1 part KNO_3 or with about 4 g Na_2O_2, using part of the flux as a cover. In the latter case a very moderate heat is sufficient. Extract with cold water, nearly neutralize with HNO_3 and boil for a few moments. Add (say) 10 ml. of saturated lead acetate solution. (Or make just acid with HNO_3, boil, add lead acetate and 1–2 g sodium acetate.) Stir and digest hot for some time, allow the yellow precipitate of basic lead vanadate to settle, filter, wash with hot water containing a little acetic acid. Dissolve the precipitate in HNO_3. Add excess H_2SO_4. Evaporate to dense white fumes. Cool, dilute, filter off $PbSO_4$, washing with cold H_2SO_4 (1 : 9). Evaporate filtrate to a small bulk, finally transfer to a weighed platinum crucible, evaporate to dryness, ignite at moderate temperature and weigh as V_2O_5.

To separate from As, Se and Te fuse with Na_2CO_3 + K_2CO_3. Extract with water. Acidify with dilute HCl. Pass SO_2 into the hot liquid, Se and Te are precipitated. Then saturate with H_2S, As is precipitated as As_2S_3. Filter; boil off excess H_2S, evaporate filtrate with HNO_3, make alkaline with Na_2CO_3, nearly neutralize and precipitate V with lead acetate as above.

2. Measured reduction from the vanadic to the vanadyl states followed by quantitative reoxidation using standard $KMnO_4$ solution

Of the many reducing agents which may be used (SO_2, H_2S, HCl, oxalic acid, alcohol and ferrous salts) the last named is by far the most popular. Tungsten is prevented from interfering by convertion to a soluble fluoride (otherwise WO_3 precipitate may occlude V) in the initial acid attack whereas any Se and Te must be removed by SO_2 precipitation otherwise these elements undergo reduction/oxidation and vitiate the result.

The use of oxidized sodium diphenylamine sulphonate as an internal indicator (Willard and Young, *Ind. Eng. Chem.* Anal. Edn., 1933. **5**. 158) has made this method both rapid and accurate even in the presence of Cr, Mn and most other metals found in irons and steels. [The same authors (*Ind. Eng. Chem.* Anal. Edn., 1934. **6**. 48) have also brought forward the use of an initial perchloric acid attack on Cr/V steels which gives direct oxidation to chromic acid and meta vanadic acid on fuming.]

In the more usual methods (for irons and steels) solution of 0·5–2 g of the sample is obtained with 25% H_2SO_4 with a few ml. HF present to deal with W. After solution is complete, oxidation of ferrous iron is brought about by small additions of conc. HNO_3. On adding 1 g ammonium persulphate and boiling, complete solution of complex carbides (including V) is obtained and conversion of vanadium to meta vanadic acid (HVO_3). Cool to about 70° C. and add N/10 ferrous ammonium sulphate solution until all V (and Cr) is reduced (as shown by the green colour of the solution) to vanadyl sulphate thus:

$$2FeSO_4 + 2HVO_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 2(VO)SO_4 + 4H_2O.$$

About 5 ml. excess reducing agent is added, cool to 20° C. and titrate to a pink flush with N/10 $KMnO_4$ (the pink colour should persist at least one minute). This reoxidizes V to meta-vanadic acid:

$$10(VO)SO_4 + 2KMnO_4 + 12H_2O = 10HVO_3 + 7H_2SO_4 + K_2SO_4 + 2MnSO_4.$$

Any small excess of $KMnO_4$ is next destroyed by treatment with the minimum volume of 5% sodium or potassium nitrite solution (not more than 5 drops excess)—this converts any permanganate to manganous sulphate thus:

$$5KNO_2 + 2KMnO_4 + 3H_2SO_4 = 5KNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

Treatment with 1–2 g urea will destroy any excess nitrite thus: $2HNO_2 + NH_2CO.NH_2 = CO_2 + 2N_2 + 3H_2O$ and 3–5 ml.

HF decolorizes the ferric ion and intensifies the indicator reaction.

Stand 5 minutes, add 5–10 drops of the oxidized indicator (for preparation of the oxidized indicator, see under 'Vanadium in Steels'), allow 10 minutes for the purple colour to develop and titrate to an apple-green end-point with N/40 or N/50 ferrous ammonium sulphate. This coloration develops only after all meta vanadic acid has been reduced to vanadyl sulphate (equation of reaction as above).

It is found that under the conditions stated there is no interference from As, Ni, Cr, Cu, Co, Mo, W, Ti, B, Be, Cb, Ta, Zr and Ce, but Se and Te undergo oxidation with $KMnO_4$ and reduction with ferrous solution. Cerium although susceptible to oxidation/reduction in hot solutions, no appreciable reaction is observed in the cold.

1 ml. N/40 ferrous ammonium sulphate = 0·00127 g V.

The method is equally applicable to ores in which case fuse 1–2 g ore with 6–8 g Na_2O_2 in an iron crucible, extract with water, acidify with H_2SO_4 to give 20% acid, boil out excess oxygen and proceed as in method above by cooling and carrying out the first reduction with ferrous ammonium sulphate.

In the presence of Se and Te (Pigott, loc. cit.).—Evaporate the initial HCl solution of the steel to low bulk after oxidation with HNO_3. Filter off SiO_2 and WO_3, adjust the filtrate to 10% HCl, heat to 80° C. and pass SO_2 for 30 minutes. Filter off Se and Te, wash with water. Evaporate filtrate to low bulk, add 20 ml. conc. H_2SO_4 and fume strongly for 5 minutes. Cool, dilute to 100 ml. with water, warm to dissolve salts, add 1 g ammonium persulphate and proceed as in method above.

Note : For estimation of V and Cr together, see under 'Chromium'—Vignal's method, Note 7 ; also see under 'Vanadium in Irons and Steels'.)

3. Comparison of the brown coloration produced with H_2O_2 with that produced with standards of known vanadium content

The method is most suitable to materials of V content less than 0·5% with less than 0·5% each of Cr, Co, Ni, Cu and Mo since these give coloured solutions, any excess over this figure must be added to the standard solution prior to oxidation and matching—thus Ni, Cr, Cu and Co are added as solutions of their sulphates and Mo as its equivalent in ammonium molybdate solution. Alternatively for the standard use a V free steel containing the correct amount of these alloying elements.

With low Cr, etc., steels a 15% H_2SO_4 solution attack is often sufficient (use a 1 g sample) followed by conc. HNO_3 oxidation of iron and carbides. The solution is boiled to remove NO_2 then diluted to 150 ml. and oxidized with strong $KMnO_4$ solution (or ammonium persulphate). Destroy excess oxidizing agent with H_2SO_3, boil out SO_2, and to the cold solution add 5 ml. syrupy phosphoric acid (to decolorize iron) and 2–5 ml. of 10 volumes H_2O_2 to form a brown solution of pervanadic acid sulphate $[(VO_2)_2(SO_4)_3]$.

Prepare a standard by treating a V-free steel (or other material) as above and adding slowly a known amount of standard ammonium meta vanadate solution, shaking and allowing 2 minutes after each addition for the full colour to develop. Match in Nessler glasses by diluting the stronger solution.

A convenient standard vanadium solution is one containing 1·148 g ammonium metavanadate/litre : 1 ml. = 0·0005 g V.

Note : If Ti is suspected add 3 ml. HF to assay and standard solutions before matching. The HF will decolorize pertitanic acid but does not affect pervanadic acid. (See also under 'Vanadium in Steel'.)

ZINC

(Zn) Atomic Weight = 65·38

Metallurgical Occurrence

Minerals (sulphide, oxide, carbonate and silicate)—often associated with Ag, Au, Cu, Pb, Fe, Mn, Cd
Aluminium and magnesium alloys
White metals
Copper-based alloys (brasses, nickel silvers, gunmetals etc.)
Iron and steel ('galvanized iron')

Source of Metal as Standard

Pure electrolytic zinc = 99·99% Zn (Imperial Smelting Corporation Ltd., London).

Methods of Determination

GRAVIMETRIC

1. *Precipitation as sulphide and ignition to oxide*
   (applicable to most materials with fairly low zinc content, e.g. aluminium and magnesium alloys, iron and steel, white metals. Groups II, III and IV metals must be removed or held in solution).
2. *Precipitation as phosphate and ignition to the pyrophosphate*
   (a better method than [1] since ZnS is difficult to filter. General application including Cu-based alloys. For zinc contents up to 25%. Groups II, III, IV metals also magnesium and other metals forming insoluble phosphates must be removed or held in solution).

3. *Precipitation as zinc quinolate, drying and weighing same or use a volumetric finish* (an alternative to (2)
(the reagent forms insoluble compounds with Fe, Mn, Ni, Co, Ti, which should be removed. Al, Mg, Cd and Ca may interfere, but with care may be prevented from precipitating).

VOLUMETRIC

4. *Titration with potassium ferrocyanide using a uranium salt as external indicator. Alternatively use a ferro-ferricyanide solution with an internal indicator*
(for high zinc contents, particularly minerals and concentrates. Cu, Pb, Cd, Ni, Co, Fe, Mn, As, Sb, Sn, Bi, Cr, Al, Ag and Hg all react in some way with the ferrocyanide).

METHODS

1. Precipitation as sulphide and ignition to oxide

The principles of the method are to use the most suitable acid mixture (nitric acid or *aqua regia* for ores, aluminium alloys, etc., and 10% sulphuric acid for steels) for initial solution followed by 'fuming' with sulphuric acid (Pb and SiO_2 removed here). Group II metals removed by H_2S from acid solution and Group III may be held up by the addition of tartaric acid. Finally zinc is precipitated as ZnS from weak acid solution (1% H_2SO_4, or formic acid—formate solutions) under these conditions the sulphide precipitate is more easily filterable.

Ignition to oxide must be conducted with care, first at 500° C. to burn off carbon in the filter and finally not above 850° C. since the volatility of the residue is appreciable above 900° C.

With irons and steels (Pigott, loc. cit.) the sulphate solution (obtained after fuming the sulphuric acid solution used for initial attack) is diluted, treated with Na_2CO_3 solution until a precipitate just forms, clear with minimum 10% H_2SO_4, cool, pass H_2S for 20 minutes and filter off sulphides of Cu, Zn, As, Sb, Mo. Ignite at 500–600° C., dissolve in minimum HCl, add 5 ml. H_2SO_4 and 'fume', dilute to give 10% acidity, warm and pass H_2S—Group II metals precipitate free from zinc in this stronger acid solution. Filter and wash with 1% H_2SO_4. To the filtrate add methyl red and exactly neutralize with ammonia. Add 10 ml. N/10 H_2SO_4, dilute to 100 ml., cool and pass H_2S for 20 minutes. Add filter pulp and allow precipitate to settle. Filter, wash with cold water and ignite carefully. Weigh as ZnO ($\times$ 0·8034 = Zn).

Alternatively the final ZnS precipitate may be dissolved in 10% HCl, boiled (to remove H_2S), cooled, made just ammoniacal, neutralized with 50% HCl (using methyl red), add 2 drops excess, heat to 80° C., add 15–25 ml., 10% diammonium phosphate solution, boil 20–30 minutes, stand at 80° C. for 1 hour. Filter zinc ammonium phosphate and ignite to the pyrophosphate as in next method. (See also under 'Zinc' in 'Aluminium and Magnesium Alloys' and 'White Metals'.)

2. Precipitation as phosphate and ignition to the pyrophosphate

With ores, digest with HNO_3 and HCl and finally fume with H_2SO_4. If the residue is not clean ($PbSO_4 + SiO_2$) it may require fusion with $KHSO_4$ or Na_2CO_3 mixtures (+ Na_2O_2 or KNO_3)—the extract is added to the main solution. Adjust H_2SO_4 concentrate to 15% and boil with Al strips, this precipitates the bulk of the Cu, Sb, Bi, Pb, Cd and leaves Zn in solution. With the Al strips still in the solution (and in the filtrate), filter and wash with water. Neutralize filtrate with sodium bicarbonate using methyl orange and then acidify with 20% formic acid or 15% hydrochloric acid to give about 1–2% acidity. Dilute to about 100 ml. for each 0·1 g Zn present and retain Fe in solution by adding 1–3 g NH_4CNS. Remove Al strips, heat to boiling and saturate with H_2S. A pure white easily filterable precipitate of ZnS should be obtained. Wash with water, dissolve in minimum HCl, boil out H_2S, make just ammoniacal then just acid with HCl, add sufficient NH_4Cl to keep Mg in solution (say about 10 g). Then add a large excess (about twenty times the amount required by theory to precipitate the zinc) of $(NH_4)_2HPO_4$ or $NaNH_4HPO_4$. Neutralize very carefully with NH_4OH, then add a very slight excess. The zinc is precipitated as follows:

$$ZnCl_2 + (NH_4)_2HPO_4 + NH_4OH = ZnNH_4PO_4 + 2NH_4Cl + H_2O.$$

Add 1 ml. of acetic acid, warm and stir. The precipitate settles and changes into a crystalline form which may be easily filtered. Settle thoroughly, filter, wash with hot water. Dry, ignite paper separately and add ash. Ignite in a porcelain crucible, gently at first, finally for a few minutes at redness and weigh as $Zn_2P_2O_7$.

($Zn_2P_2O_7 \times 0{\cdot}4290 = Zn$.)

(For separation of uranium and zirconium, see under these metals.)

With Cu based alloys, 0·5–2 g alloy is dissolved in nitric acid and after filtering off Sn, Sb, As and P as hydrated oxides (as in the 'Gravimetric estimation of Tin') follow by fuming the filtrate with H_2SO_4 to remove Pb (if necessary). With little Pb, electrolysis of a weak HNO_3 solution removes Cu (cathode) and Pb (anode), otherwise remove Cu as sulphide (Method 1), on Al strips (as above) or titrate with the usual iodide—thiosulphate method and filter off Cu_2I_2.

The filtrates from these methods contain the zinc (and Ni in nickel silvers). The Ni may be estimated with demithylglyoxine or KCN and the filtrate in the first case evaporated with concentrated HNO_3 to destroy excess organic reagent, neutralize with

NH_4OH, just acid with HCl and precipitate zinc as zinc ammonium phosphate with 1 g microcosmic salt ($NaNH_4HPO_4$). Treat the precipitate as above (see also under 'Zinc in Brasses, Gunmetals, etc.').

The cyanide solution from Ni titration with 10 ml. excess N/10 KCN added is warmed to 80° C. and a slight excess (20–30 ml.) of a 2% alcoholic solution of 8-hydroxyquinoline is added with stirring. The yellow quinolate precipitate is treated as in Method 3 below.

With slight modifications to the method (see below) Mg, Al, Ca and Cd do not interfere.

3. Precipitation as zinc quinolate, drying and weighing same or use a volumetric finish (*B.D.H. Book of Organic Reagents*, 1948, and other references quoted therein)

For zinc in bronzes, gunmetals, brasses, etc., dissolve 0·2–0·5 g sample in 10 ml. 25% H_2SO_4 + 2 ml. concentrated HNO_3 (all metals are thus kept in solution). Evaporate to 'fumes' of SO_3 (filter off Pb if present) dilute and to the cool solution add 20 ml. 30% NaK tartrate and make alkaline to phenolphthalein with 10% NaOH solution, add 15 ml. excess and 45 ml. of 5% KCN solution (again all metals present are kept in solution as tartrates or complex cyanides). The solution containing not more than 0·05 g Zn is diluted to 200 ml., and add 20 ml. of 2% 8-hydroxyquinoline in N acetic acid slowly to the zinc solution held just short of boiling. Stand half an hour and filter on a tared sintered glass crucible or on a No. 40 Whatman filter. Wash with 1% ammoniacal tartrate solution and with hot water.

Either dry at 120° C. for 1 hour and weigh as $Zn(C_9H_6NO)_2$ containing 18·49% Zn, or dissolve in minimum 3N . HCl, dilute to 150 ml., add an excess of N/10 bromate-bromide solution and 1 g KI and titrate the iodine liberated with N/10 sodium thiosulphate using starch as indicator.

Under these conditions : 1 ml. N/10 bromate-bromide solution = 0·008173 g Zn.

Potassium bromate-bromide solution : 2·784 g $KBrO_3$, 12·00 g KBr } per litre

As Al, Mg, and Ca are liable to interfere, separate as follows (Cd is very difficult to separate effectively with this reagent).

With Ca present dissolve the zinc quinolate precipitate in dilute HCl and reprecipitate with NH_4OH.

Separation of Magnesium and Zinc.—Precipitate zinc quinolate from a solution (containing Zn and Mg) adjusted to have 5%

ammonium acetate and 3% acetic acid. Heat to boiling and add a 5% solution of the reagent in 2N acetic acid slowly with stirring. After filtering off the zinc complex, the Mg in the filtrate may be precipitated by adding 25–30 ml. of 5N . NaOH solution.

Separation of Aluminium from Zinc.—Precipitate zinc quinolate from a solution made just alkaline with NaOH and containing sodium tartrate. This retains Al in solution which may be precipitated later by neutralizing with HCl and then making ammoniacal.

4. Titration with potassium ferrocyanide using external or internal indicator

Owing to the various reactions of the majority of the common base metals with potassium ferrocyanide, preliminary removal or inhibition is essential, so that the solution for titrating is substantially freed from all metals except zinc.

Separation of interfering metals may be effected in a variety of ways (e.g. those outlined in Methods 1 and 2 above; basic acetate separation ; group separation, or Low's method—see below).

The pure zinc solution is then made just acid (2% acidity) with HCl or H_2SO_4 (nitrates must be absent) and titrated warm (about 50–60° C.) with standard potassium ferrocyanide solution using a 10–15% solution of uranyl acetate or nitrate as external indicator. The end-point is the formation of a brown coloration due to potassium uranyl ferrocyanide. The use of external indicators is tedious and requires experience for accurate determinations.

In this respect it is often advisable to reserve a portion (a quarter or less) of the zinc solution, titrate the balance and add the reserved portion in small portions to the main solution, titrating to the end-point in each case.

As an alternative to uranyl acetate indicator solution, a 1–3% aqueous ammonium molybdate solution may be used. In this case the zinc solution being titrated must be boiled free of any H_2S (see below in Low's method) otherwise an early end-point is obtained due to the formation of brown molybdenum sulphide instead of the ferrocyanide.

The use of an internal indicator in zinc titration is more speedy and no less accurate. Formerly a 1% solution of diphenylamine or diphenylbenzidine in concentrated H_2SO_4 was used (5 drops), but these solutions do not keep and have more recently been replaced by barium or sodium diphenylamine sulphonate (0·3% in water).

These indicators are used with a titrating solution of potassium ferrocyanide containing a small quantity of potassium ferricyanide and the effect is to produce a deep blue colour when the indicator

is oxidized by the ferricyanide during titration (the ferrocyanide being consumed in precipitating the zinc) and at the end-point (first drop of excess ferro-ferricyanide solution) the blue oxidation colour is reduced to apple-green. The change is quite sharp.

The acid concentration and temperature of titration are important and should be closely adhered to in both assays and standards, since concentration affects the constitution of the precipitated ferrocyanide and temperature of titration affects the titration value (e.g. cold solutions need much shaking and tend to give high results ; boiling solutions give rapid reaction, but rate of cooling is liable to affect the titration figure).

Useful conditions for consistent work are : about 0·1% zinc concentration, 2% HCl or H_2SO_4 concentration and temperature about 50° C. (by adding 75 ml. cold water and 100 ml. boiling water).

The main reactions involved are :

$$6ZnCl_2 + 3K_4Fe(CN)_6 = 3Zn_2Fe(CN)_6 + 12KCl$$
$$3Zn_2Fe(CN)_6 + K_4Fe(CN)_6 = 2K_2Zn_3[Fe(CN)_6]_2$$

with external indicator

$$(UO_2)(C_2H_3O_2) + K_4Fe(CN)_6 = K_2(UO_2)Fe(CN)_6 + 2KC_2H_3O_2$$

Low's Method for Ores, Concentrates, etc.—0·5 g finely crushed ore is digested with 10 ml. concentrated HCl + 5 ml. concentrated HNO_3 (+ 2 ml. HF for very siliceous materials). Evaporate to a paste, add 5 ml. concentrated HNO_3 and evaporate again to expel HCl. 10 ml. concentrated HNO_3 are next added followed by 10 ml. water and warm to take salts into solution. Add 5 g $KClO_3$ and evaporate *just* to dryness. Cool and leach with 35 ml. of the following solution (200 g NH_4Cl + 500 ml. concentrated NH_4OH + 750 ml. water) with gentle simmering until the cake is disintegrated. Add 10–25 ml. of bromine water and boil for 5 minutes. This causes complete precipitation of Fe and Mn as hydrated oxides. Filter and wash the residue with 50 ml. of the following solution (100 g NH_4Cl, 50 ml. concentrated NH_4OH ; dilute to 1 litre with water). Neutralize the filtrate with HCl (use litmus indicator or Cu if appreciable present), add 3–4 ml. concentrated HCl excess, dilute to about 200 ml., heat to boiling, saturate with H_2S (Cu and other Group II metals are precipitated) and filter off precipitation if bulky. Boil out all H_2S from the filtrate, adjust temperature to about 50° C. and titrate with potassium ferrocyanide solution if external indicators are used, or with potassium ferro-ferricyanide solution if internal indicators are used.

Convenient Potassium Ferrocyanide Solutions are:

21·53 g pot. ferrocyanide/litre : 1 ml. = 0·005 g Zn (External Indicator)

21·53 g pot. ferrocyanide + 0·3 g pot. ferricyanide/litre 1 ml. = 0·005 g Zn (Internal Indicator)

The ferrocyanide solutions should be standardized by dissolving 0·2 g pure electrolytic zinc (or 0·25 g 'Analar' ZnO) in 10 ml. 50% HCl dilute to 250 ml., adjust temperature of solution as before and titrate exactly as described for the assay.

ZIRCONIUM

(Zr) Atomic Weight = 91·22

Metallurgical Occurrence

In irons and steels
Minerals and refractories (as zircon [$ZrSiO_4$] and zirconia [ZrO_2])
Used for manufacture of rayon spinnerettes (as a substitute for Pt)
In the radio valve industry (as a 'getter')
15% Zr/Cu alloys (competes with Be/Cu alloys)

Source of Metal as Standard

Metallic zirconium is obtainable = 99% + Zr (New Metals & Chemicals Ltd., London, W.C.2) but never used as a standard due to difficulty of solution. The gravimetric methods used do not require the use of a standard.

Methods of Determination

GRAVIMETRIC

1. *Fusion with alkaline flux and precipitation as phosphate*
   (suitable for ores and steels, Fe, Ti, W, Sn, Cb, Cr, Ta, Al, Ni are prevented from interfering, but U and Hf may contaminate the precipitate [see 'Cupferron Separation'])
2. *Precipitation as zirconyl propylarsonate and ignition to ZrO_2*
   (very suitable for steels and may be applied to alloys since only Sn, Cb and Ta are co-precipitated and Ti, Al, Cr, Co, Ni, Cu, U, V, Mo and W do not interfere).

Four other methods of separation from interfering elements are given below and in each the residue may be ignited and weighed as ZrO_2. These methods however are of less general application than the two selected above.

METHODS OF SEPARATION

(*a*) From Ti, Cb and Ta—Tannin precipitation.

(*b*) From Al, Cr, U, Mn, Ni, Co, Zn and Be—Cupferron precipitation.

(*c*) From Group II metals—H_2S precipitation in acid solution.
(*d*) From Fe^{++}, Zn, Ni, Co and Mn—$(NH_4)_2S$ precipitation.
Hf as HfO_2 is nearly always present with zirconium minerals and is very difficult to separate.

(a) **Tannin precipitation** (Fe present in excess of 0·05 g should be removed as ferrous sulphide from ammoniacal tartrate solution otherwise contamination of precipitate results)

Fuse an amount of mineral which contains not more than 0·25 g ZrO_2 with five times the weight of potassium bisulphate. Leach the melt with 100 ml. 10% ammonium oxalate solution and filter off SiO_2. Add NH_4OH to the filtrate until a faint precipitate forms, clear with the minimum of dilute HCl. Add 5 drops concentrated HCl per 200 ml. solution followed by 150 ml. saturated NH_4Cl solution. Boil and add drops of 5% aqueous tannin solution until all Ti, Cb and Ta are precipitated. Stand 1 hour, filter on a No. 40 paper and wash with 5% NH_4Cl containing 1% ammonium oxalate.

The filtrate containing Zr (+ Th, Al, Be, U, V and Fe if present) has Zr (+ other metals) precipitated as a dirty grey complex by adding 0·5 g tannin after diluting to 300 ml. and making ammoniacal. Stand 1 hour at 70° C., filter and wash with 2% ammonium nitrate solution. Ignite at 800–1000° C. to ZrO_2, weigh as such. (HfO_2 is almost certain to be present in the precipitate and is difficult to remove.) ($ZrO_2 \times 0{\cdot}7403 = Zr$.)

(b) **Cupferron precipitation** (United Steel Company's method)

5 g steel are dissolved in 75 ml. 25% H_2SO_4, dilute to 100 ml., cool in ice-water and precipitate Zr (+Ti, Fe^{+++}, V, Cb, Ta, Cu) which should be a clean white precipitate (unless contaminated), filter and wash with 5% H_2SO_4 (containing a little cupferron) and finally with 5% NH_4OH (dissolves out W, Cu, and Mo from the complex).

Dry and ignite the precipitate in a Pt crucible at 650° C., cool, add 2 ml. 50% H_2SO_4 and 5 ml. HF and evaporate to dryness to remove SiO_2. Fuse the residue with 2 g potassium bisulphate, cool and extract with 50 ml. 10% H_2SO_4 and 10 ml. 50% tartaric acid solution. Adjust acidity to 1% H_2SO_4 with NH_4OH and pass H_2S. Add 15 ml. 50% NH_4OH and continue passing H_2S. Filter off ferrous sulphide and wash with ammonium sulphide solution (freshly made). Acidify the filtrate with 50% H_2SO_4 and boil out H_2S. Adjust to 10% H_2SO_4, cool in ice-water, add a little paper pulp and precipitate zirconium with 6% aqueous cupferron until a white precipitate of excess reagent shows. Filter, wash as

before with 5% H_2SO_4 (+ little cupferron) and finally with 5% NH_4OH, dry and ignite in a silica crucible first at about 300° C. and finally at 1000° C. Weigh as ZrO_2. ($ZrO_2 \times 0{\cdot}7403 = Zr$.)

Any Ti in the residue is determined colorimetrically after fusion with potassium bisulphate (see under 'Titanium'), convert to TiO_2 and deduct.

Any Cb and Ta in the precipitate is determined by tannin precipitation following potassium bisulphate fusion and extraction in oxalic acid. Convert to Cb_2O_5 or Ta_2O_5 and deduct.

(c) **Arsenate precipitation** (Schumb and Nolan, *Ind. Eng. Chem.* Anal. Edn., 1937. **9.** 371

A weight of finely powdered ore containing not more than 0·1 g ZrO_2 is fused with five times the weight of K_2CO_3. Extract with hot water and fuse the residue (ZrO_2) with potassium bisulphate. Leach with hot water, filter off SiO_2 and make the filtrate ammoniacal. Filter off white gelatinous impure $Zr(OH)_2$, dissolve in 40% HCl, dilute to 350 ml. and add 50 ml. 1% ammonium arsenate solution dropwise. Filter off zirconium arsenate, dissolve in 80% HCl and reprecipitate with more ammonium arsenate solution. Wash final precipitate with 10% HCl and hot water and finally ignite at 1000° C. to ZrO_2.

W, Ti and Hf may contaminate the final residue, W must be removed by the alkali carbonate fusion but Ti must be estimated colorimetrically and deducted as in (b) above. HfO_2 is most difficult to separate and may usually be ignored.

(d) **Selenious acid precipitation** (Simpson and Schumb, *Analyst*, 1931. **56.** 337

Decompose the mineral by double fusion and precipitate the hydroxide with NH_4OH (as in [c] above). Dissolve in 40 ml. 50% HCl, add 20 ml. alcohol, warm to 70° C., dilute to 500 ml. and to the boiling solution add about 20 ml. 10% selenious acid for each 1 g ore. The precipitate of zirconium selenite $Zr(SeO_3)_2$ is filtered off after standing 2 hours at 60° C. Wash with hot water. Reprecipitation is advisable to complete the separation from Ti, Al, Cr, V, Co, Ni, Cu and U. For this, dissolve the selenite precipitate in 15 ml. concentrated HCl, add 20 ml. 3% H_2O_2 ('10 vols.') to oxidize Ti, dilute to 500 ml. and add selenious acid as before. Ignite the final precipitate at 1000–1200° C. and weigh as ZrO_2. HfO_2 may be present as may ThO_2. The latter may be removed by dissolving the selenite precipitate (prior to ignition) in 50% HCl and precipitate Th as oxalate with oxalic acid (see under 'Thorium').

METHODS

1. Fusion with alkaline flux and precipitation as phosphate

Fuse 2 g of the ore with 10 to 12 g Na_2CO_3 and 0·5 g KNO_3 in a platinum crucible. (If sulphides were present, the ore should previously be roasted.) Take up the melt in water, add alcohol, to reduce manganates, filter, wash with dilute Na_2CO_3. Residue contains Zr, Ba, etc. Digest with dilute H_2SO_4. Filter; most of the Zr passes into the filtrate. Wash, ignite residue, evaporate with HF + H_2SO_4, take up with dilute H_2SO_4, filter and add solution to previous filtrate. Add H_2O_2 and a sufficient amount of Na_2HPO_4 to precipitate Zr. Allow to stand twenty-four to forty-eight hours. The amount of free H_2SO_4 should not exceed 1% of the solution. Zr is precipitated as phosphate, with a trace of Ti, leaving Fe and Al in solution. Ignite precipitate, fuse with Na_2CO_3, extract with water and filter. (Ti is in the filtrate.) Fuse residue with $K_2S_2O_7$, extract with hot dilute H_2SO_4. To the solution add a little 3% H_2O_2 and Na_2HPO_4. Allow to stand one to two days; filter, ignite, weigh as $xZrO_2 . yP_2O_5$, containing 51·8% ZrO_2 or 38·28% Zr. (See also under 'Zirconium in Steel'.)

2. Precipitation as zirconyl propylarsonate and ignition to ZrO_2 (Geist and Chandler, *Ind. Eng. Chem.* Anal. Edn., 1937. 9. 169, and Pigott, loc. cit.)

N-propylarsonic acid [$C_3H_7ASO(OH)_2$] is almost a specific precipitant for Zr from dilute HCl solution (about 5% HCl).

For steels an initial mixed acid attack followed by an alkali carbonate fusion is usually sufficient to break up complex zirconium compounds and gives insoluble zirconates whereas W, Cr, V and most of the Sn are in solution.

With about five times excess of the organic reagent, white flocculent zirconyl propylarsenate is precipitated [$ZrO(C_3H_7ASO_3)_2$]. A double precipitation is usual to overcome possible adsorption from large amounts of iron and Ti if present.

Final ignition at 1100° C. gives pure ZrO_2 (in the absence of Sn, Ta and Cb). Tin if present is removed by adding 1 g ammonium iodide and igniting to volatilize tin iodide—repeat to constant weight. Alternatively fuse the precipitate with alkali carbonate, extract with water and filter off insoluble zirconates leaving Sn in solution as stannate.

With appreciable Cb and Ta, either carry out a tannin separation (as in [a] above) or fuse the ZrO_2 (impure) in a nickel crucible with 5 g KOH, filter, ignite precipitate and re-fuse with potassium

pyrosulphate in a porcelain crucible. Extract with 1% H_2SO_4, add 10 ml. concentrated HCl, dilute to 200 ml. and reprecipitate Zr with 10 ml. of 5% aqueous solution of n-propylarsonic acid. This procedure takes Cb and Ta into solution as potassium tantalate and columbate. (For specific details in steel analysis see under 'Zirconium in Steel'.)

PART THREE

Analysis of Commercial Metals, including Aluminium, Antimony, Copper, Lead, Nickel, Tin, Zinc.

Analysis of Non-Ferrous Alloys, including Light Alloys, Bronzes, Brasses, etc., Bearing Metals, Zinc Base Alloys, Platinum Metals and Alloys.

Analysis of Iron and Steel and of Ferro Alloys.

CHAPTER V

ANALYSIS OF COMMERCIAL METALS

Solvents used in the Analysis of Non-Ferrous Alloys

(For *general methods* of solution and separation see Chapter II.)

As a general rule it is advisable to estimate the constituents of an alloy on separate samples, since the actual amounts of the constituents present in an industrial alloy vary to a great extent, thus making the procedure of carrying out all the estimations on one sample weight practically impossible.

This method of separate estimations also conduces to greater accuracy, since it provides to some extent a method of checking results ; the method also permits of a wider range of solvents.

The usual solvents are, of course, nitric acid, sulphuric acid, and hydrochloric acid. In special cases caustic alkali may be used as a solvent, or the material may be fused.

Nitric Acid

Can be usefully employed for copper alloys in general, since the electrolytic or the 'Iodide' method of estimation can be performed in a solution so obtained, but in the case of the bronzes which contain tin a much better solvent is HCl, with a few crystals of $KClO_3$ or *aqua regia.* Since the residue of 'metastannic acid' produced by the use of HNO_3 may be impure, careful washing is necessary when this is to be used for the estimation of tin with P absent (or it may be used for phosphorus estimation); also a nitric acid solution of a bronze is not suitable for the subsequent estimation of other constituents. Nitric acid of 1·2 sp. gr. is also suitable for lead alloys.

Hydrochloric Acid

Is a suitable solvent for white metals, especially if a crystal of $KClO_3$ be added ; tin and antimony may be estimated directly in such solutions. It is also suitable for magnesium-aluminium alloys.

Sulphuric Acid

Will dissolve very few alloys directly, but either as a part solvent or by addition after solution in either of the above it is a very useful acid, as it separates lead and provides a solution suitable for 'gassing' with H_2S.

It, however, is an excellent solvent for bearing metals (in the direct estimation of antimony) and for chrome steel.

Aqua Regia

Not necessarily in the standard proportions of $3HCl : 1HNO_3$, but almost any mixture of the two acids is a very effective solvent for many non-ferrous alloys and also for iron and steel. The use of this solvent should usually be followed by evaporation to fumes with H_2SO_4.

Caustic Alkali

Caustic soda is the best solvent for aluminium alloys (if magnesium is absent) and may also be used for zinc base alloys.

Fusion

This method is most applicable to refractory materials, slags, and many ores; it may be used, however, in the case of silicon alloys.

The usual reagents employed are caustic soda or sodium peroxide for tin ores, chrome iron ores, aluminium ores; fusion mixture for siliceous materials and slags; potassium bisulphate is also a very useful reagent for ores of iron, aluminium and titanium.

THE ANALYSIS OF COMMERCIAL ALUMINIUM

The most usual impurities to be determined are copper, iron, silicon and manganese. Lead, zinc and titanium may also occur in very small quantities.

Calcium, magnesium, nickel and sodium may be present in minute amounts but are not normally determined.

In the case of super-pure aluminium the elements determined are copper, iron and silicon, these occurring in amounts from 0·0005% to approximately 0·005%. Some difference in analytical methods is advisable for this material, these being indicated at the end of this section.

Sampling

Many varieties of fabricated aluminium may be sampled by sawing, drilling or milling of the material. In cases where segregation is suspected a 'dip' sample should be taken and the metal thus withdrawn from a melt cast into a chill mould or as a 'splash' sample.

In the case of super-pure aluminium a small sample is cast into an aluminium mould and milling taken from the resultant billet.

For iron determinations the sample is best obtained by taking a single piece of approximately 2 g weight, remove the surface by immersion in hot hydrochloric acid, wash well and dry.

Preliminary Note.—In the following recommended methods the *colorimetric* finish is usually chosen but if the amount of any individual element is considerable the methods given under 'Analysis of Commercial Light Alloys' may be employed.

If the amount of the particular element is very small it is recommended that the final comparison of colour be made by means of absorptiometric methods such as the Spekker.

Determination of Copper (greater than 0·01% Cu.)

Reagents

Ammonium hydroxide	1 : 2
Citric acid	30%
Ferric citrate solution	Dissolve 4 g of ferric chloride in 10 ml. HCl, add 300 ml. of water and then add 30 g of citric acid. Make just ammoniacal
Gum arabic	1% in water
Hydrochloric-nitric acid mixture	5 vols. hydrochloric acid and 1 vol. nitric acid in 4 vols. of water
Sodium diethyldithiocarbamate	0·1% solution
Sodium hydroxide	20% solution
Standard copper solution (from pure copper or copper sulphate)	1 ml. = 0·0001 g copper

Method—Assuming a copper content of 0·01% take 0·2 g of sample and attack with 10 ml. acid mixture in a 250 ml. beaker. When solution is complete cool, add 10 ml. of citric acid and make ammoniacal (15 ml.). Cool and transfer to a 100 ml. Nessler comparison tube, add 3 ml. of gum arabic, and dilute to 100 ml.

Prepare a blank solution of the reagents and, if necessary, add ferric citrate solution until the colour matches that of the sample solution.

Add 5 ml. of the sodium diethyldithiocarbamate solution to both and add standard copper solution to the blank until the colour matches that of the test solution.

Determination of Copper (less than 0.01% Cu)

Reagents

Ammonium hydroxide	1 : 1
Gum Arabic	1% solution; prepared cold and freshly filtered
Hydrazine hydrochloride	10% solution
Nitric acid	1 : 1
Sodium diethyldithiocarbamate	0·1% solution; freshly prepared and filtered
Sodium hydroxide	20% solution
Standard copper solution	1·0 ml. ≡ 0·10 mgm. Cu. Attack 1·0 gram electrolytic copper with 20–30 ml. nitric acid. When attack is complete, wash down, add 20 ml. sulphuric acid (1 : 1) and evaporate to fuming. Cool, wash down and dilute to 1·0 litre. Dilute this stock solution tenfold

Method.—Attack 1·0 gram metal in a 250 ml. squat beaker with 20 ml. sodium hydroxide solution (20%). When solution is complete dilute immediately to 200 ml. with recently boiled distilled water, add 5 ml. hydrazine hydrochloride solution (10%) and filter off insoluble iron and copper on a pulp pad. Wash the beaker an . pad six times with distilled water, discard the filtrate and pla the original beaker under the funnel.

Drop 5 ml. warm nitric acid (1 : 1) round the funnel and ove the pad. Then drop a little hydrochloric acid on the pad to dissolve any iron left unattacked and wash six times with cold distilled water.

Remove the beaker containing the filtrate, add a small piece of litmus paper and add, from a burette, ammonium hydroxide (1 : 1) until neutral, then 3 ml. excess. Heat the solution to boiling and filter immediately on the original pulp pad. Wash six times with ammonium hydroxide wash liquor (5%).

Cool the ammoniacal filtrate to room temperature, add 1 ml. gum arabic solution (1%), transfer to a Nessler glass and make bulk up to 95 ml., mix well and add 5 ml. sodium diethyldithiocarbamate solution (0·1%) again mixing well.

Carry out a blank determination on the reagents with each batch. Add standard copper solution to the blank, mixing after each addition, until the colour matches that of the sample solution.

Alternatively the determination can be completed absorptiometrically using a wavelength of 436 mμ.

Determination of Iron (volumetric method)

Reagents

Potassium thiocyanate	50% solution
Sodium carbonate,	
Sodium hydroxide	20% solution
Sulphuric acid	1 : 1
Potassium permanganate	N/56 solution. 1 ml. = 0·001 iron
Standard steel	99·7% iron
Standard titanous chloride	150 ml. of a 15% solution is added to 200 ml. of hydrochloric acid (sp. gr. 1·16). Boil for 2 minutes, cool. Make up to 5 litres. Keep in an aspirator connected with a hydrogen generator

Method.—Take 1 to 2 g, according to iron content of sample and attack with 30 ml. of sodium hydroxide. When action is complete add 30 ml. of sulphuric acid (1 : 1). Shake until all aluminium salts dissolve. Cool.

Titrate with potassium permanganate in the usual manner. Add 3 ml. of potassium thiocyanate and titrate rapidly with titanous chloride until red colour is just discharged.

The potassium permanganate and titanous chloride solutions are standardized by dissolving 0·2006 g of the standard steel (Fe = 99·7%) in sulphuric acid in the presence of a little sodium carbonate using a flask fitted with a bunsen valve. Make up to a definite volume. Titrate 5 ml. of the thus standard steel solution with the permanganate. Now add 3 ml. KCNS solution and titrate with the titanous chloride. 1 ml. standard steel solution = 0·001 g Fe.

Determination of Silicon (gravimetric Regelsberger method)

Reagents

Hydrochloric acid	1 : 1
Hydrofluoric acid	
Sodium hydroxide	20% solution (made up in a nickel dish)
Sulphuric acid	1 : 2

Method.—Presuming the absence of columbium, attack 2 g of metal of normal silicon contents in a 200 ml. nickel crucible (with cover) using 20 ml. of sodium hydroxide. When action is completed evaporate to a pasty mass, cool, dilute with 5 ml. of water and transfer to a 450 ml. beaker containing 30 ml. sulphuric acid. Wash out well and clean out crucible with 5 ml. sulphuric acid.

Evaporate to fumes, fume 10 minutes, cool, dilute to 200 ml. with hot water, boil for 10 minutes and filter off the precipitated silica onto an ashless pulp pad. Wash well with hot water, then with hot hydrochloric acid and finally ten times with hot water.

Remove to a porcelain crucible, dry and ignite for 1 hour at 900° C. Brush residue into a weighed platinum crucible and re-weigh. Treat with 10 drops of sulphuric acid and 10 drops hydrofluoric acid and fume carefully. Ignite for 10 minutes and determine the loss in weight. (Factor = 0·4672.)

Determination of Titanium (colorimetric method)

Reagents

Hydrogen peroxide	3% ('10 vols.')
Phosphoric acid	
Sodium hydroxide	20% solution
Sulphuric acid	1 : 2
Standard titanium solution ..	1·0 ml. ≡ 0·10 mgm. Ti Heat 0·737 gram potassium titanyl oxalate with 20 ml. sulphuric acid and 0·5 gram ammonium sulphate, gently at first and finally allowing to boil for ten minutes. Cool, dilute by pouring into distilled water, cool, filter and dilute to 1·0 litre

Method.—Attack 1·0 gram metal in a 400 ml. squat beaker with 20 ml. sodium hydroxide solution (20%). When in solution dilute to 150 ml. and boil. Allow the residue to settle, filter on a pulp pad and wash well with hot water containing a little sodium hydroxide.

Extract the residue on the pad with 30 ml. sulphuric acid (1 : 2) in three lots of 10 ml. and wash with hot water after each extraction. Adjust bulk to about 60 ml., cool and transfer to a Nessler glass. Add 10 ml. hydrogen peroxide (3%) and dilute to

100 ml. Add standard titanium solution to a blank containing 30 ml. sulphuric acid (1 : 2) and 10 ml. hydrogen peroxide (3%) until the colour matches that of the sample.

Note 1.—If much iron is present in the samples, add 5 ml. phosphoric acid to both samples and blank before adding the hydrogen peroxide.

Note 2.—If an absorptiometric finish is preferred use a wavelength of 425 mμ and correct for the extinction due to the iron content of the sample.

Determination of Zinc (colorimetric method)

Reagents

Alcohol	
Ammonium hydroxide	1 : 1
Dithizone (diphenylthiocarbazone) ..	0·01% and 0·002% solutions in carbon tetrachloride
Hydrochloric acid	1 : 1 and N/50
Sodium acetate-acetic acid buffer solution	1 vol. sodium hydroxide [N], 1 vol. acetic acid [5N]
Sodium hydroxide	10% solution
Sodium thiosulphate	2% solution
Sofnol No. 2 indicator	0·6% solution in alcohol
Tartaric acid	25% solution
Standard zinc solution (from pure zinc or zinc sulphate) ..	1 ml. = 0·005 mg. Zn

Method.—Attack 0·05 g of metal in a test-tube, with 2 ml. hydrochloric acid, heat in boiling water, add 2 ml. tartaric acid solution. Add 5 drops of Sofnol indicator, 1 ml. alcohol and ammonium hydroxide until nearly neutral, cool and continue the neutralization until the colour of the indicator matches that of a reference tube containing the same amount of indicator buffered at pH 6·9. Now add 5 ml. dithizone (0·01%) and shake vigorously. Draw off the carbon tetrachloride layer with a pipette and transfer the carbon tetrachloride solution to a second tube. Rinse out the pipette with a 5 ml. dithizone and add to main solution in the second tube.

Shake the combined extracts for 3 minutes with 5 ml. hydrochloric acid $\frac{N}{50}$ and draw off the layer as before transferring to the first tube. Repeat as before. Add successively 1 ml. sodium

thiosulphate solution, 2 ml. sodium acetate—acetic acid buffer solution and 10 ml. dithizone (0·002%) solution to the test solution and also to a blank. Shake the tubes for 1 minute and match the colours produced in the test and blank by adding standard zinc solution to the blank.

Note.—A distillation–polarographic method has now been introduced by the British Aluminium Co. See also: McCamley, Scott & Smart "Analyst", 1951, **76**, 200.

Determination of Lead (colorimetric method)

Reagents

Ammonium hydroxide	1 : 1
Diphenylthiocarbazone (Dithizone)	0·001% solution in chloroform
Hydrazine hydrochloride	10% solution
Hydrochloric—nitric acid mixture	See under 'Copper'
Potassium cyanide	20% solution containing a few drops of 20% sodium hydroxide to stabilize
Tartaric acid	25% solution
Thymol Blue	0·02% solution in alcohol
Standard lead solution	0·01831 g lead acetate in water containing a little acetic acid and dilute to 1 litre. 1 ml. = 0·00001 g Pb

Method.—Attack 1 g of metal with 30 ml. of the acid mixture in a 400 ml. beaker. When action is complete boil and cool. Transfer to a 200 ml. flask and dilute to mark. Pipette a suitable aliquot part (20 ml.) into a comparison tube, add a few drops of hydrazine hydrochloride and then add (2·5 ml.) tartaric acid.

Now add a few drops of the thymol blue and NH_4OH dropwise until colour changes from yellow to blue neglecting any slight precipitate of aluminium hydroxide. Add 1 ml. potassium cyanide and immediately add 10 ml. dithizone solution.

Prepare a blank solution in the same way with the reagents and agitate both test sample and blank for three minutes. Add the standard lead solution to the blank until the colour of the chloroform layer matches that of the test solution. Shake well after each addition.

Determination of Manganese (colorimetric method)

Reagents

Potassium periodate	
Sodium hydroxide	20% solution
Sulphuric acid	1 : 1
Standard manganese solution ..	Dissolve 0·0288 g of potassium permanganate in water, acidify with sulphuric acid, reduce with sulphur dioxide. Boil off excess of sulphur dioxide, cool, dilute to 1 litre. 1 ml. = 0·00001 g Mn

Method.—Attack 1·0 g of metal in a 600 ml. beaker with 20 ml. sodium hydroxide. Add 20 ml. nitric acid and evaporate to crystallization. Dilute and add 15 ml. nitric acid and 10 ml. sulphuric acid. Boil until solution is clear and add 0·2 g potassium periodate. Boil for one minute and allow to stand on hot plate. Cool, transfer to a Nessler colour tube and match the colour against a series of manganese standards.

To prepare the standards pipette suitable quantities of the standard solution into a series of beakers, add 15 ml. nitric acid and 10 ml. sulphuric acid and oxidize as in the test solution with 0·2 g potassium periodate. Boil, dilute and transfer to stoppered bottles or tubes.

ANALYSIS OF SUPER-PURITY ALUMINIUM

For copper, iron and silicon.

Sampling

Special precautions are necessary as explained under 'Commercial Aluminium'.

Determination of Copper

The method already given under 'Commercial Aluminium' may be employed, but using a more dilute standard copper solution.

Determination of Iron

Reagents

Hydrochloric acid	1 : 1
Hydrogen peroxide	3%
Mercuric chloride	5%
Potassium thiocyanate	30%
Standard iron solution (0·432 g ferric ammonium alum with 10 ml. HCl, dilute to 10 litres) ..	1 ml. = 0·000005 g Fe

Method.—Attack 1 g with 30 ml. hydrochloric acid in a covered 600 ml. beaker. Add 5 drops of mercuric chloride solution. Filter off the mercury through a sintered glass funnel. Transfer to a Nessler tube, add 2 drops of hydrogen peroxide, dilute to 100 ml. Add 10 ml. potassium thiocyanate.

Prepare a blank solution from the reagents, adding HCl and $HgCl_2$ as before, evaporate to 10 ml., add 2 drops of hydrogen peroxide dilute and add potassium thiocyanate. Add the standard iron solution until the colour matches the sample solution.

Determination of Silicon

Reagents

Ammonium molybdate	10% solution (fresh and filtered)
Nitric acid	1 : 2
Sodium hydroxide	15% solution
Standard picric acid	0·134 g of picric acid in 1 litre of water, dilute tenfold. 1 ml. = 0·00001 g silicon

Method.—Attack 1 g with 25 ml. of sodium hydroxide in a covered nickel crucible, boil, dilute to 80 ml., transfer to a beaker containing 43 ml. of nitric acid. Mix well and boil, with stirring, until all the aluminium hydroxide is dissolved. Cool, filter and transfer solution to a Nessler tube, dilute to 140 ml., add 10 ml. of ammonium molybdate, mix well and allow colour to develop for 10 minutes. Compare the colour produced with that of the standard picric acid by adding measured quantities of the latter to 150 ml. water. This is standardized against a solution of a standard aluminium sample whose silicon content is known.

Carry out a blank on reagents using only 22 ml. Nitric acid.

Addendum.—The non-metallic elements usually present are

carbon, nitrogen, oxygen, phosphorus, and sulphur. The amounts are minute and do not vary much. These elements are not sufficiently important as to warrant regular determination. If it is desired to estimate them however reference to some standard work should be made. Some indication of the methods is given in Publication No. 405 of the British Aluminium Company Ltd.

METHOD OF ANALYSIS OF ANTIMONY METAL

for Antimony, Lead, Iron and Arsenic

Antimony

Weigh 0·2 g of finely ground metal into a 400 ml. beaker, add 5 ml. conc. HCl and liquid bromine and warm slightly to dissolve. When dissolved heat to remove excess bromine. Add 100 ml. 1 : 1 HCl, insert a capillary 'boiling tube' or glass beads to prevent 'bumping' and 1 g sodium sulphite crystals. Boil down with a cover on the beaker to approximately 10 ml. Wash down the cover and sides of beaker with 20 ml. chlorine free conc. HCl and then with boiling water. Dilute to 150 ml. with boiling water. Add 1 drop of 0·1% aqueous methyl orange solution and titrate with N/10 $KBrO_3$ which has been standardized against pure antimony or antimony potassium tartrate. It is advisable to boil the solution again just before the end-point is reached.

1 ml. N/10 $KBrO_3$ = 0·00609 g Sb.

Lead

Dissolve 2 g of finely ground metal in HCl and bromine. Evaporate nearly to dryness, add 50 ml. water and 5 g tartaric acid, boil and add HCl to give a clear solution. Make up separately a solution containing 100 ml. water, 15 g NaOH and 10 ml. of 10% Na_2S. While this solution is still warm pour the antimony solution into it slowly with stirring. Filter on an asbestos pad washing with weak NaOH + Na_2S solution (one tenth of above strength). Dissolve the lead sulphide with 1 : 2 HNO_3 saturated with bromine, finally washing the pad with hot water. Add 5 ml. conc. H_2SO_4, take to fumes, cool and dilute to 100 ml. with water. Stand overnight, filter and weigh as $PbSO_4$.

If the lead content is small proceed as above as far as fuming with 5 ml. H_2SO_4 and diluting to 100 ml. with water then add 50 ml. methylated spirit and stand overnight. Filter on a retentive paper and wash with 5% H_2SO_4 solution in a mixture of 1 part

methylated spirit to 2 parts water. Dissolve the lead sulphate with two successive portions of 10 ml. boiling 30% ammonium acetate solution. Wash with hot water, cool and make up to 100 ml. Take an aliquot portion, dilute to 50 ml., add 5 ml. 0·88 ammonia, and 1 ml. 10% KCN solution, boil and cool. Transfer to a Nessler tube, add 4 drops of 10% Na_2S solution and compare the colour with standards prepared with the same amounts of ammonia, ammonium acetate and KCN with standard lead solution. (1 ml. = 0·0001 g Pb.)

Iron

Dissolve 1 g of finely ground metal in HCl and bromine. Boil off excess bromine. Add 20 ml. conc. HCl and make up to 100 ml. Take an aliquot portion, add 10 ml. conc. HCl and 20 ml. 20% potassium thiocyanate solution, transfer to a Nessler tube and dilute to 100 ml. Compare with standards containing the same amounts of HCl and KCNS, and standard ferric chloride solution (1 ml. = 0·0001 g Fe) to match the colour.

Arsenic

Weigh 2 g of finely powdered material into the flask of an arsenic distillation apparatus. Add 120 ml. 'ferric chloride mixture'.* Warm gently until all metal has dissolved, then distil briskly until thermometer (dipping in liquid) registers 120° C. Add concentrated hydrochloric acid to the distillate until the concentration is at least 20% HCl, then pass H_2S through the solution for 1 hour. Filter through an acid-resistant paper, wash six times with conc. HCl. Wash free from chlorides with cold distilled water. Place 10 ml. conc. H_2SO_4 in 250 ml. Pyrex flask, place this under funnel. Pierce paper with glass rod. Wash bulk of precipitate through into flask, then dissolve remainder off paper with a few ml. 10% KOH, finally washing with water. Evaporate contents of flask until fuming, then cover and heat strongly until white. Cool, dilute, nearly neutralize with ammonia, cool. Add excess $NaHCO_3$. Titrate with N/50 iodine, adding starch near end point.

Standardize using N/50 As_2O_3 (dissolve in NaOH solution, acidify with H_2SO_4 and make up).

* *Ferric chloride mixture*
300 g. ferric chloride
600 g calcium chloride
600 ml. hydrochloric acid (sp. gr. 1·16)
dilute to 1 litre with water.

ANALYSIS OF PURE COPPER

Sampling

Fine drillings obtained by drilling right through the ingots should be used after cleansing from grease and oil.

The usual determinations are : bismuth, lead, arsenic, phosphorus, iron, nickel, sulphur and non-metallic inclusions. Antimony, tin, silver, tellurium and oxygen are sometimes required but rarely in normal analyses of this metal.

Determination of Iron (colorimetric method with thioglycollic acid)

Weigh 10 g of drillings into a 600 ml. beaker and dissolve in 150 ml. of nitric acid (sp. gr. 1·2). Boil off the brown fumes, add 5 g of ammonium chloride. Add ammonia solution until a permanent dark blue colour develops, add 10 ml. in excess. Boil for a few minutes and filter on a No. 4 Whatman paper. Wash with boiling water and then with dilute ammonia solution until the filtrate is free from copper. Dissolve the precipitate with hot hydrochloric acid (1 : 1) and wash the filter paper thoroughly with hot water. Add 5 ml. of concentrated sulphuric acid and evaporate to fumes. Dilute with cold water and transfer the solution to a 100 ml. standard flask. Pipette a 10 ml. aliquot part of this solution into a 50 ml. Nessler tube, add 0·5 g of citric acid, and 5 ml. of ammonia solution (1 : 1) and make up the volume to about 50 ml., add 0·1 ml. of thioglycollic acid. Compare the pink colour produced with a range of iron standards in 50 ml. tubes. These are made with a standard iron sulphate solution treated exactly as the sample and arranged so that they cover the amount of iron expected in the sample. Calculate the percentage of iron in the sample from the figures obtained. The standard iron solution is made by dissolving 0·1 g of pure iron in dilute sulphuric acid and making the volume up to one litre. 1 ml. = 0·0001 g iron.

Note: Coloured discs are available which remove the necessity of preparing iron standards.

Determination of Bismuth (colorimetric method with potassium iodide)

Proceed as in the determination of iron taking a 10 ml. aliquot part of the solution obtained after fuming with sulphuric acid and diluting to 100 ml. The 10 ml. are transferred to a 50 ml. Nessler tube and 1 ml. of sulphurous acid added. Make up the volume to about 45 ml. and add 5 ml. of a 5% solution of potassium iodide. Compare the yellow colour produced with that obtained from

standard bismuth solutions as follows. Prepare a set of standards by taking suitable aliquot parts of a bismuth solution made by dissolving 0·1 g of bismuth in 5 ml. of *dilute* HNO_3 and evaporating to dryness. Add 10 ml. of concentrated sulphuric acid subsequently making the volume to 1 litre with 20% sulphuric acid. 1 ml. = 0·0001 g bismuth. The tube contents should be treated exactly as the sample and should cover the expected bismuth content of the sample which is to be compared with them.

From the figures obtained the percentage bismuth content of the sample is calculated.

Note: Coloured discs are available which remove the necessity of preparing bismuth standard.

Determination of Lead

Gravimetric, colorimetric and electrolytic methods are available.

Of these the electrolytic is recommended for normal practice, the gravimetric method, as usually applied to lead determinations, can be used with some slight modifications and the colorimetric method, based upon the use of diphenylthiocarbazone, is recommended for great accuracy in 'referee analyses'.

Electrolytic Method.—Weigh 10 g of drillings into a 600 ml. beaker and attack with 100 ml. of nitric acid (sp. gr. 1·2). Boil off the brown fumes and evaporate the solution to about 10 ml. Transfer to a 250 ml. beaker and dilute to 150 ml. Electrolyse at a P.D. of 3·5 volts until all the copper has been removed. The *anode* is to be weighed in this operation since it is on this electrode that the lead will be deposited. Wash and remove the anode without switching off the current, dry and weigh in the usual manner. Lead dioxide is deposited as a chocolate-brown stain. Care should be taken in handling since the deposit does not adhere firmly to the electrode.

$$\text{Weight of lead dioxide} \times 0{\cdot}866 = \text{weight of lead.}$$

Note: The identity of the deposit should be confirmed since if manganese is present in an appreciable amount it will be deposited on the anode with the lead.

Gravimetric Method.—Weigh 10 g. of drillings into a 600 ml. beaker and attack with 100 ml. of nitric acid (sp. gr. 1·2). Boil off brown fumes and evaporate to a pasty condition. Cool and add 20 ml. of concentrated sulphuric acid. Evaporate to fuming. Allow to cool, dissolve the copper salts with 300 ml. of water and allow to settle overnight if possible. Filter, collecting the lead sulphate on a Whatman No. 42 paper, wash free from copper salts with 4% sulphuric acid and then with minimum washings of

cold water to remove acid. Place approximately 10 g of ammonium acetate into the filter paper with the lead sulphate and wash through with a small amount of boiling water into a 400 ml. beaker. Wash thoroughly with water and dilute the filtrate to 100 ml. Boil the solution, add one or two ml. of acetic acid and then add slowly 5 ml. of a 10% solution of ammonium molybdate. Allow the precipitated lead molybdate to settle for 30 minutes on a warm plate and then filter through a pulp pad or a No. 40 Whatman paper. Wash with warm water, place the precipitate and paper in a porcelain crucible and carefully burn off the paper. The operation must not be hurried and the temperature must not exceed 600° C. or the precipitate may be reduced or fused. (Factor for conversion to lead is 0·5643.)

Determination of Nickel

Dissolve a 10 g sample in 100 ml. of the following acid mixture : 240 ml. of concentrated sulphuric acid, 600 ml. of water, 160 ml. of nitric acid. Warm to expel nitrous fumes. Cool and dilute to 300 ml. with water and electrolyse at 1 to 1·3 amperes to remove copper. When deposition of copper is complete, wash electrodes and evaporate the residual electrolyte and washings to about 250 ml. Neutralize with ammonia adding 5 ml. in excess, bring to the boil and filter off any iron and bismuth hydroxides. Add about 20 ml. of a 1% alcoholic solution of dimethylglyoxime to the ammoniacal filtrate, allow the red precipitate to stand for several hours on a warm plate and then filter through a tared sintered glass crucible. Wash well with water and dry for 1 hour at 110° C. Cool and weigh.

$$\text{Weight of precipitate} \times 0{\cdot}2032 = \text{nickel.}$$

If small this precipitate may be converted to nickel oxide by ignition in the usual manner.

Determination of Arsenic

Distillation Method.—Weigh 3 g of drillings into a dry 250 ml. distillation flask, and pour directly onto the sample, 150 ml. of special ferric chloride solution. This solution consists of 300 g of ferric chloride and 600 g of calcium chloride dissolved in 600 ml. of concentrated hydrochloric acid, and made up to 1 litre.

Fit the flask with a condenser and warm the contents to effect solution. Then distil almost to dryness in the normal manner collecting the distillate in a 250 ml. flask immersed in water.

Neutralize the distillate with 20% caustic soda solution and make just acid with concentrated hydrochloric acid using litmus

as an indicator. Cool, add 3 g of sodium carbonate. Add a few drops of potassium iodide and 5 ml. of starch solution and titrate with N/100 iodine solution to a permanent blue colour.

The iodine solution is made by dissolving 5 g of potassium iodide in the minimum amount of water and adding 1·27 g of iodine. When solution is complete make up to 1 litre with water.

The iodine solution may be standardized in the usual manner against arsenious oxide.

A blank assay should be run on arsenic-free copper using the same reagents as in the sample analysis.

1 ml. N/100 iodine ≡ 0·0004 g As.

Determination of Phosphorus

Gravimetric Method.—Weigh 5 g of drillings into a 500 ml. conical beaker and dissolve in a mixture of 20 ml. of hydrochloric acid and 30 ml. of nitric acid (sp. gr. 1·2). When solution is complete digest at just below boiling point for one hour and then dilute to 200 ml. with hot water.

Add 0·5 ml. of 10% ferric chloride (the object of which is to form ferric phosphate), and make alkaline with ammonia solution adding about 10 ml. of this reagent in excess. Boil for about one minute and filter through a No. 541 fluted Whatman filter paper. Wash alternately with hot water and a dilute ammonia solution (1 : 10). Dissolve the precipitate into the original beaker with hot hydrochloric acid (1 : 1) and make up solution to 100 ml. Add 10 g of ammonium chloride and make just alkaline with ammonia, and then just redissolve the precipitated ferric hydroxide with nitric acid. Raise the temperature of the solution to about 70° C. Add 40 ml. of ammonium nitro-molybdate solution (see note below). Allow the precipitate to settle until the supernatant solution is clear and filter through a pulp pad. Wash the precipitate six times with 3% nitric acid, to remove all traces of iron, and then with 3% potassium nitrate until acid free. Transfer the precipitate back to the original beaker and add 10 ml. of N/20 sodium hydroxide solution and 50 ml. of cold water. Shake well until the precipitate has completely dissolved in the sodium hydroxide solution and titrate the excess of sodium hydroxide with an equivalent solution of hydrochloric acid (N/20) using 2 drops of phenolphalein solution as the indicator.

Calculation. (ml. of sodium hydroxide — ml. of hydrochloric acid) × 0·0000674 = phosphorus content in grams.

Note: For the preparation of nitro-molybdate solution, see Appendix.

The nitro molybdate reagent should be added slowly to the phosphorus containing solution which should be just off boiling. It should not be brought to boiling point again as there is a danger of molybdic acid separating which may be recognized as a white granular precipitate.

Determination of Sulphur

Gravimetric Method.—Dissolve 10 g of fine drillings contained in a 400 ml. beaker with 100 ml. nitric acid (1 : 1). Evaporate to dryness. Redissolve in 50 ml. of hydrochloric acid (concentrated) and evaporate to a low volume. Filter on a No. 40 Whatman paper and wash well with dilute hydrochloric acid and finally several times with hot water. Fuse the residue with fusion mixture, cool, extract the melt with water, dilute to about 100 ml. and filter as before. Mix the two filtrates. Raise to boiling on hot plate and add 10% barium chloride solution with stirring. Allow to stand for several hours. Filter on a No. 40 Whatman paper and wash well as before. Dry the precipitate and ignite in a porcelain crucible. Weigh as barium sulphate. ($BaSO_4 \times 0{\cdot}1374 = S$.)

Note: An evolution method of analysis may be used and the effluent gas absorbed in cadmium acetate. The analysis being completed by titration with iodine and sodium thiosulphate as usual but the above method is accurate and easier of manipulation.

Determination of Non-Metallic Inclusions

Weigh 10 g of drillings into a 500 ml. conical flask, add 250 ml. of alcohol and 80 ml. of bromine and allow to stand in a cool place until solution is complete. When this is accomplished filter through a Whatman paper (No. 1) using alcohol to wash the paper free from bromine. Transfer to a porcelain crucible and burn off the paper at about 500° C. Cool and weigh.

The nature of the precipitate, which is usually of a siliceous nature, may be determined by qualitative means.

Determination of Cuprous Oxide (approximate)

Weigh 3 g of drillings into a 400 ml. beaker and pour over them 100 ml. of a 2% solution of silver nitrate. Allow to stand in a cool place for one hour. Filter through a Whatman paper No. 1 and wash well with water. Transfer precipitate to a porcelain dish and treat with sulphuric acid (1 : 1). Filter and determine the copper in the filtrate by any method desired.

1 part of copper ≡ 1·68 parts of cuprous oxide.

A very accurate method of determining total oxygen in copper is by heating a prepared sample in hydrogen and measuring the water vapour pressure produced. (Baker, *Metallurgia*, 1949. **40.** 188.)

Determination of Tellurium

Gravimetric Method.—Dissolve 10 g in the minimum amount of nitric acid, evaporate on a water bath to dryness, redissolve in hydrochloric acid. Dilute to 200 ml. with hot water. Adjust acidity of hydrochloric acid present to 5%, warm to keep any traces of lead in solution and pass sulphur dioxide. Filter off the precipitate of tellurium which is produced. Wash well with water, filter through a tared sintered glass crucible and dry at 105° C. Weigh as metallic tellurium.

Note: If there is any considerable quantity of lead and bismuth present the procedure as from the obtaining of a solution of 200 ml. should be as follows :

Make the solution just ammoniacal then just acid with acetic acid which should be in sufficient quantity as to keep copper and lead in solution. Boil and a white precipitate of tellurium dioxide is produced. Filter through a sintered glass crucible, wash with warm water and dry at 105° C. Factor for conversion to tellurium is 0·8.

METHOD OF ANALYSIS OF PIG LEAD

For Antimony, Copper, Bismuth and Zinc.

Preparation of Sample.—Cut the lead into small pieces (about a quarter of an inch square) and wash with benzene or other suitable solvent to remove grease. Afterwards wash the sample with dilute hydrochloric acid (1 part acid to 10 parts water), followed by distilled water until the lead is free from acid. Finally dry the sample in air.

Solution of the Sample

Weigh 500 g into a 3000 ml. beaker. Add 1500 ml. water, then while stirring add cautiously 500 ml. concentrated nitric acid. Place the beaker on a warm plate and heat until dissolved.

Note 1 : The solution should be clear but if any residue remains it may contain antimony and tin. Filter if necessary and dissolve the residue in a few ml. of hydrochloric acid. Dilute to 20 times its volume with hot water and saturate with hydrogen sulphide.

Allow to stand overnight. Filter and reserve the precipitate for determination of antimony and tin. The filtrate can now be discarded.

Preliminary Separation of Antimony, Copper, Bismuth and Zinc

In order to remove the bulk of the lead, add while stirring hot dilute sulphuric acid made by carefully adding 175 ml. 98% sulphuric acid to 500 ml. water. Allow to cool and filter off the lead sulphate precipitate on a large Buchner funnel, washing the precipitate with 500 ml. cold dilute sulphuric acid (5% by weight). This lead sulphate precipitate can now be discarded. It is now necessary to evaporate the large bulk of filtrate, and this is best done in a porcelain dish in a fume cupboard. The liquid is evaporated to 10 ml. and allowed to cool. Transfer to a 200 ml. beaker and dilute to 100 ml. with water. Heat to boiling and allow to cool. Filter and wash the insoluble with a little dilute sulphuric acid (5%).

The precipitate on the paper now referred to as *Precipitate* (*A*) and the filtrate referred to as *Filtrate* (*A*) are dealt with as follows:

Precipitate (*A*).—Rinse off the paper with hot water and dissolve in as small amount of hot hydrochloric acid as is required to obtain a clear solution. Pour this solution into 20 times its bulk of hot water and saturate with hydrogen sulphide. Allow to stand in a warm place for an hour then filter and wash once with warm water, discard the filtrate and reserve the precipitate which is now referred to as *Precipitate* (*B*).

Filtrate (*A*).—Nearly neutralize with ammonia, dilute with water to 150 ml. and add a few drops of sulphurous acid solution and 2 ml. dilute sulphuric acid (1:1). Heat to boiling to remove excess of sulphur dioxide, cool and saturate with hydrogen sulphide. Allow to stand overnight, then filter. The precipitate on the paper is now referred to as *Precipitate* (*C*), and the filtrate as *Filtrate* (*B*). These are dealt with as described below.

The two precipitates (B) and (C) are now combined, together with precipitate from treating any insoluble residue which may have been found when the lead was dissolved in nitric acid as explained in Note 1. Boil with 50 ml. dilute potassium hydroxide solution (2%), then filter and wash with hot water. The filtrate now referred to as *Filtrate* (*C*) contains all the antimony and is dealt with as described below. The precipitate left on the paper now referred to as *Precipitate* (*D*) containing copper and bismuth is treated as described later.

Determination of Antimony

Neutralize *Filtrate* (*C*) with hydrochloric acid (1:1) and add 5 ml. of hydrochloric acid saturated with bromine. Evaporate the solution to 20 ml. Add 20 ml. hydrochloric acid and 1 g sodium sulphite crystals. Cover the beaker and boil down gently to about 15 ml. Now add 20 ml. of hydrochloric acid and 150 ml. hot water. Bring just to boiling and titrate hot with N/20 potassium bromate solution using methyl orange (3 drops of methyl orange solution, 0·1 g in 100 ml. water) as indicator. The end-point is shown when 1 drop of potassium bromate solution discharges the methyl orange colour.

1 ml. N/20 potassium bromate = 0·00304 g Sb.

Determination of Bismuth

Dissolve *Precipitate* (*D*) in hot nitric acid (1:1) containing bromine and evaporate the solution to about 10 ml. Add 10 ml. hydrochloric acid and 20 ml. water, boil and filter, using hot 1:5 hydrochloric acid to wash the residue on the filter. This residue can be discarded. The bismuth in the filtrate is next precipitated as bismuth oxychloride as follows :

Add ammonia until nearly neutral, cool the solution and dilute to 100 ml. Adjust the acidity of the solution using 3 drops methyl orange solution as indicator, and adding ammonia until yellow followed by hydrochloric acid until 1 drop of hydrochloric acid just changes the colour of the indicator from yellow to red. Dilute the solution to 350 ml. with water, heat to boiling and allow to stand in a warm place until the bismuth oxychloride settles. Filter and wash with hot water. Reserve the filtrate, referred to later as *Filtrate* (*D*), for copper determination. Dissolve the bismuth oxychloride in a little hot dilute hydrochloric acid (1:1). Add 20 ml. dilute sulphuric acid (1:1) and evaporate to fuming. Cool, dilute to 50 ml. with water and filter into a 250 ml. graduated flask. Make up to the mark with dilute sulphuric acid (5%). The bismuth is determined colorimetrically as follows :

Add a measured quantity of the solution to a 100 ml. Nessler tube. The quantity of the solution taken should be such that not more than 2 ml. of standard bismuth solution is required to match the colour produced later. The correct amount to be taken is best ascertained by a preliminary test. Now add to the solution in the Nessler tube 50 ml. water, 5 ml. sulphuric acid (10%), 5 ml. freshly made 5% potassium iodide solution, and 2 drops of sulphurous acid solution (one part saturated solution to 10 parts water). Mix the solution and dilute exactly to the 100 ml. mark. Next take a

second Nessler tube and measure the same quantity of acid, water, potassium iodide solution and sulphurous acid as is present in the first tube, then add standard bismuth solution from a burette until the yellow colour in the two tubes is exactly the same. For the preparation of standard bismuth solution dissolve 0·1 g of pure bismuth in 20 ml. sulphuric acid, cool and dilute exactly to one litre.

1 ml. = 0·0001 g Bi.

Determination of Copper

Heat *Filtrate* (*D*) nearly to boiling and saturate with hydrogen sulphide. Filter and dissolve the precipitate in nitric acid (1 : 1). Add 20 ml. sulphuric acid (1:1) and evaporate to fuming. Cool, dilute with water to 100 ml., boil, and allow to stand overnight. Filter and wash with dilute sulphuric acid (1:10). Saturate the filtrate with hydrogen sulphide and allow to stand until the precipitate settles. Filter and wash with water containing a little hydrogen sulphide. Ignite the precipitate in a porcelain crucible at dull red heat. Dissolve the residue in 2 ml. nitric acid and determine copper colorimetrically as follows. Dilute the solution and add an excess of ammonia. Transfer to a Nessler tube and dilute to 100 ml. Compare colour with that produced by a measured quantity of standard copper solution in ammonia. Standard copper solution is made by dissolving 1 g copper in 10 ml. nitric acid, and diluting to 1 litre.

1 ml. = 0·001 g Cu.

Determination of Zinc

Boil *Filtrate* (*B*), containing the zinc, free from hydrogen sulphide. Add slight excess of bromine water to oxidize the iron, then boil off the excess bromine. Add 10 ml. ammonium chloride solution (10%), and slight excess of ammonia. Filter and wash with hot water. Neutralize the filtrate exactly with hydrochloric acid, using methyl orange as indicator. Add 1 drop acetic acid (30%) and saturate with hydrogen sulphide. Allow precipitate to settle, filter and wash with water. Rinse the precipitate from the paper into a small beaker, add 2 ml. dilute sulphuric acid (1:1) and evaporate to fuming. Cool, dilute with 20 ml. water then neutralize exactly with ammonia, using methyl orange as indicator. Make just acid to methyl orange with sulphuric acid, (not more than 2 drops N/10 sulphuric after the solution was yellow to methyl orange). Saturate the solution with hydrogen sulphide and allow to settle overnight. Filter, burn off and weigh as zinc oxide.

METHOD OF ANALYSIS OF INGOT TIN

for Copper, Lead, Bismuth, Iron, Nickel, Cobalt, Zinc, Cadmium, Antimony, Arsenic, Silver and Sulphur

General Note

In view of the small amounts of impurities present in high-grade tin, reagents used must be of the best quality available and blank determinations must be carried through with every assay.

Preparation of Sample

In order to obtain the sample in a form convenient for analysis, granulate bars of the metal by melting in a sulphur-free flame and allowing the molten metal to fall into water. Dry and thoroughly mix the granulated material.

Solution of Sample and Removal of Bulk of the Tin

Reagents required

Hydrobromic acid (sp. gr. 1·49).
Hydrochloric acid (sp. gr. 1·18).
Liquid bromine.
Nitric acid (sp. gr. 1·42).

Method.—Weigh 100 g sample into a 700 ml. Pyrex flask, add 100 ml. water, 100 ml. hydrobromic acid (sp. gr. 1·49), 100 ml. hydrochloric acid (sp. gr. 1·18) and bromine a little at a time, while cooling the flask, until the sample is in solution. Evaporate first on a sand bath then over a naked flame, swirling vigorously, to incipient dryness, but avoid baking. Dissolve in 10 ml. hydrochloric acid (sp. gr. 1·18), clear with a few drops of nitric acid (sp. gr. 1·42), then dilute to 100 ml. in a standard flask.

Prepare a similar blank solution on reagents, but evaporate off most of the bromine before adding the acids.

Determination of Copper

Reagents required

Ammonium citrate (20%).—Dissolve 20 g ammonium citrate in water and dilute to 100 ml.
Ammonium hydroxide (sp. gr. 0·880).

Gum arabic (1%).—Dissolve 1 g gum arabic in warm water, and dilute to 100 ml.

Sodium diethyldithiocarbamate (0·1%).—Dissolve 0·1 g reagent in water and dilute to 100 ml.

Standard copper solution.—Dissolve 0·1 g pure copper in 2 ml. nitric acid (sp. gr. 1·42), boil out fumes and dilute to 1000 ml. Dilute 20 ml. of this solution to 100 ml. immediately before use.

1 ml. = 0·00002 g copper.

Method.—Pipette 10 ml. sample solution into a 100 ml. beaker, evaporate to low bulk to remove excess acid, dilute a little, transfer to a 50 ml. Nessler glass, add 5 ml. ammonium citrate (20%), 2 ml. ammonium hydroxide (sp. gr. 0·880) 10 ml. gum arabic (1%) and 1 ml. sodium diethyl-dithiocarbamate solution (0·1%). Estimate the copper by adding standard copper solution to a similar Nessler glass containing the same reagents, until the colours match.

Determination of Lead

Reagents required

Ammonium citrate (20%).—Dissolve 20 g ammonium citrate in water and dilute to 100 ml.

Ammonium hydroxide (sp. gr. 0·880).

Potassium cyanide (20%).—Dissolve 20 g potassium cyanide in water and dilute to 100 ml.

Diphenylthiocarbazone solution (0·1%).—Dissolve 0·2 g diphenylthiocarbazone in 100 ml. chloroform without heating. Transfer to a separating funnel, add 100 ml. water and 5 ml. ammonium hydroxide (sp. gr. 0·880). Shake thoroughly, discard the chloroform layer, wash the aqueous layer with two 5 ml. portions of chloroform, then add 200 ml. chloroform and hydrochloric acid (sp. gr. 1·18) until the aqueous layer after shaking is colourless. Discard the aqueous layer, wash the chloroform solution twice with water.

Perchloric acid (60%).

Hydrogen peroxide (20 vol.).

Hydrochloric acid (sp. gr. 1·18).

Potassium dichromate solution (N/10).—Dissolve 4·9033 g potassium dichromate in water and dilute to 1000 ml.

Ammonium hydroxide (1 : 1).—Dilute one volume ammonium hydroxide (sp. gr. 0·880) with an equal volume of water.

Acetic acid (1 : 1).—Dilute one volume glacial acetic acid with an equal volume of water.

Potassium nitrate (2%).—Dissolve 2 g potassium nitrate in water and dilute to 100 ml.

Nitric acid (1 : 1).—Dilute one volume nitric acid (sp. gr. 1·42) with an equal volume of water, boil to remove nitrous acid, cool.

Diphenylcarbazide solution (0·1%).—Dissolve 0·1 g diphenylcarbazide in 50 ml. glacial acetic acid and dilute to 100 ml. with water.

Potassium dichromate solution (N/1000).—Dilute 10 ml. potassium dichromate solution (N/10) to 1000 ml. with water.

1 ml. = 0·000069 g lead.

Method.—Pipette 5 ml. sample solution into a 100 ml. beaker, evaporate to low bulk to remove excess acid, transfer to a separating funnel, add 5 ml. ammonium citrate (20%) sufficient ammonium hydroxide (sp. gr. 0·880) to make the solution alkaline, and 2 ml. potassium cyanide (20%). Extract with successive 10 ml. portions diphenylthiocarbazone solution (0·1%) until the last extract is green in colour, combine the extracts and wash three times with water. Discard the aqueous layer and washings.

Transfer the chloroform solution to a 150 ml. beaker, evaporate almost to dryness, add 2 ml. perchloric acid (60%) and 2 ml. hydrogen peroxide (20 vol.), and heat to destroy organic matter and until all perchloric acid is expelled. Dissolve the residue in six drops hydrochloric acid (1 : 1), add 5 ml. water, 5 ml. potassium dichromate solution (N/10), ammonium hydroxide (1 : 1) until the colour turns to yellow green, acetic acid (1 : 1) dropwise until orange and three drops in excess. Boil for 10 minutes, cool and allow to stand overnight.

Filter on a sintered glass crucible (porosity 4) and wash thoroughly with potassium nitrate (2%). Dissolve through into a 50 ml. Nessler cylinder with 10 ml. nitric acid (1 : 1, free from nitrous acid), wash lightly with water, cool and add 5 ml. diphenylcarbazide solution (0·1%). Estimate the lead by adding standard potassium dichromate solution (N/1000) to a similar Nessler glass containing the same reagents, until the colours match.

Determination of Bismuth

Reagents required

Solutions for extraction.—As for lead.

Sulphuric acid (sp. gr. 1·84).

Nitric acid (sp. gr. 1·42).

Potassium iodide (20%).—Dissolve 20 g potassium iodide in water and dilute to 100 ml.

Starch solution (0·5%).—Make a paste of 0·5 g soluble starch with cold water, pour into 100 ml. boiling distilled water, boil for a few minutes and cool. Prepare freshly as required.

Sodium thiosulphate solution (2%).—Dissolve 2 g sodium thiosulphate in water and dilute to 100 ml.

Sulphuric acid (1 : 9).—Pour 10 ml. sulphuric acid (sp. gr. 1·84) into 50 ml. water, cool and dilute to 100 ml.

Standard bismuth solution.—Dissolve 0·1 g pure bismuth in 10 ml. sulphuric acid (sp. gr. 1·84), cool and dilute to 1000 ml. Dilute 10 ml. of this solution to 100 ml. immediately before use.

1 ml. = 0·00001 g bismuth.

Amyl alcohol-ethyl acetate (3 : 1).—Mix 75 ml. amyl alcohol and 25 ml. ethyl acetate.

Method.—Extract a 10 ml. portion of the sample solution with diphenylthiocarbazone solution exactly as for lead. Evaporate off the chloroform, add 4 ml. sulphuric acid (sp. gr. 1·84), heat to fumes, clear the solution by the dropwise addition of nitric acid (sp. gr. 1·42), then heat strongly to eliminate nitric acid. Cool, add 20 ml. water, cool, add 3 ml. potassium iodide (20%), a few drops of starch solution (0·5%) and sufficient sodium thiosulphate (2%) to discharge any blue colour. Dilute to 50 ml. with sulphuric acid (1 : 9). Estimate the bismuth by adding standard bismuth solution to a similar Nessler glass containing the same reagents, until the colours match.

If the bismuth iodide colour is very weak, add 5 ml. amyl alcohol-ethyl acetate (3 : 1) to both sample and standard, shake thoroughly and compare the colour of the extract.

Determination of Iron

Reagents required

Potassium thiocyanate (30%).—Dissolve 30 g potassium thiocyanate in water and dilute to 100 ml.

Standard iron solution.—Dissolve 0·1 g pure iron wire in 10 ml. nitric acid (1 : 1), boil out fumes and dilute to 1000 ml. Dilute 10 ml. of this solution to 100 ml. immediately before use.

1 ml. = 0·00001 g iron.

Method.—Dilute 5 ml. of the sample solution to 50 ml. in a standard flask. Pipette 5 ml. of the diluted solution into a 100 ml. Nessler cylinder, add 1 drop hydrochloric acid (sp. gr. 1·18), dilute to 90 ml. and pipette in 10 ml. potassium thiocyanate solution (30%). Estimate the iron by adding standard iron solution to a similar Nessler glass containing the same reagents until the colours match.

Determination of Nickel

Reagents required

Ammonium citrate (20%).—Dissolve 20 g ammonium citrate in water and dilute to 100 ml.

Dimethylglyoxime solution (0·1%).—Dissolve 0·1 g dimethyl glyoxime in 50 ml. ammonium hydroxide (sp. gr. 0·880) and dilute to 100 ml.

Bromine Water (saturated).

Method.—Pipette 5 ml. sample solution into a 50 ml. Nessler cylinder, add 5 ml. ammonium citrate (20%), 5 ml. dimethylglyoxime solution (0·1%), 1 ml. bromine water, and dilute to 50 ml. Estimate the nickel by comparison with standards containing varying amounts of nickel treated similarly to the sample.

Determination of Cobalt

Reagents required

Sodium acetate (50%).—Dissolve 50 g sodium acetate in water and dilute to 100 ml.

Nitroso-R-salt (0·5%).—Dissolve 0·5 g nitroso-R-salt in water and dilute to 100 ml.

Method.—Pipette 5 ml. sample solution into a 50 ml. beaker and evaporate almost to dryness. Add 4 ml. sodium acetate (50%) 5 ml. water and 2 ml. nitroso-R-salt (0·5%). Boil for 45 seconds, add 1·5 ml. hydrochloric acid (sp. gr. 1·18) and boil for further 45 seconds. Compare with suitable standards, treated similarly.

Determination of Zinc

Reagents required

4·75 *buffer solution.*—Mix equal volumes of 2N acetic acid and 2N sodium acetate. Remove heavy metals by extraction

with diphenylthiocarbazone solution (0·1% in chloroform). Filter off chloroform droplets.

Sodium thiosulphate solution (25%).—Dissolve 25 g sodium thiosulphate in water and dilute to 100 ml.

Diphenylthiocarbazone solution (0·001%).—Prepare diphenylthiocarbazone solution (0·1%) as described for the determination of lead. Dilute 10 ml. to 1000 ml. with chloroform.

Method.—Pipette 5 ml. sample solution into a 50 ml. beaker and evaporate almost to dryness. Add 10 ml. water, 5·0 ml. 4·75 buffer solution and 1·0 ml. sodium thiosulphate solution (25%). Shake vigorously with 5·0 ml. diphenylthiocarbazone solution (0·001%) and observe the colour. Compare with the following table:

Quantity of Zinc $g \times 10^{-6}$	*Colour*
0	Green
1	Blue
2	Purple violet
3	Violet
4–5	Red violet

Confirm if necessary by treating standards containing known amounts of zinc in the same way.

Determination of Cadmium

Reagents required

Diphenylthiocarbazone solution (0·005%).—Prepare diphenylthiocarbazone solution (0·1%) as described for the determination of lead. Dilute 5 ml. to 100 ml. with chloroform.

Sodium hydroxide (10%).—Dissolve 10 g sodium hydroxide in water and dilute to 100 ml.

Sodium potassium tartrate solution (20%).—Dissolve 20 g sodium potassium tartrate in water and dilute to 100 ml.

Sodium Hydroxide (2%).—Dissolve 2 g sodium hydroxide in water and dilute to 100 ml.

Method.—Pipette 5 ml. sample solution into a 50 ml. beaker and evaporate almost to dryness. Dilute to 10 ml. and extract with two 5 ml. portions of diphenylthiocarbazone solution (0·005%). Discard the extract. Add to the aqueous layer an equal volume of sodium hydroxide (10%) and 5 ml. sodium potassium tartrate (20%). Shake with three successive 5 ml. portions of dithizone, or until

extraction is complete, discard the aqueous layer, wash the chloroform layer with two 10 ml. portions sodium hydroxide (2%) to extract excess dithizone. Finally shake the chloroform layer with 50 ml. water made just acid with hydrochloric acid. This converts the unstable cadmium dithizone complex to free dithizone, the colour of which is then compared with standards treated similarly.

Determination of Antimony

Reagents required

Hydrochloric acid (sp. gr. 1·18).
Liquid bromine.
Oxalic acid.
Sodium hypophosphite.
Sodium peroxide.
Ammonium nitrate (1%).—Dissolve 10 g ammonium nitrate in water and dilute to 1000 ml.
Sulphuric acid (sp. gr. 1·84).
Nitric acid (sp. gr. 1·42).
Gum arabic (1%).—Dissolve 1 g gum arabic in warm water and dilute to 100 ml.
Potassium iodide (20%).—Dissolve 20 g potassium iodide in water and dilute to 100 ml.
Pyridine (10% v/v).—Dilute 10 ml. pyridine to 100 ml. with water.
Sulphurous acid (1 : 9).—Saturate 10 ml. water with sulphur dioxide and dilute to 100 ml.
Sulphuric acid (1 : 3).—Pour 250 ml. sulphuric acid (sp. gr. 1·84) into 500 ml. water, cool and dilute to 1000 ml.
Standard antimony solution.—Dissolve 0·1 g pure antimony by heating with 10 ml. sulphuric acid (sp. gr. 1·84), cool and dilute to 1000 ml.

1 ml. = 0·0001 g antimony.

Method.—Dissolve 20 g tin in a mixture of 150 ml. water, 100 ml. hydrochloric acid (sp. gr. 1·18) and 20 ml. bromine. Boil to remove excess bromine, dilute to 400 ml., add 10 g oxalic acid and 10–15 g sodium hypophosphite. Boil and if appreciable amounts of arsenic are precipitated, filter. Insert a piece of clean copper foil, about 6 inches × 1 inch, rolled into a coil, into the solution and boil gently for 2 hours. Carefully remove the coil and wash by immersion in cold water. Transfer to a 50 ml. beaker, cover with distilled water and add 0·5–1·0 g sodium peroxide. Allow to

stand 10–15 minutes, warm gently so that the coil becomes coated with a layer of oxide, decant off the liquid and wash the coil with water.

Confirm that the antimony is completely removed by immersing the coil in sulphuric acid (1 : 3) when the oxide stain is removed and any dark colour due to residual antimony may be observed.

Pass a rapid stream of hydrogen sulphide through the solution for 15 seconds and allow to stand on a water bath for 30 minutes. Filter on a small paper pulp pad and wash lightly with ammonium nitrate (1%). Add 5 ml. sulphuric acid (sp. gr. 1·84) and evaporate to fumes, introducing a few drops of nitric acid (sp. gr. 1·42) to oxidise organic matter. Add 15 ml. water, boil and cool. Filter if necessary.

Prepare the following mixture in a 50 ml. Nessler cylinder :

2 ml. gum arabic (1%)
1 ml. potassium iodide (20%)
0·2 ml. pyridine (10%)
0·2 ml. sulphurous acid (1 : 9)
12 ml. sulphuric acid (1 : 3)

Pour the assay solution into this and compare with a standard containing similar amounts of reagents, but 18 ml. sulphuric acid (1 : 3). Run in standard antimony solution until the colours match.

Determination of Arsenic

Reagents required

Mercuric chloride (1·5%).—Dissolve 1·5 g mercuric chloride in water and dilute to 100 ml.

Potassium permanganate (0·1%).—Dissolve 0·1 g potassium permanganate in water and dilute to 100 ml.

Hydrochloric acid (sp. gr. 1·18).

Sulphuric acid (1 : 5).—Pour one volume sulphuric acid into five volumes of water.

Ammonium molybdate (1%).—Dissolve 1 g ammonium molybdate in 10 ml. water + 90 ml. sulphuric acid (1 : 5).

Hydrazine sulphate (0·15%).—Dissolve 0·15 g hydrazine sulphate in water and dilute to 100 ml.

Ammonium molybdate/hydrazine sulphate reagent.—Prepare immediately before use by mixing 10 ml. ammonium molybdate (1%) with 10 ml. hydrazine sulphate (0·15%) and diluting to 100 ml.

Standard arsenic solution.—Dissolve 0·132 g arsenious oxide in 1 g sodium hydroxide dissolved in 20 ml. water and dilute to 1000 ml. Dilute 10 ml. of this solution to 100 ml. before use.

1 ml. = 0·00001 g As.

Method.—Weigh 5 g tin into a small evolution apparatus with ground glass joints. Place in the absorbing vessel, which should contain glass beads or small pieces of glass tube, a mixture of 10 ml. mercuric chloride (1·5%), 1·5 ml. potassium permanganate (0·1%) and 2·0 ml. sulphuric acid (1 : 5). Add 25 ml. water and 25 ml. hydrochloric acid (sp. gr. 1·18) to the tin sample, connect up the apparatus and warm until all is dissolved. (A trace of an antimony compound may be added to catalyse the reaction.) Add 2–3 g zinc (arsenic free) and warm until dissolved.

To the distillate, add 50 ml. ammonium molybdate/hydrazine sulphate reagent, heat for 15 minutes on a water bath, cool and dilute to 250 ml. Prepare a standard, containing 0·0002 g arsenic, by treating 20 ml. standard arsenic solution in the same way. Compare the two by taking a known volume of the sample solution in a 100 ml. Nessler and run the standard solution into a similar Nessler until the colours match when diluted to 100 ml.

Determination of Silver

Reagents required

Hydrobromic acid (sp. gr. 1·49).
Hydrochloric acid (sp. gr. 1·18).
Liquid bromine.
Sodium carbonate.
Litharge.
Argol.
Nitric acid (1 : 1).—Dilute one volume of nitric acid (sp. gr. 1·42) with an equal volume of water.
Nitric acid (*approx.* N/20).—Dilute 4 ml. nitric acid (sp. gr. 1·42) to 1000 ml.
p-Dimethylamino-benzal-rhodanine (0·05%).—Dissolve 0·05 g p-dimethylamino-benzal-rhodanine in 100 ml. ethyl alcohol.
Standard silver solution.—Dissolve 0·1 g silver in 10 ml. nitric acid (1 : 1), boil out fumes and dilute to 1000 ml. Dilute 10 ml. of this solution to 100 ml. before use.

1 ml. = 0·00001 g Ag.

Method.—Dissolve 200 g sample in a mixture of 150 ml.

hydrobromic acid (sp. gr. 1·49) and 150 ml. hydrochloric acid (sp. gr. 1·18), adding bromine as necessary to keep the solution oxidised. Evaporate to low bulk, about 10 ml., add excess solid sodium carbonate and evaporate to dryness on a sand bath. Thoroughly mix the dry residue with 100 g litharge, 30 g argol, 30 g anhydrous sodium carbonate, transfer to a fireclay pot, heat in a furnace until the melt is quiescent, then pour into button mould. When cold, clean the lead button and scorify by heating in a furnace in a current of air to oxidise tin. When the surface of the button is covered with oxide, add borax, allow to fuse then pour into a button mould. Clean and cupel the resultant lead button, but remove from the muffle before cupellation is complete. About 20–30 milligrammes of lead should be left and allowance must be made for the fact that a button several times this size will cool to the required dimensions while the cupel is cooling.

Dissolve the button of lead in nitric acid (1 : 1) evaporate gently to dryness, and take up the residue in 50 ml. nitric acid (N/20). Add from a pipette 0·50 ml. p-dimethylamino-benzal-rhodanine (0·05%), and compare with a standard containing similar amounts of reagents, adding standard silver solution until the colours match.

Determination of Sulphur

Reagents required

Hydrochloric acid (sp. gr. 1·18).

Liquid bromine.

Barium chloride (10%).—Dissolve 10 g barium chloride in water and dilute to 100 ml.

Apparatus.—The apparatus used for this determination is all glass, and consists of a 1500 ml. reaction flask fitted with tap funnel, lead in for hydrogen generated in a Kipps apparatus, and a delivery tube leading to the absorption train, which is made up of two bubblers, containing liquid bromine and two Dreschel bottles containing a layer of liquid bromine covered with water.

Method.—Weigh 200 g sample into the reaction flask, displace air from the apparatus by means of a current of hydrogen, then reduce the flow and dissolve the tin by the addition of 700 ml. hydrochloric acid (sp. gr. 1·18), warming or cooling as necessary to moderate the velocity of the reaction. A little antimony salt may be added if solution is slow. When all the tin is dissolved, increase the flow of hydrogen to flush out all hydrogen sulphide.

Wash the contents of the bubblers into a beaker, warm gently

to expel excess bromine, then evaporate to low bulk. Neutralize with ammonium hydroxide (sp. gr. 0·880) using methyl orange indicator, add an excess of 2 ml. hydrochloric acid (sp. gr. 1·18) and dilute to 200 ml. Bring to the boil and add, while boiling, 5 ml. barium chloride (10%). Boil for 10 minutes, allow to stand overnight, filter on a small paper pulp filter and wash thoroughly with hot water. Transfer to silica crucible, dry and ignite to barium sulphate.

Factor: $BaSO_4 \times 0{\cdot}1374 =$ sulphur.

METHOD OF ANALYSIS OF ZINC

for Arsenic, Iron, Lead, Aluminium, Tin, Cadmium, Copper

1. **Preparation of Sample.**—Drillings or sawings should be taken right through the ingots (at points along one diagonal) and mixed together. These should be freed from mechanically entangled iron by a magnet, washed with benzene and kept in a well stoppered sample bottle until required.

2. **Solution of Sample.**—Since the determinations of the various elements listed above are made on separate samples the method of solution is given under the individual procedures recommended.

Determination of Arsenic (Gutzeit method)

SOLUTIONS

Sodium hydroxide solution.—Dissolve 20 g of sodium hydroxide in 50 ml. of distilled water, cool, and dilute to 100 ml.

Stannous chloride solution.—Dissolve 100 g of stannous chloride in 100 ml. hydrochloric acid and dilute to 1 litre with distilled water.

Copper sulphate solution.—Dissolve 100 g of copper sulphate in distilled water, and dilute to 1 litre.

Lead acetate solution.—Dissolve 100 g of lead acetate in distilled water, and dilute to 1 litre.

Mercuric chloride solution.—Dissolve 25 g of mercuric chloride in distilled water and dilute to 1 litre.

PREPARATION OF THE STANDARDS

The arsenic solution

1. Weigh 1·320 g of resublimed arsenious oxide (As_2O_3) into a 400 ml. conical beaker.

2. Dissolve the arsenious oxide in 25 ml. of 20% sodium hydroxide solution.
3. Neutralize the free sodium hydroxide with dilute sulphuric acid using phenolphthalein as indicator.
4. Dilute to a bulk of 1 litre in a graduated flask with freshly distilled water containing 10 ml. of concentrated sulphuric acid per litre.
5. Dilute 100 ml. of this solution to 1 litre with distilled water containing 10 ml. of concentrated sulphuric acid per litre.
6. Similarly dilute 10 ml. of solution from (5) to 1 litre.
7. 1 ml. now contains 0·000001 g arsenic.

The mercuric chloride paper

1. Soak a sheet of good quality drawing paper or Whatman No. 1 filter paper in distilled water for 2 hours.
2. Allow to drain.
3. Soak the sheet of paper in the mercuric chloride solution contained in a dish which is gently rocked so that there is a slight motion in the liquid.
4. Continue for 1 hour.
5. Remove the sheet of paper and replace it the other side up.
6. Continue the soaking for another hour.
7. Lift out the paper and remove the excess liquid by lightly rolling with a 'squeegee' roller, and allow to dry.
8. Cut up the paper into strips of the required lengths (i.e. $\frac{1}{8}$ inch $\times$ 3 inches).
9. The papers should be prepared in as pure an atmosphere as possible to avoid subsequent interference with the test.
10. The papers should be kept in a closed receptacle in a dark place.

The lead acetate paper

Prepare the lead acetate paper in a similar manner to the mercuric chloride paper.

PREPARATION OF THE STANDARD STAINS

1. Prepare eleven 150 ml. extraction flasks.
2. Conduct No. 1 flask as a 'blank' on the reagents which should, of course, be arsenic free, and in the other flasks, commencing with No. 2, place 1 ml., 2 ml., 3 ml., etc., up to 10 ml. of the arsenic solution.
3. Dilute the solution in each flask to 100 ml. with distilled water.

4. Add 5 ml. of pure concentrated sulphuric acid.
5. Oxidize the solution with N/10 potassium permanganate until a permanent pink coloration is given.
6. Add 5 ml. of the stannous chloride solution and 2 drops of copper sulphate solution.
7. Place a mercuric chloride paper in the top of the tube of the apparatus.
8. Add about 5 g of zinc (arsenic free) to the flask.
9. Run the test for 45 minutes.
10. Remove the papers and place them in a large tube containing solid calcium chloride. They are kept out of contact with the calcium chloride by means of a piece of filter paper.
11. The tube is then sealed and kept in the dark.
12. Fresh standards should be prepared at least every 3 months, or sooner if any fading is apparent.

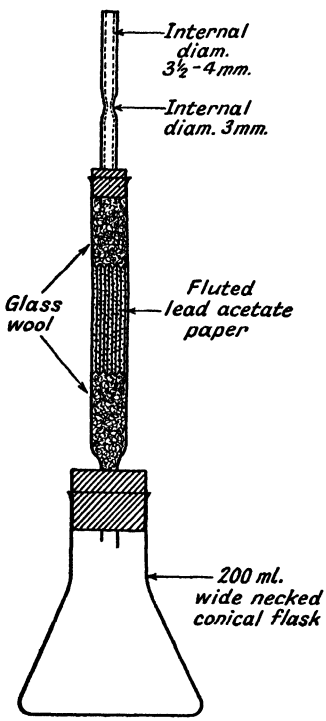


FIGURE 4.
Diagram of Gutzeit apparatus.

Reagents

Sulphuric acid, A.R. quality (sp. gr. 1·840).

Stannous chloride solution (10% [w/v] in 10% [v/v] hydrochloric acid).

Copper sulphate solution (10% [w/v]).

N/10 potassium permanganate solution (approx.).

Method

1. Place 100 ml. distilled water in the flask of the Gutzeit apparatus and add 5 ml. concentrated sulphuric acid. Cool the solution.
2. Add N/10 potassium permanganate solution until a permanent pink coloration is produced.
3. Add 5 ml. stannous chloride solution, and 2 drops of copper sulphate solution.
4. Place a mercuric chloride paper in the top of the tube of the apparatus.

5. Add 1 g of the degreased sample "fines" together with 5 g. Zn (As free) to the solution and replace the bung.
6. Allow the test to run for 45 minutes.

Any stain on the paper indicates the presence of arsenic in the zinc and should be matched against the standard stains.

Calculation.—Stain × 0·0001 = % As (for a 1 g sample).

Determination of Iron

STANDARD SOLUTION REQUIRED

Titanous chloride.—200 ml. of concentrated hydrochloric acid are added to 140 ml. of titanous chloride (15% solution) and the mixture diluted to 4 litres with distilled water. The solution is stored under an atmosphere of hydrogen, and standardized against ferrous ammonium sulphate.

1 ml. = 0·0016 g Fe (approx.).

INTERNAL INDICATOR

10% ammonium thiocyanate solution.

Reagents

Hydrochloric acid (sp. gr. 1·16).
Nitric acid (sp. gr. 1·42).
Ammonia (sp. gr. 0·880).
Sulphuric acid (20% by volume).
N/10 *potassium permanganate.*

Method

1. 50 to 100 g of sample are placed in a litre beaker and 200 or 400 ml. (according to the weight taken) of hydrochloric acid (sp. gr. 1·16) added.
2. When the reaction has nearly ceased 25 ml. nitric acid (sp. gr. 1·42) are added and the solution allowed to stand until the metal has dissolved. Dilute with 100 ml. water.
3. Neutralize with ammonia, and add sufficient excess to keep the zinc salts in solution, boil for about five minutes, and allow to stand on a hot plate for about thirty minutes.
4. Filter while hot, and wash twice with hot water (discard the filtrate).
5. Dissolve the precipitate by pouring hot 20% H_2SO_4 over the paper, wash with hot water. Cool, and dilute to about 200 ml. with water.

6. Add N/10 potassium permanganate until a permanent pink colour is obtained, then 10 ml. of ammonium thiocyanate, and titrate with titanous chloride.

Calculation

$$\frac{(\text{ml. } TiCl_3 \times \text{Fe equivalent}) \times 100}{\text{Weight Taken}} = \% \text{ Fe}$$

Notes:

(1) Iron-free reagents must be used.

(2) The amount to be taken as sample depends on the purity of the zinc. The weight suggested in the determination is suitable for high quality metal but for commercial zinc 25 g is to be taken. In this case some adjustment of quantity of acid for solution is necessary.

Determination of Lead

STANDARD SOLUTION REQUIRED

Ammonium molybdate.—Approximately 9 g of A.R. ammonium molybdate are dissolved in distilled water, diluted to 1 litre and standardized against pure lead sulphate.

EXTERNAL INDICATOR

Tannic acid solution.—Dissolve 1·0 g of tannic acid in distilled water and dilute to 100 ml.

Reagents

Sulphuric acid concentrated (sp. gr. 1·840).

Nitric acid concentrated.

Ammonium acetate solution slightly acidified with Acetic Acid. (Prepared by mixing equal volumes of concentrated ammonia liquor sp. gr. 0·880 and glacial acetic acid and then adjusting the acidity.)

Method

1. Weigh out 10·0 g of the sample into a 650 ml. conical beaker, add 100 ml. of distilled water and 25 ml. of concentrated sulphuric acid. Cover with watch glass and allow to stand overnight.
2. Filter through a 15 cm. 633 E, English Postlip filter paper and wash well with cold water. Discard filtrate.
3. Wash spongy mass back into the original beaker with hot water pour 15 ml. of concentrated nitric acid over paper and wash again with hot water.

4. Evaporate to about 10 ml., cool and add 10 ml. concentrated sulphuric acid. Heat until copious white fumes of sulphur trioxide are evolved. Allow to cool, dilute with distilled water to about 15 ml., boil, cool, and allow lead sulphate to settle.
5. Filter through a No. 633 E, 12·5 cm. English Postlip filter paper washing well with cold distilled water slightly acidified with sulphuric acid, finally washing with cold water.
6. Wash the lead sulphate precipitate back into the original beaker with hot water, and pour 15 ml. of hot ammonium acetate solution over the paper, again washing well with hot water. Dilute to about 150 ml. with water, bring to boil, and titrate with standard ammonium molybdate solution, using a freshly prepared 1% solution of tannic acid as external indicator. The end point is reached when a faint yellow colour develops in the indicator.

Calculation.—ml. × 0·01 × 10 = % Pb.

Determination of Aluminium

Reagents required

Hydrochloric acid (50% v/v).
Nitric acid, concentrated (sp. gr. 1·42).
Ammonium chloride A.R.
Ammonium hydroxide 2*N* (approx.).
Sulphuric acid (25% v/v).
8-*hydroxyquinoline solution.*—Dissolve 2·5 g 8-hydroxyquinoline in 5 ml. acetic acid and make up to 100 ml. with distilled water.
Ammonium acetate solution.—Dissolve 400 g ammonium acetate in 1 litre of distilled water.
Methyl red indicator.
Ammonium Chloride Wash Solution (2% solution).

Method

1. Weigh 50 g of sawings and transfer to a 650 ml. conical beaker.
2. Add 350 ml. (1 : 1) hydrochloric acid, and when reaction has subsided add 5 ml. of concentrated nitric acid. Boil and cool. Filter if necessary.
3. Add 10 g ammonium chloride and when dissolved add 2 N. ammonium hydroxide until just alkaline to methyl red indicator. Boil.
4. Filter off precipitate and wash with hot 2·5% ammonium chloride solution.

5. Redissolve precipitate into original beaker with dilute hydrochloric acid, dilute with water.
6. Add a few drops of methyl red indicator and then 2 N. ammonium hydroxide until colour change just takes place. Boil.
7. Filter off precipitate and dissolve in minimum amount of dilute sulphuric acid (1 : 3 by volume). Add methyl red indicator and neutralize with (1 : 1) ammonium hydroxide and re-acidify with (1 : 1) sulphuric acid (about 1 ml.).
8. Electrolyse in any modern type of mercury cathode cell, e.g. the Melaven cell using Pt gauze cylinder as rotating anode. Cover the cell with split watch glasses having a central hole. Adjust volume of solution to 175 ml.
9. Electrolyse for 45 minutes at a current of 6 amperes or correspondingly longer at lower currents.
10. On completion of the electrolysis, switch off the current and immediately run off the mercury through the two-way tap, separating sharply from the solution.
11. Withdraw solution and wash cell and anode thoroughly with the minimum quantity of water (about 25 ml.).
12. Adjust volume of solution to 200 ml.
13. Warm to 50–60° C. and add 30 ml. of 2·5% oxine solution from a burette, swirling the contents of the beaker.
14. Add 100 ml. of ammonium acetate solution slowly with stirring. Stand for 10 minutes.
15. Filter through a tared No. 4 sintered glass crucible. Wash with hot water, until washings show no yellow colour.
16. Dry for 1½ hours at 140° C. Cool. Weigh.

Calculation.—Weight of oxinate × 0·05871 × 2 = Weight of aluminium.

Determination of Tin

Reagents required

Hydrochloric acid (50% v/v).
Nitric acid, concentrated (sp. gr. 1·42).
Ammonium hydroxide (0·88 S.G.).
Ammonium chloride A.R.
Ammonium chloride (2% w/v solution).
Antimony chloride solution.—Dissolve 0·5 g of antimony chloride in 100 ml. of dilute hydrochloric acid (1 : 2).
Sodium bicarbonate (10% solution).
Potassium iodide (10% solution).

Starch (1% solution).
Standard potassium iodate (0·01N solution).

1 ml. = 0·0005935 g tin.

Method

1. Weigh 50 g of sawings and transfer to a 650 ml. beaker.
2. Add hydrochloric acid (1 : 1) in small quantities until reaction ceases. (About 350 ml. is required.) Add a little nitric acid to complete the solution of the assay.
3. Add 10 g ammonium chloride and a slight excess of ammonium hydroxide. Boil, filter and wash with hot 2% ammonium chloride solution.
4. Redissolve precipitate with about 150 ml. of hot hydrochloric acid (1 : 1) by pouring on to the filter and catching the solution in a 500 ml. wide mouth Erlenmeyer flask. Wash with hot water.
5. Add 2 ml. of antimony chloride solution. Bring to just boiling and add 0·5 g of aluminium foil in small quantities. Before the last piece dissolves, insert rubber bung, fitted with two-right-angled-bend delivery tube in neck of flask.
6. Boil for half an hour. Cool under water tap whilst the end of the delivery tube is immersed in 200 ml. of sodium bicarbonate solution contained in a 350 ml. beaker.
7. When cold, remove the bung, add the remainder of the sodium bicarbonate solution, 10 ml. of potassium iodide solution and 5 ml. of starch solution and titrate immediately with potassium iodate solution until a permanent blue colour just appears.

Calculation.—ml. of $KIO_3 \times 0{\cdot}0005935 \times 2 = \%$ tin.

Notes:

(*a*) A blank determination, containing an equivalent amount of tin-free zinc, should be carried out with each series of determinations, and allowance made to the test results.

(*b*) When the metal sample is low in iron, as in the case of high-grade zinc, some ferric chloride solution should be added to the assay, prior to the addition of ammonium hydroxide (Paragraph 3), so that the precipitated iron hydroxide serves as a carrier for the tin hydroxide.

Determination of Cadmium

Of the several methods available, viz. : chemical, electrolytic and polarographic, the electrolytic is recommended for the normal determination in commercial metal.

Reagents

Hydrochloric acid, concentrated (sp. gr. 1·16).
Nitric acid (sp. gr. 1·42).
Ammonia (sp. gr. 0·880).
Sodium sulphide solution.—Prepared by dissolving 100 g of sodium hydroxide in water, diluting to 2·5 litres and passing hydrogen sulphide through the solution until saturated.
Dilute sulphuric acid.—50% (vol.).
Hydrogen sulphide water.

Method

1. Attack 10 g of the sample with 40 ml. of concentrated hydrochloric acid in a 650 ml. conical beaker. Allow to stand for a few minutes on hot plate and then add 7 ml. of concentrated nitric acid. Boil to expel nitrous fumes.
2. Dilute the solution with 50 ml. cold distilled water then add *slowly* 50 ml. ammonia. Boil, and again add *slowly* 5–10 ml. sodium sulphide solution. Shake well.
3. Filter through a No. 633 E, 15·0 cm. English Postlip filter paper into a 650 ml. conical beaker. Do not wash at this stage. Discard filtrate.
4. Wash precipitate back into the original beaker with hot distilled water, and pour 15 ml. concentrated nitric acid over the paper, again washing well with hot water.
5. Add 15 ml. dilute sulphuric acid to the solution, place on hotplate and heat until copious white fumes of sulphur trioxide are evolved. Allow to cool, dilute with distilled water to about 150 ml., boil and allow precipitate to settle until cold.
6. Filter through a No. 633 E, 15·0 English Postlip filter paper, into a 650 ml. conical beaker, washing precipitate well with cold distilled water slightly acidified with sulphuric acid, finally washing with cold water. Discard precipitate unless required for lead determination.
7. Dilute filtrate with distilled water to about 400 ml., place on hotplate and raise to boiling.
8. Gas with hydrogen sulphide for half an hour, adding a few drops of ammonia to ensure complete precipitation of cadmium sulphide. Allow precipitate to settle.
9. Filter through a No. 5, 15·0 cm. Whatman filter paper and wash precipitate well with cold distilled water. Discard filtrate unless required for iron determination.
10. Wash the precipitate of cadmium sulphide, etc., back into the original beaker with hot water. Pour 10 ml. hot concentrated hydrochloric acid over the paper and again wash well with

hot water. Raise to boiling, add 2–5 ml. of saturated hydrogen sulphide water and filter through a No. 1, 15·0 cm. Whatman filter paper, washing well with hot water. Discard precipitate.

11. Boil the filtrate to remove all hydrogen sulphide and reduce the volume to about 100 ml. Transfer the solution to a 400 ml. squat beaker.

12. Add 5 drops of B.D.H. 4·5 Indicator and a strong solution of caustic soda (*not* ammonia) until the solution just turns blue, then add 2% sulphuric acid from a dropping bottle until the neutral point (grey) is reached, followed by the addition of the following solutions from pipettes, in the order given :

    5 ml. acetic acid solution. (50 ml. of glacial acetic acid to 1 litre of distilled water.)
    2 ml. hydrazine hydrochloride solution. (100 g of the salt in water, filtered, made up 400 ml. with distilled water.)
    25 ml. zinc sulphate solution. (200 g of the salt in water, made up to 500 ml.)
    5 ml. sodium acetate solution. (200 g of the salt in water, made up to 500 ml.)

INTERNAL ELECTROLYSIS* (modified Sand's apparatus)

The solution should be clear and with a greyish blue colour. It is recommended to flush out the anode compartment with an anolyte consisting of a solution obtained by dissolving 100 g of ammonium chloride in water and adding 104 g of anhydrous zinc chloride, making up to 1 litre.

The solution to be electrolysed is now brought under the electrodes, heated to 70° C. and maintained at this temperature while the electrolysis is carried out for 30 minutes. The solution should be mechanically stirred by any convenient means. Lower the beaker and remove the Pt gauze cathode, wash in hot water, rinse in alcohol and then in ether and dry in hot air oven for 10 minutes. Cool for 10 minutes and weigh. Increase in weight of cathode = Cd.

Determination of Copper

STANDARD SOLUTIONS

Copper sulphate. Dissolve 3·8966 g A.R. cupric sulphate in distilled water containing 5 ml. H_2SO_4 and dilute to 1 litre

* For description of apparatus see E. M. Collin "*Analyst*" 1930, **55**, 495, and J. G. Fife "*Analyst*" 1936, **61**, 681.

with distilled water in a standard graduated flask. 1 ml. = 0·001 g Cu. Dilute 10 ml. of the above solution to 1 litre with distilled water. 1 ml. = 0·00001 g Cu.

Reagents required

Hydrochloric acid, concentrated (sp. gr. 1·16).
Potassium chlorate crystals, A.R.
Ammonium citrate.—500 g of citric acid dissolved in 500 ml. of ammonia (sp. gr. 0·880) and made up to 1 litre with distilled water.
Ammonium hydroxide (sp. gr. 0·880).
Sodium diethyl-dithio-carbamate (0·1% aqueous solution).
Fused calcium chloride (granular).

Method

1. Weigh 25 g of zinc into a 650 ml. beaker.
2. Add 100 ml. concentrated hydrochloric acid.
3. When action has almost ceased place on hot plate and heat nearly to boiling.
4. Add potassium chlorate a little at a time until solution is complete.
5. Evaporate to a bulk of 50 ml.
6. Cool and make up to 500 ml. in a graduated flask. In some cases lead chloride will separate, but this may be ignored, the supernatant liquor only being used for subsequent tests. A blank on all the reagents should be prepared in the same manner.
7. Take 20 ml. of the solution prepared above (equivalent to 1 g of original metal), add 10 ml. of ammonium citrate solution, 50 ml. of ammonium hydroxide and 15 ml. of sodium diethyl-dithio-carbamate solution. Mix and make up to 100 ml. with distilled water.
8. Extract this solution with successive portions of 10 ml. carbon tetrachloride, adding 15 ml. of sodium diethyl-dithio-carbamate each time, until the extract is colourless.
9. Combine the extracts and make up to 100 ml. with carbon tetrachloride in a graduated flask.
10. Add a few lumps of fused calcium chloride as a drying agent.
11. Prepare a similar extract of the blank on the reagents.
12. Using a Spekker Absorptiometer measure the light absorption of the test extract using 4 cm. cells, Ilford spectrum blue filters No. 602 and a blank setting of 0·6, a tungsten filament being used as light source. The copper content of the aliquot taken is read from the appropriate graph.

Calibration Graph for 'Spekker' Absorptiometer.—Into a number of 100 ml. graduated flasks measure quantities of 0 to 10 ml. in increments of 1 ml. of standard copper solution from a burette. To each flask add 10 ml. of ammonium citrate solution, 20 ml. of 20% ammonium hydroxide and 10 ml. sodium diethyl-dithiocarbamate solution. Make up to 100 ml. with distilled water and mix thoroughly. Extract each solution with carbon tetrachloride as previously described.

Measure the light absorption of these extracts as before and graph the results obtained.

An alternative (but less accurate) method is to compare visually the colours of carbon tetrachloride extracts of both assays and standards, using Nessler glasses.

Standards may be prepared from standard copper sulphate solution, exactly as described in above paragraph for calibrating the 'Spekker' absorptiometer.

ANALYSIS OF NICKEL

		Range
1.	Nickel ..	80·0 to 99·9%
2.	Cobalt ..	0·01 to 1·00%
3.	Silicon ..	0·01 to 6·00%
4.	Iron ..	0·01 to 1·00%
5.	Manganese ..	0·01 to 5·0%
6.	Copper ..	0·01 to 1·0%
7.	Sulphur ..	0·001 to 0·01%
8.	Carbon ..	0·01 to 2·0%

Determination of Nickel

Reagents

Perchloric acid ($HClO_4$) 70%.

Tartaric acid (300 g per litre).

Dimethylglyoxime (10 g per litre of industrial methylated spirit).

Special Apparatus

A Jena fritted glass crucible of No. 4 porosity 30 to 50 ml. capacity.

Procedure.—Transfer 0.1000 g to a 400 ml. beaker cover and add 20 ml. of nitric acid (1 : 1) and heat gently until action ceases. Add 10 ml. of perchloric acid (70%) and evaporate solution

to dense white fumes. Replace cover and continue heating until the perchloric acid refluxes and the silicic acid has been dehydrated (10 minutes' boil should suffice). Allow the beaker to cool, add 100 ml. water and 10 ml. hydrochloric (1 : 1) and boil. Filter through a medium filter paper into a 600 ml. beaker washing first with hot 5% hydrochloric and then with hot water. (Small residues can be discarded but if more than 1% of silicon is present treat as follows. Ignite the paper in a platinum crucible, cool, add 2 ml. of perchloric and 5 ml. of hydrofluoric acid and evaporate to dense fumes of $HClO_4$. Cool, dilute and add to main filtrate.) Add 10 ml. of tartaric acid solution and neutralize with NH_4OH adding 1 ml. in excess. Dilute to 400 ml. and heat to 60° to 70° C. Add, while stirring vigorously, 60 ml. of dimethylglyoxime solution, cover and stand for 1 hour on low heat (60° C.). Filter through a tared Jena crucible and wash well with hot water. Dry at 110° C. to constant weight. Cool and weigh as nickel dimethylglyoxime. Factor = 0·2032.

Alternatively, the nickel-glyoxime precipitate may be filtered through a filter paper washed well with hot water, redissolved in H_2SO_4, evaporated to fumes and any carbonacious matter destroyed with HNO_3. Cool, dilute and make ammoniacal adding 25 ml. NH_4OH (0·880) in excess and electrolyse, preferably overnight at 0·2 to 0·3 amp. per sq. dm.

Determination of Cobalt

Reagents

Perchloric acid (*$HClO_4$*) 70%.

Zinc oxide.—Suspension of finely ground ZnO in distilled water. Shake well before using.

Alpha-nitroso-beta-naphthol solution.—7 g per 100 ml. of glacial acetic acid, and filter. Prepare this just before using.

Procedure.—Weigh 5 g of sample into a 400 ml. beaker and dissolve in 70 ml. dilute HNO_3 (1 : 1). Add 25 ml. of $HClO_4$ (if an appreciable amount of Si is present add sufficient HF to dissolve it), remove cover and evaporate to dense white fumes. Cover beaker and boil for 5 minutes. Add 1 ml. of HCl in order to reduce any chromic acid and remove from heat. Add 300 ml. of hot water and digest until the solution is clear. Stir vigorously and add small amounts of ZnO suspension until a slight excess of ZnO is present. Heat gently for 15 minutes and filter into a 600 ml. beaker washing well with hot water. Heat the filtrate to boiling and add 10 ml. of the alpha-nitroso-beta-naphthol solution

and boil for 5 minutes. Allow to stand at 60° C. for 1 hour and filter on a low ash medium filter paper, washing well with 5% HCl hot. Ignite in a tall form porcelain crucible and cool. Fuse with 1 to 2 g of potassium pyrosulphate and leach out in 100 ml. of water to which has been added 10 ml. of HCl. Dilute to 200 ml. and reprecipitate the Co as previously described. Ignite the precipitated cobalt in a tared porcelain crucible and weigh as Co_3O_4. If more than 0·5% of Cu is present in sample, fuse the weighed residue in potassium pyrosulphate and dissolve in 10% H_2SO_4. Saturate with H_2S, filter and wash with 1% H_2SO_4 saturated with H_2S and ignite at 900° C. to 1000° C. Cool and weigh. Subtract the weight of this from the first residue weight to give Co_3O_4. *Factor* = 0·7342.

Determination of Silicon and Iron

Reagents

Perchloric acid ($HClO_4$).—70%.

Ammonium thiocyanate.—100 g. dissolved in 500 ml. water.

Ammonium persulphate.—2·5 g dissolved in 500 ml. water.

Stannous chloride.—0·5 $SnCl_2$ $2H_2O$ in 10 ml. HCl and dilute to 100 ml.

Mercuric chloride.—80 g in 1 litre of hot water. Cool and use saturated solution.

Sulphuric-phosphoric acid.—150 ml. H_2SO_4 + 150 ml. H_3PO_4 (sp. gr. 1·75) to 700 ml. water.

Sodium-diphenylamine-sulphonate indicator.—Dissolve 0·32 g of barium diphenylamine sulphonate in 100 ml. of sodium sulphate (100 g per litre) and filter off $BaSO_4$.

Standard potassium dichromate solution.—0·02 N.

Procedure.—Weigh 2 g of sample into a 250 ml. beaker and dissolve in 40 ml. of dilute HNO_3 (1 : 1). When solution is complete add 20 ml. $HClO_4$, remove cover and evaporate to dense white fumes. Replace cover and increase heat until the $HClO_4$ boils and continue boiling for 10 minutes. Cool and add 50 ml. water and 5 ml. of HCl. Boil and filter through medium low ash paper washing well with hot 5% HCl and finally with hot water. Ignite paper in a silica or platinum crucible to constant weight. If the above procedure is carried out carefully the SiO_2 can usually be accepted as pure for routine work. However, for highest accuracy, treat with HF and H_2SO_4 and regard the loss in weight as true

SiO_2. Factor is 0·4762. Make filtrate ammoniacal and boil. Filter through medium filter washing well with hot water. For Fe values of 0 to 0·5% follow section (*a*). For Fe content of 0 to 5% follow section (*b*).

(*a*) Dissolve hydroxides off paper in 10% HCl. Dilute to 200 ml. and pipette off two 10 ml. aliquots. Add to one aliquot, 10 ml. of ammonium persulphate solution and 10 ml. of ammonium thiocyanate solution and dilute to 100 ml. To the other aliquot add 10 ml. of ammonium persulphate solution only and dilute to 100 ml. Fill a 2 cm. cell with the solutions and measure the absorption on a 'Spekker' absorptiometric apparatus using Ilford spectrum green No. 604 filters and a water setting of 1·0. Read the drum difference on a calibrated graph for Fe%.

(*b*) Redissolve hydroxides in HCl and again reprecipitate with ammonia, boil, filter and wash with hot water. Dissolve in hot 10% HCl washing paper well. Bring solution to the boil and add slowly stannous chloride solution until solution is colourless and add 3 to 5 drops excess. Cool to tap water temperature and dilute to 100 ml. Add 15 ml. of mercuric chloride solution and stir well. After a 5 minute period, add 30 ml. of phosphoric-sulphuric solution and 3–5 drops of sodium-diphenylamine-sulphonate solution and titrate with 0·02N $K_2Cr_2O_7$ solution until solution turns a permanent reddish violet. The $K_2Cr_2O_7$ solution should be standardized against a known iron standard. (The use of British Chemical Standard No. 150, prepared by the Bureau of Analysed Samples Ltd., Middlesbrough, is recommended.)

Determination of Manganese

Potentiometric titration

Acid solvent:

Water.—1335 ml.

Sulphuric acid (sp. gr. 1·84).—250 ml.

Phosphoric acid (sp. gr. 1·75).—315 ml.

Nitric acid (sp. gr. 1·42).—600 ml.

Silver nitrate solution (8 g per litre).

Ammonium persulphate.—250 g per litre.

Sodium arsenite solution.—2·72 g of sodium arsenite and 5 g of potassium bicarbonate are dissolved in 150 ml. hot water. Cool, filter, if necessary, and dilute to 1 litre. Solution is approx. N/20. For Mn content below 0·20% use N/40.

Procedure

0 to 0·2% weigh 2 g sample
0·2 to 2·0% weigh 1 g sample
2·0 to 4·0% weigh 0·5 g sample
4% upwards, fractionate by pipette 0·1 g from 1 g sample.

Dissolve in 30 ml. of acid solvent in a 250 ml. covered beaker, and boil gently until all nitrous fumes have been removed. Filter, if necessary, washing with 1% cold HNO_3. Dilute to 150 ml. and heat nearly to boil. Add 10 ml. of silver nitrate solution and 10 ml. of ammonium persulphate solution. Boil for 1 minute exact (timed). Cool to 20° C. and dilute to 200 ml. if Mn is over 1% and titrate at once. Employ the Cambridge Potentiometric Titration Apparatus using a mercurous sulphate electrode. The sodium bismuthate method gives equally good results but is somewhat longer than the above.

Determination of Copper (0 to 0·1%)

Weigh 20 g into a 800 ml. beaker, cover and add in small portions 125 ml. of HNO_3. Allow each portion to react until spent before adding next. If a large amount of gelatinous silicic acid is present, add just enough HF to dissolve it. Heat gently until action ceases, remove cover and evaporate the solution until it comes syrupy and a thin scum forms over the surface. Add 100 ml. hot water and heat until the syrup dissolves. (Ti and Zr may precipitate in which case stir well and add HF until precipitates dissolve.)

Filter through a medium paper and wash with hot water. Dilute to 300 ml., heat to 60° C. and pass H_2S through hot solution. Continue gassing until cold. Add a little filter pulp and filter, washing with a 1% H_2SO_4 solution saturated with H_2S. Transfer paper to beaker, add 15 ml. HNO_3 and 10 ml. $HClO_4$ (70%) and evaporate slowly to dense white fumes. Cover and boil gently for 5 minutes. Cool, add 100 ml. water and 2 ml. of HNO_3 and boil until the salts dissolve. Cool, filter if necessary and electrolyse overnight at 0·3 to 0·4 amp. per sq. dm. (A higher amperage can be employed if using a rotating anode in which case Cu should be completely deposited in 1 hour.) Wash and dry the electrode and weigh as metallic Cu.

Determination of Sulphur

Reagents

Potassium nitrate.
Granulated zinc.—Highest purity possible.

Barium chloride (10% aqueous solution).
Potassium sulphate (0·10% aqueous solution).

Procedure.—Weigh 5 g of sample into a 600 ml. beaker with a cover. Add a few crystals of potassium nitrate and 35 ml. of HNO_3 (sp. gr. 1·42) and carefully pour in 25 ml. of HCl (sp. gr. 1·16). With the cover still on evaporate to dryness and bake at 250° C. for 30 minutes. Cool and add 1 g of granulated Zn and 35 ml. of HCl (sp. gr. 1·16) and evaporate to a syrupy consistency. Dilute with 50 ml. of hot 1:20 HCl and boil. Filter through a pulp pad washing with hot 1:20 HCl and discard the pad. Dilute the filtrate to 300 ml., add from a pipette 10 ml. of potassium sulphate 0·10% and boil. Add slowly to the boiling solution 20 ml. of barium chloride 10% and boil for 1 minute and then stand in cold overnight. Filter through a compact pulp pad washing with warm 1:20 HCl containing a little barium chloride and finally with warm water. Ignite residue in a porcelain crucible at 700° C. and weigh as $BaSO_4$. With the assay run a blank treating this in exactly the same manner as above. Subtract the weight of the blank from that of the test to give the true $BaSO_4$ which multiplied by 2·75 is the % of S in the sample using a 5 g sample.

The combustion method for routine work may also be used. In this method the sample is burnt in a liberal supply of oxygen at 1400° C. in a platinum wound electric furnace, the gases are passed through a potassium sulphate-hydrogen peroxide solution for 3 minutes. The furnace is then by-passed for 3 minutes allowing any C in the solution to be converted to CO_2 and dispelled. The solution is then titrated potentiometrically. The results are remarkably consistent with the gravimetric method and the experiment only takes 6 minutes to complete.

Determination of Carbon (by direct combustion method)

Normal carbon combustion train is employed. Weights of 5 g to 10 g of fine drillings are placed into unglazed porcelain boats (previously ignited under oxygen for 5 minutes at 1000° C.) lined with 'alundum' or alumina. Add an equal weight of pure tin or lead millings as an accelerator and place cover over boat. Transfer to hot zone of furnace 1200–1400° C. and burn for 30 minutes with oxygen supply at about 1 litre per minute.

Pack the absorption bulbs with 'Sandarite' or 'Carbosil'. In the event of very low C 10 g may be weighed into two boats. For higher ranges 2·729 g or 1·3645 g may be employed. A careful blank is required on all reagents used.

CHAPTER VI

TECHNICAL ANALYSIS OF NON-FERROUS ALLOYS

Section I

ALUMINIUM AND MAGNESIUM ALLOYS

Commercially pure aluminium which is manufactured almost exclusively by the electrolytic process of Hall and Heroult always contains small amounts of silicon, iron and copper. Traces of other elements may be detected by the spectrograph, but in practice the analyst is rarely called upon to determine these with the possible exception of titanium.

The elements commonly alloyed with aluminium are eight in number, comprising copper, magnesium, silicon, nickel, iron, zinc, manganese, and titanium. Tin and chromium are occasionally added, or together with lead may be present as adventitious contaminations, particularly in material which has been remelted or blended from scrap.

Select methods for these eleven elements which are given below are based on the carrying out of many thousands of determinations.

Details for the determination of uncommon and rare elements in aluminium alloys may be found elsewhere [1, 2, 30, 31, 32, 33] and several other useful publications dealing with the analysis of aluminium and its alloys are available.[3, 4, 5, 6, 7]

Indications are given where determination of more than one element may be made from a single sample weighing.

Examples of determinations which may be expeditiously and reliably accomplished by physical devices such as the Spekker absorptiometer [8, 9, 10, 11, 12, 34] and the polarograph [24, 25, 26] are included where these procedures have been sufficiently tested. For information concerning spectrographic technique of aluminium alloy analysis the appropriate section of this book should be consulted.

Where only one procedure is stated for any element it may be assumed that this has been found to be the most reliable although not necessarily the most rapid available.

The base metal aluminium is rarely determined directly, because

reliable methods are not available. If required, it is calculated by difference after determination of all other elements present.

COPPER

Copper is present in commercially pure aluminium in amounts generally not exceeding 0·1%, and in alloys from 0·1 to 14%. In addition hardener or key alloys containing up to 50% of copper are also manufactured.

(A) Volumetric Method

Copper contents 0·1 to 50%

Principle.—The sample is dissolved in mixed acids, and silica removed by fuming and subsequent filtration. Copper in the filtrate is then precipitated as copper sulphide, which is converted to oxide by ignition. The copper oxide is dissolved in acid, and copper determined by titration with sodium thiosulphate in the presence of potassium iodide.

Note: Although somewhat tedious, this method if conscientiously carried out can be thoroughly recommended as an accurate basic one for standard samples, e.g. for preparing calibration graphs for Method (C). It is not recommended for large scale routine determinations. The copper-free filtrate can be conveniently used for determination of several other elements, e.g. iron and nickel.

Reagents

Nitric acid	Concentrated
Hydrochloric acid	Concentrated
Sulphuric acid	Concentrated
Hydrogen sulphide gas	
Ammonia	S.G. 0·880
Acetic acid	Glacial
Potassium iodide	Pure crystals or 50% solution
Sodium thiosulphate	Standard solution 7·840 g crystals dissolved and made up to 1 litre. Add 1–2 g sodium carbonate per litre to stabilize. Standardize against electrolytic copper. 1 ml. = approx. 0·002 g copper.
Starch solution	
Electrolytic copper	

Procedure.—Attack suitable weight of sample (200 mg. to 2 g. depending on copper content) with 20 to 60 ml. *aqua regia* in a conical 300 ml. beaker.

When solution is complete add 5 to 15 ml. sulphuric acid and evaporate to fumes.

Cool, and add 30 to 60 ml. hot distilled water, and boil until the solution is clear.

Filter the silicon residue off on a pulp pad or a Whatman 540 paper which contains a pulped accelerator; collect the filtrate in a 500 ml. conical beaker, and wash the residue thoroughly with hot water.

Heat the filtrate to about 70° C., pass a steady stream of hydrogen sulphide for about 10 minutes.

Collect the copper sulphide on a pulp pad or a Whatman 541 paper containing an accelerator, and wash at least eight times with 0·2% sulphuric acid previously saturated with hydrogen sulphide.

Dry and ignite the copper sulphide in a porcelain or silica crucible at 600–700° C.

Brush the resulting copper oxide into the previously used 500 ml. beaker, and add 5 ml. nitric acid and 5 drops sulphuric acid to the crucible.

Heat the crucible and pour into the beaker containing the copper oxide.

Digest to complete solution, and then carefully evaporate to fumes, finally heating until all the fumes have ceased, but not so strongly that copper oxide is reformed.

Cool, dilute to 10 ml. with distilled water; add ammonia from a dropping bottle until there is one drop in excess of the amount required to produce the blue cupric ammonium compound.

Add 3 ml. acetic acid and allow to cool.

Add 2 g. potassium iodide (measured with a spoon) or 4 ml. potassium iodide solution, and titrate against standard sodium thiosulphate solution, adding starch solution as an indicator just before the end-point is reached.

(B) Electrolytic Method

Principle.—The alloy is attacked with sodium hydroxide solution to separate most of the aluminium. The copper is removed by filtration and re-dissolved in nitric and sulphuric acid mixture. This solution is then electrolysed to determine the copper.

Reagents

Sodium hydroxide	20% solution.
Acid mixture	Water 600 ml., sulphuric acid 180 ml., nitric acid, 180 ml.
Hydroxylamine sulphate ..	5% solution.
Acetone	
α-benzoin oxime	Dissolve a small crystal in acetone as required.

Procedure.—Attack 1 g. of sample with 10 ml. sodium hydroxide solution in a tall-form beaker. Allow the reaction to subside, and wash down the side of the beaker to remove adhering metal.

Warm the mixture until solution is as complete as possible.

Add 100 ml. of water and boil; filter through a pulp pad or a Whatman 541 paper.

Dissolve the residue which consists mainly of metallic copper, nickel, iron, etc., with perhaps some oxide or hydroxide, in 16 ml. of hot acid mixture, and wash thoroughly.

Boil the solution until nitrous fumes are no longer evolved, and then dilute with distilled water to a volume sufficient to cover the accurately weighed platinum electrodes.

Electrolyse for 15 minutes with a current density of 2 amps. per 100 sq. cm. of cathode surface and an E.M.F. of 3·5–6 volts at a temperature of 20–30° C., using a motor-driven stirrer, or rotating electrodes.

Add 1 ml. of hydroxylamine sulphate as a depolarizer at the commencement of the deposition, and a second 1 ml. after 10 minutes. Wash down the sides of the electrolyte beaker after this second addition.

After 15 minutes test for complete removal of copper by transferring a minute quantity of the electrolyte with a rod or capillary to a piece of test paper. Hold the test paper over an ammonia bottle and add one spot of freshly made solution of α-benzoin oxime. A green coloration indicates copper still present, in which case continue electrolysis for a further period.

When the electrolyte is completely free from copper as indicated by the above test, lower the beaker, but continue the current and stirrer, and wash the electrodes with a constant stream of hot water.

Switch off the current and stirrer; detach the electrodes and dehydrate the cathode by immersing into each of two acetone bottles, and dry in an air oven for one minute.

The increase in weight of the cathode gives the amount of copper deposited.

Note: If preferred electrolysis may be carried out on an acid solution following removal of silicon, providing that hydrochloric acid is not added. In this case add 3–4 ml. concentrated nitric acid before commencing electrolysis. It is also necessary to ensure that the final washing of the cathode is carried out meticulously because of possible contamination from aluminium salts.

(C) Rapid Photometric Method[11]

For Copper Contents up to 5%

Principle.—Photometric measurement of the brown complex of copper with sodium diethyldithiocarbamate in ammoniacal citrate solution. Citric acid is added to prevent interference by aluminium and iron.

Reagents

Nitric acid	Concentrated.
Hydrochloric acid	Concentrated.
Citric acid	30% aqueous solution.
Ammonia	S.G. 0·880.
Gum arabic	1% aqueous solution.
Sodium diethyldithiocarbamate	0·1% aqueous solution.

Procedure.—Weigh 100 mg. sample into a 150 ml. tall-form beaker, and attack with 5 ml. nitric acid, and 5 ml. hydrochloric acid.

When solution is complete, wash down sides of beaker with distilled water.

Filter off any undissolved silicon, and transfer to a 200 ml. wide necked flask (sugar flask).

Dilute to mark and mix very thoroughly.

Pipette into a 100 ml. graduated flask a 10 ml. aliquot (copper contents 0·2–5·0%); for copper contents below 0·2% take a larger aliquot, or adjust sample weight as required.

Add 5 ml. citric acid, and 15 ml. ammonia, followed by 5 ml. gum arabic, and 10 mi. sodium diethyldithiocarbamate.

Dilute to 100 ml., mix well and measure the absorption in a 4 cm. cell on a Spekker absorptiometer, using Ilford Violet 601 filter.

Deduct value for 'blank' on the same quantity of reagents similarly treated. and convert to copper from appropriate calibration graph.

Note: Nickel and iron may be conveniently determined on the same sample weighing as the copper (see photometric methods for nickel and iron).

MAGNESIUM

Magnesium is rarely present in commercially pure aluminium. In alloys it may be present in amounts from less than 0·10 to 11·0%.

Pyrophosphate Method

(1) *Determination of Magnesium in Aluminium Alloys (excluding those containing calcium)*

Principle.—For low silicon content alloys an initial sodium hydroxide attack to remove the major part of the aluminium is sufficient. With high silicon alloys, > 2%, an initial weak sodium hydroxide separation is used to remove aluminium, followed by a stronger one to remove silicon. The insoluble residue containing the magnesium is dissolved in *aqua regia* and the last traces of silicon removed by fuming. Most other interfering elements are separated using the mercury cathode. An ammonium hydroxide separation removes aluminium and titanium, followed by a bromine separation of the remaining manganese in the presence of a small amount of added iron. The magnesium is finally precipitated as magnesium ammonium phosphate and ignited to the pyrophosphate.

Reagents

Sodium hydroxide	A.R. pellets 1% wash solution
Aqua regia	3 parts hydrochloric acid, 1 part nitric acid
Hydrogen peroxide	20 vol.
Sulphuric acid	50% A.R.
Mercury	
Hydrochloric acid	A.R.
Ammonium hydroxide	A.R.
Bromo cresol purple indicator	
Ammonium chloride	1% solution, just ammoniacal to bromo cresol purple
Bromine	A.R.
Ammonium phosphate	10% aqueous solution
Ferric chloride	0·1 g dissolved in 100 ml. water
Ammonium persulphate ..	A.R.

Procedure

Wt. of sample > 2% Mg	0·5 g.
1–2% Mg	1·0 g.
0·5–1% Mg	2·0 g.
< 0·5% Mg	4·0–5·0 g.

(2) *Solution of Low Silicon Content Alloys*

Dissolve the sample in 4–8 g. sodium hydroxide pellets and 20–30 ml. warm water. Boil into solution, dilute to 150–200 ml., boil gently 5 minutes and filter on a Whatman 540 paper. Wash thoroughly with hot 1% sodium hydroxide.

(3) *Solution of High Silicon Content Alloys*

Weigh sample into a 500 ml. conical beaker and add 400 ml. warm water (50–60° C.). Add gradually 20–30 g. sodium hydroxide pellets, allow the alloy to dissolve and then boil gently 10 minutes. Stand on a water bath for 1 hour. Filter on a Whatman 541, 15 cm. and wash three times with hot 1% sodium hydroxide solution, wash once with hot water.

Wash back the residue off the paper into the original beaker with cold water. (Retain the paper.) Add 20–25 g. sodium hydroxide pellets and dilute to 50–100 ml. and boil 10–15 minutes with additions of hydrogen peroxide (5 ml.) to assist complete solution of the silicon.

Refilter on the original Whatman 541 and wash thoroughly with 1% sodium hydroxide solution. Pierce the paper and wash the precipitate into the original beaker with hot water. Wash round the paper with 15 ml. hot *aqua regia* then thoroughly with hot water.

To the extract, add 5 ml. 50% sulphuric acid and evaporate to fumes. Fume 5 minutes, cool and dilute with 75 ml. hot water. Boil the salts into solution and then filter on a Whatman 541, washing with hot water containing a little dilute sulphuric acid. Collect the filtrate and washings in a 250 ml. squat beaker (solution bulk 150–200 ml.)

Add 15 ml. clean mercury to the beaker and electrolyse using a platinum anode, and the simple type of cathode connection recommended by Chirnside, Dauncey and Proffitt[50] for 30 minutes. A current of 4–5 amps. is normal.

Siphon off the electrolyte into a tall 500 ml. beaker and wash beaker and electrodes 3–4 times with hot water. Siphon the washings into the main electrolyte. Filter if cloudy.

Evaporate to 150–200 ml. and add 10 ml. concentrated hydrochloric acid. Bring the solution just ammoniacal to bromo-cresol purple indicator. Boil for 1 minute, stand several minutes and

filter through a Whatman 541, retaining the filtrate in a second 500 ml. beaker.

Wash the hydroxides 5 times with hot ammonium chloride wash solution. Transfer funnel to the original beaker, pierce the paper and wash through the precipitate with hot water. Wash round the paper with 50 ml. 50% hydrochloric acid + 2 ml. nitric acid and then hot water. Reprecipitate as before. Filter on a Whatman 541 into the previous filtrate.

Evaporate the combined filtrates to 70–100 ml. bulk, cool, add 10 ml. ferric chloride solution, 10–15 ml. bromine water and make ammoniacal with 15 drops excess. Add 1–2 g. ammonium persulphate.

Boil 2 minutes, stand 10–15 minutes in a warm place and filter the coagulated precipitate on a Whatman No. 1 containing a small accelerator pad. Wash with hot 1% ammonium chloride solution containing 5 ml. ammonium hydroxide per litre.

Bring the filtrate just acid with hydrochloric acid, evaporate to 150 ml., cool, add 10 ml. 10% ammonium phosphate, bring just ammoniacal with ammonium hydroxide and then add sufficient excess to adjust the volume to 5% ammonium hydroxide.

Stand overnight.

Filter on a Whatman 40 or 540 containing an accelerator. 'Police' the beaker and wash the precipitate 15 times with cold 5% ammonium hydroxide solution.

Dry thoroughly and ignite slowly at 400° C. until all the carbonaceous matter is destroyed, then ignite at 1000–1100° C. for 30 minutes.

$$Mg_2P_2O_7 \times 0{\cdot}2184 = Mg.$$

The ignition is carried out in good quality silica crucibles.

Notes:

(1) The mercury cathode separation of interfering heavy metals is recommended as the most efficient and elegant of the available procedures. G. E. Smith's method[4] however has been found satisfactory. See also[16] for method employing 8-hydroxyquinoline.

(2) Any calcium present in the alloy will be precipitated along with magnesium as calcium phosphate by the above procedure.

In general, no appreciable error results as the calcium content is usually $< 0{\cdot}01\%$. If however it is desired to determine or remove the calcium it may be precipitated by adding 10 ml. of saturated ammonium oxalate following the bromine separation. Boil for 1 hour; stand several hours or preferably overnight; filter on Whatman 42. Ignite to calcium oxide and weigh, or determine volumetrically as preferred.

(3) *Photometric Determination of Magnesium.*—Where the number of daily determinations to be carried out is large the photometric method of Stross[15] based on the use of titan yellow is highly recommended. The conditions of separation of interfering metals, and colour development are however very critical, and therefore because of its rather specialized application, details are not given here. It should be pointed out however that at least two large light alloy laboratories (including that of the author) have been operating the process with great success for a considerable period. It is possible by this method to obtain a single magnesium result within 30 minutes.

SILICON

Commercially pure aluminium always contains silicon up to 0·5%. Alloys at present in use contain up to 13·5% or even higher amounts of silicon either with or without added elements such as copper, magnesium, nickel, iron and manganese.

(A) Alkali Attack Method

Principle.—The sample is attacked with sodium hydroxide solution in a nickel crucible. The solution is then transferred to perchloric acid, and evaporated to fumes. The silicon is then determined gravimetrically as SiO_2.

Reagents

Sodium hydroxide	30% solution
Hydrogen peroxide	10 vol. solution
Perchloric acid	50% solution
Hydrochloric acid	50% solution
Hydrofluoric acid	40–60% solution
Sulphuric acid	50% solution

Procedure.—Adjust sample weight to contain not more than 60 mg. and not less than 0·5 mg. of silicon.

Attack the sample in a covered nickel crucible with 15 ml. 30% sodium hydroxide.

When the reaction is complete wash down the sides of the crucible and the lid, with distilled water, and evaporate on the hot plate until the solution becomes pasty.

Cool and add 50 ml. water, and 3 ml. of hydrogen peroxide, and boil to ensure complete solution.

Cool and wash the contents of the crucible into a squat 600 ml. beaker containing 30 ml. of 50% perchloric acid (see Note 1).

'Police' the crucible thoroughly with a mixture of 50% hydrochloric acid and a few drops of hydrogen peroxide.

Evaporate the solution to fumes, and fume for 10 minutes.

Add 300 ml. 10% hydrochloric acid ; boil and filter on a Whatman 541 containing a pulped accelerator. 'Police' the beaker to remove all SiO_2.

Wash alternately with hot 50% hydrochloric acid and hot water (3 times each).

If lead is present wash with hot 25% ammonium acetate solution.

Finally wash 6 times with hot water.

Evaporate the filtrate to fumes once more, and treat the precipitate exactly as before, but filter on a Whatman 540.

Transfer the two precipitates to a platinum crucible and ignite at 1100–1150° C.

Add a few drops of concentrated sulphuric acid, and heat the crucible until no more fumes are evolved, and then heat to red heat (900° C.) to convert everything to oxide. Cool and weigh. Moisten the precipitate with water, add 2–3 ml. hydrofluoric acid and a few drops of concentrated sulphuric acid, and cautiously evaporate until no more fumes are evolved ; finally ignite at 1100–1150° C.

Cool and reweigh.

The loss in weight represents SiO_2.

$$SiO_2 \times 0{\cdot}4672 = Si.$$

Carry out a parallel blank determination using identical quantities of all reagents, and following the same procedure.

Notes:

(1) It is quite safe to use perchloric acid as specified above, provided that it is not brought into contact with organic matter, finely divided aluminium or silicon.

(2) If either tin or antimony are present in amounts exceeding 1% it is advisable that dehydration be carried out with 30 ml. sulphuric acid (33%) because of the oxidizing effect of perchloric acid.[4] Perchloric acid is normally preferred because it is a more efficient dehydrating agent than sulphuric acid and gives a more granular and easily filterable silica residue.

(3) When columbium is present the silica residue will contain some columbium pentoxide. In this case fuse the residue with potassium bisulphate, and extract the columbium with tartaric acid solution. Then proceed as above.[1]

(4) Rapid photometric methods have been described for the determination of silicon in aluminium alloys up to 15% content.[9, 10, 17, 18, 19, 20, 21, 22, 23]

Such methods are being used fairly extensively, but it is felt that until further investigations have been completed, which it is hoped may prove their reliability, they cannot justifiably be described as ' select' methods.

NICKEL

Nickel is rarely present in commercially pure aluminium, but is used in alloys up to 2·8%.

(A) Volumetric Method

Principle.—Nickel is precipitated in the filtrate from the copper sulphide precipitation or in the electrolyte following deposition of copper by dimethylglyoxime in the presence of tartaric acid.

Reagents

Tartaric acid	25% solution
Nitric acid	
Ammonium hydroxide	
Dimethylglyoxime	1% alcoholic solution. 10 ml. is sufficient excess to precipitate 20 mg. of nickel. Use additional 5 ml. for each further 5 mg. nickel
Hydrochloric acid	1 : 1
Hydrogen peroxide	20 volume solution
Potassium iodide	
Potassium cyanide	Standard solution (see Note 1)
Silver nitrate	Standard solution containing 5·789 g. A.R. reagent per litre

Procedure.—Boil the copper sulphide filtrate (see copper) for 15 minutes to remove hydrogen sulphide; add 5 ml. nitric acid and boil for a further 5 minutes. In the case of the copper electrolyte, boiling is obviously not necessary.

Add 30 ml. tartaric acid; adjust volume to about 250 ml.; make just ammoniacal to litmus paper.

Add dimethylglyoxime; bring just to boiling point, and allow to stand 30 minutes in a warm place.

Filter on Whatman 541; wash with hot water. Test filtrate with dimethylglyoxime to ensure complete removal of nickel.

Dissolve nickel dimethylglyoxime into original beaker with hot hydrochloric acid ; add 2 ml. hydrogen peroxide, and evaporate carefully to a syrup to destroy excess dimethylglyoxime.

Take up in the minimum of water ; add two drops of tartaric acid solution ; make faintly but distinctly ammoniacal by dropwise addition of 50% ammonia.

Dilute to 50 ml. and cool.

Add 5 fragments of potassium iodide to serve as indicator.

From a burette add about 1 ml. standard silver nitrate, and then add standard potassium cyanide until the turbidity is just cleared ; then add a further 2 ml.

Back-titrate with standard silver nitrate, detecting the end-point which is the first faint opalescence, against a black background.

Deduct total silver nitrate used from total potassium cyanide.

1 ml. potassium cyanide = 1 mg. nickel.

Notes:

(1) It is advisable to take an excess weight (4·75 g.) of potassium cyanide over theoretical (4·438 g. per litre) ; add 1 g. potassium hydroxide per litre.

Find by titration the strength of the potassium cyanide in terms of the silver nitrate ; add the calculated amount of water to the cyanide solution, and on a second titration the cyanide and silver nitrate solution should exactly balance. Check against pure nickel or a standard nickel-bearing aluminium alloy.

(2) If the nickel content is less than 0·5% take 2–5 g. sample as required.

If the nickel content is less than 0·1% allow the nickel dimethylglyoxime to coagulate overnight.

(3) The above volumetric finish is prefered to a gravimetric one, such as drying the complex at 110–120° C., or alternatively igniting it to nickel oxide.

(B) Rapid Photometric Method[11,13]

Nickel Contents 0·2–3·0%

Reagents

Nitric acid	Concentrated
Hydrochloric acid	Concentrated
Citric acid	30% solution in water
Ammonia	S.G. 0·880
Gum arabic	1% solution in water
Dimethylglyoxime	0·2% solution in alcohol
Iodine	N/20

Procedure.—Attack 100 mg. sample with a mixture of 5 ml. concentrated nitric acid, and 5 ml. concentrated hydrochloric acid in a 150 ml. tall beaker.

Warm if necessary and wash down the sides of the beaker when solution is complete.

If silicon is present filter through a Whatman 31 paper for low silicon alloys or a Whatman 40 paper for high silicon alloys into a 200 ml. wide-neck flask (sugar flask).

Wash the filter paper twice and the funnel once with distilled water into the filtrate.

If no filtering is necessary, wash direct into 200 ml. flask.

Dilute to the mark and mix thoroughly.

Pipette 10 ml. into another 100 ml. Nessler tube.

Add, in the following order:

5 ml. of 30% citric acid
15 ml. of 0·880 ammonia
5 ml. of M/20 iodine
10 ml. of 0·2% dimethylglyoxime

Dilute to the mark and mix well.

Measure the extinction in a Spekker absorptiometer, using a filament lamp, 4 cm. cell, and Ilford Violet Number 601 filter.

Measure 'blank' extinction of the same volume of reagents similarly treated.

Subtract the 'blank' extinction from the extinction of the sample and convert resulting figure into percentage of nickel from a calibration graph prepared from a solution of pure nickel, or samples of known content processed in the above manner.

Notes:

(1) The procedure is identical with that already described for the photometric determination of copper (Method C) except for the different reagents used to develop the colour. Thus copper and nickel may be conveniently determined on a single sample weighing of 100 mg.

(2) In the case of low nickel content (less than 0·2%) arrange sample weight so that 100 mg. sample is present in final solution. In this case, 40 ml. of citric acid and 20 ml. of ammonia are required.

IRON

Iron is always present in commercially pure aluminium up to 0·6%, and may be added to alloys up to 1·5%.

(A) Volumetric Method

Principle.—The sample is dissolved in mixed acids, and silica

removed by fuming and subsequent filtration. Copper in the filtrate is removed by hydrogen sulphide precipitation. The iron in the filtrate is then determined by titration with titanous chloride.

Reagents

Nitric acid	Concentrated
Hydrochloric acid	Concentrated
Sulphuric acid	Concentrated
Hydrogen sulphide gas	
Potassium permanganate ..	N/56 solution. 1 ml. = 0·001 g iron
Potassium thiocyanate	10% solution
Titanous chloride	1 ml. = 0·001 g iron

Procedure.—Follow the directions given for the determination of copper (volumetric procedure A).

Evaporate the filtrate from the separation of copper to a low bulk to ensure removal of all hydrogen sulphide.

Add 100 ml. of water, and cool the solution.

Oxidize the iron by titration with N/56 potassium permanganate solution.

Add 10 ml. potassium thiocyanate indicator, and titrate with standard titanous chloride solution.

Notes:

(1) *Preparation and Preservation of Titanous Chloride Solution.*[1]—Boil 110 ml. of 15% titanous chloride solution with 200 ml. of concentrated hydrochloric acid for 10 minutes.

After rapid cooling pour into a dark-coloured 5 litre aspirator which is already almost full of cold, boiled, distilled water.

Mix thoroughly by shaking, and immediately connect to burette having side connection for automatically filling to zero.

Displace all air from aspirator-burette system by means of hydrogen from a Kipps generator.

Seal all connections with paraffin wax.

Stand overnight, and standardize against A.R. iron wire (assay value 99·9%) or a standard sample of aluminium alloy.

(2) If the silicon content of the sample is high (more than 3%), some iron may be incorporated in the silica-silicon residue.

To recover this treat the residue after ignition in a platinum crucible with 2 ml. concentrated nitric acid ; 1 ml. concentrated sulphuric acid, and a few drops of hydrofluoric acid. Evaporate to fuming and extract with water, and add to the main solution.

(B) Rapid Photometric Method

Principle. — Photometric determination of ferric ferrithiocyanate formed by reaction of potassium thiocyanate and ferric iron.

Reagents

Nitric acid	.. ..	Concentrated
Hydrochloric acid	.. ..	Concentrated
Potassium thiocyanate	.. ..	10% solution

Procedure.—Weigh 100 mg. sample into a tall form 150 ml. beaker and attack with 5 ml. nitric acid, and 5 ml. hydrochloric acid.

When solution is complete, wash down sides of beaker with distilled water. Boil to expel nitrous fumes.

Filter off silicon if necessary and transfer to a 200 ml. wide-necked flask (sugar flask).

Dilute to mark and mix very thoroughly.

Transfer 100 ml. solution to original beaker containing 25 ml. potassium thiocyanate solution.

Mix thoroughly, and measure immediately on a Spekker absorptiometer, using a 1 cm. cell and Ilford filter Number 604.

Set the instrument at drum reading 1·4.

It is necessary to run a blank determination on similar volumes of all reagents.

Prepare calibration graph from standard aluminium alloys.

Note: This may be carried out on the same sample weighing of 100 mg. as the previously described photometric methods for copper and nickel.

ZINC

Zinc is rarely present in commercially pure aluminium, and then only in amounts below 0·03%. In alloys it may be added up to 13%.

(A) Separation as Sulphide

Principle.—The sample is attacked with mixed acids ; silicon and copper are removed, and other interfering elements (aluminium, iron, manganese, and nickel) are held in solution by means of tartaric acid and ammonium formate. Zinc is then precipitated as sulphide and converted to oxide by ignition.

In the case of zinc less than 0·30% the zinc sulphide is redissolved and precipitated as zinc mercuric thiocyanate, the zinc being finally determined by titration with standard potassium iodate using chloroform as an internal indicator.

Reagents

Hydrochloric acid	Concentrated
Nitric acid	Concentrated
Sulphuric acid	Concentrated
Tartaric acid	35% solution
Ammonium hydroxide	S.G. 0·880
Formate mixture	500 g. ammonium sulphate 400 ml. formic acid 1·2 S.G. 60 ml. ammonium hydroxide Make up to 2000 ml. with water
Formate wash	25 ml. of above solution made up to 1000 ml. with water and saturate with hydrogen sulphide
Hydrochloric acid	1 : 1
Mercuric potassium thiocyanate	54 g. mercuric chloride in water 76 g potassium thiocyanate in water; make up to 2000 ml. with water
Mercuric potassium thiocyanate wash	20 ml. of above solution made up to 1000 ml. with water
Potassium iodate solution	1·964 g. potassium iodate made up to 1000 ml. with water
Chloroform	Pure

Procedure.—Attack 1 g. of sample in a 300 ml. conical beaker by adding slowly 20 ml. hydrochloric acid, followed by 10 ml. nitric acid.

Boil down until pasty: add 5 ml. sulphuric acid.

Shake well and evaporate cautiously to fuming, and fume for 10 minutes.

Cool; dilute to 100–150 ml. and boil well to ensure complete solution.

Cool to about 50° C. and saturate with hydrogen sulphide: filter through Whatman 41 pulp pad to remove copper and silicon. Wash with 1% sulphuric acid saturated with hydrogen sulphide.

Boil filtrate until free from hydrogen sulphide, dilute to 200 ml.,

add 25 ml. tartaric acid solution and make ammoniacal to methyl red plus 0·2–0·5 ml. excess.

Add 25 ml. formate mixture and dilute to 400 ml.

Bring nearly to boiling point and pass hydrogen sulphide for 15 minutes.

Allow to stand 30 minutes at a temperature of 60–70° C. then 90 minutes at room temperature.

Filter through 12·5 cm. Whatman 40 containing a pulped accelerator, wash and 'police' beaker with formate wash solution and wash thoroughly 6 times.

Ignite the zinc sulphide carefully, starting at a dull red (say 550° C. to char paper) and finally at 800° C. for 2 minutes. (If zinc less than 0·30%, see Note 2.

Cool and weigh as zinc oxide.

$$ZnO \times 0{\cdot}8034 = Zn.$$

Notes:

(1) If lead is present the zinc sulphide may be dark coloured, in this case dissolve the zinc sulphide in hot dilute (1 : 6 nitric acid); boil off the hydrogen sulphide : dilute to 100 ml. and then deposit the lead by electrolysing for 15 minutes at 5 amps. Re-precipitate the zinc sulphide in formate buffered tartaric solution as above.

(2) If the zinc content is expected to be less than 0·3% redissolve the precipitate of zinc sulphide with hot (1 : 1) hydrochloric acid.

Add 5 ml. nitric acid followed by 5 ml. sulphuric acid, evaporate and fume for 5 minutes.

Cool ; dilute to 60 ml., add 10 ml. mercuric potassium thiocyanate, stir vigorously until precipitation commences : stand overnight at room temperature.

Filter the zinc mercuric thiocyanate through a G4 or 3 X 4 Jena funnel using gentle suction. Wash 6 times with thiocyanate wash.

Extract into a clean dry vacuum flask as follows :

(1) Add 2 ml. concentrated hydrochloric acid dropwise from a pipette round the edge of the funnel without using suction, and then suck gently through.
(2) Repeat.
(3) Repeat with 1 ml. water.
(4) Repeat with 1 ml. hydrochloric acid.
(5) Repeat with 0·5 ml. water.

Add 5 ml. chloroform, then run in 3 ml. standard potassium iodate and shake vigorously : continue adding potassium iodate

dropwise with vigorous shaking until the chloroform is just colourless.

1 ml. KIO_3 = 0·001 g. Zn.

Standardization.—Treat a measured volume of a solution of known zinc content exactly as above.

Prepare standard zinc solution as follows :

Dissolve 0·1 g. pure zinc in the minimum amount of hydrochloric acid. Boil to complete solution : add 10 ml. sulphuric acid, evaporate and fume for 10 minutes.

Cool, dilute to 200 ml. ; boil to complete solution ; cool and make up to 1000 ml.

1 ml. = 0·0001 g. Zn.

For a standard use 20 ml. of this solution = 0·002 g. Zn.

Note : See [2] for quinaldinic acid method and [28] for electrolytic method.

(B) Polarographic Method[26]

Principle.—The alloy is attacked with sodium hydroxide solution to obtain in solution most of the aluminium and zinc. The residue is treated to extract the small but significant amounts of zinc retained therein. The two extracts are bulked together, and a filtration removes remaining traces of interfering elements. 2 ml. of this solution are then polarographed at a suitable sensitivity, and the zinc wave height compared with that of a standard alloy treated under identical conditions.[18]

Reagents

Sodium hydroxide	.. ..	40% solution
Sulphuric acid ..	.. ..	1 : 1 solution
Hydrogen peroxide	.. ..	20 volumes
Gelatine solution	.. ..	0·5% solution of high purity gelatine

Procedure.—Attack 500 mg. of sample with 3·5 ml. sodium hydroxide solution in a 100 ml. tall-form beaker.

After the violent reaction has ceased wash down the sides of the beaker and heat until solution is complete.

Filter through a Whatman 541 into a 100 ml. beaker : wash twice with hot distilled water.

Wash the residue back into the original beaker and dissolve with 0·5 ml. sulphuric acid and 2 ml. hydrogen peroxide : boil.

Carefully add 2·5 ml. sodium hydroxide solution, and bring to boil.

Filter through a Whatman 541 into the original extract (Note 1), transfer to a 25 ml. measuring cylinder; add 0·1 ml. of gelatine solution, and make up to 25 ml.

Mix well, and filter through a Whatman 542.

Only 2–5 ml. of filtrate need be obtained.

Place 2 ml. in a polarographic cell, and remove dissolved oxygen by passing hydrogen or nitrogen through the side arm for one minute.

Record or plot polarogram at adequate sensitivity between applied potentials—1·1 and 1·6 volts (Note 3).

For the determination of zinc contents 0·02–0·20% use sensitivity of 1/7 or 1/15.

For zinc contents 5–6% use a sensitivity of 1/200 or 1/300.

Compare wave heights with those of suitable standards similarly treated.

Notes:

(1) It has been found that not more than 1% of the zinc present in the sample is retained in the residue after this treatment.

(2) The object of this filtration is to remove faint traces of copper which are usually present as may be seen from the blue tinge of the solution before filtration.

(3) As a guide to suitable sensitivities on above sample weight for zinc contents 0·02–0·2% use 1/7 or 1/15.

For zinc contents 2–6% use 1/200 or 1/300.

(4) These sensitivities refer only to the Cambridge Polarograph, but are easily determined by experiment for any other type of instrument. The polarographic method for zinc is highly recommended where routine determinations have to be catered for.

For example 40 determinations can readily be carried out in a day by one analyst as compared with 2–2½ days required for a similar number of determinations by the previous method.

MANGANESE

Manganese is rarely present in commercially pure aluminium, it is however added to alloys up to 1·5%.

(A) Volumetric Method (Bismuthate)

Principle.—Manganese is oxidized to permanganate in cold nitric acid solution with sodium bismuthate. This permanganate is determined by titration with standard ferrous ammonium sulphate.

Reagents

Sodium hydroxide	30% solution
Nitric acid	Concentrated boiled-out solution
Sodium bismuthate	
Ferrous ammonium sulphate ..	N/10 standard solution
Potassium permanganate ..	N/10 standard solution

Procedure.—Attack 1·1 g. sample in a 400 ml. squat beaker with 15 ml. 30% sodium hydroxide.

Warm to complete solution ; add 15 ml. water, and make acid with 25 ml. of freshly boiled-out nitric acid.

Dilute to 120 ml. ; add 2 to 3 drops of hydrogen peroxide if any precipitated manganese dioxide is present and boil for 10 minutes.

Add excess sodium bismuthate to colour the solution a definite pink ; boil for 1 to 2 minutes and then clear the solution with a small crystal of ferrous sulphate. Boil 10 minutes.

Cool to room temperature ; add excess sodium bismuthate ; shake thoroughly for 1 minute.

Allow to settle and filter on an asbestos pad or on a fine sintered glass crucible using suction.

Wash the beaker by decantation with cold 2% nitric acid pouring the wsshings through the filter until colourless, but avoiding unnecessary dilution of the filtrate.

Add N/10 ferrous ammonium solution from a burette until the purple colour is just discharged, and then a further 2 to 3 ml.

Back titrate to the first permanent pink tinge with N/10 potassium permanganate.

1 ml. N/10 ferrous ammonium sulphate = 0·1% Mn on 1·1 g.

Note: For discussion of the ammonium persulphate method for manganese see [2].

(B) Photometric Method (Periodate)

Principle.—Manganese is oxidized to permanganate in acid solution with potassium periodate, and evaluated photometrically.

Reagents

Acid mixture	Nitric acid (conc.), 200 ml. Sulphuric acid (conc.), 200 ml. Water, 600 ml.
Hydrofluoric acid	Conc.
Potassium periodate	10 g. in 200 ml. 20% sulphuric acid

Procedure.—Attack 100 mg. sample in a 150 ml. tall-form beaker with 15 ml. acid mixture.

Warm to complete solution : add a few drops of hydrofluoric acid to remove the silicon.

Boil for three minutes : add 1 ml. potassium periodate solution. When the colour develops dilute slightly and boil.

Stand until cool and dilute to 100 ml. in a Nessler glass.

Mix well and measure on the Spekker absorptiometer using a 4 cm. cell and Ilford Green Filter No. 604.

An instrument setting of 1·4 has been found convenient for manganese contents up to 1·5%.

TITANIUM

Titanium may be present in commercial aluminium although usually at not more than 0·02%. It is intentionally added to certain alloys up to 0·30%.

(A) Visual Colorimetric

Principle.—Colorimetric determination based on the yellow colour of pertitanic acid produced by the addition of hydrogen peroxide to acid solutions of titanic sulphate.

Reagents

Hydrogen peroxide	20 volume
Titanium potassium oxalate ..	Standard solution. 3·71 g. of pure salt dissolved in a mixture of 20 ml. concentrated nitric acid and 20 ml. concentrated sulphuric acid. Evaporate to fumes ; dissolve in water and make up to 1000 ml. 1 ml. = 0·0005 g. titanium

Procedure.—Evaporate the filtrate from the copper sulphide separation to low bulk to remove all hydrogen sulphide.

Alternatively evaporate the electrolyte after copper deposition.

Cool ; add 2 ml. hydrogen peroxide ; dilute to 100 ml. in a Nessler cylinder.

Run a parallel blank test consisting of 2 ml. concentrated sulphuric acid diluted with water ; add 2 ml. hydrogen peroxide ; dilute in Nessler cylinder to approximately 90 ml.

Add standard titanium solution from a burette until colour matches when the volumes of test and blank are equal.

Note: If nickel is present in the sample the colour should be compensated for in the blank by adding 4 mg. nickel sulphate ($NiSO_46H_2O$) for each 1 mg. nickel in the sample.

(B) Rapid Photometric

Principle.—As for Method A, but with photometric evaluation.

Reagents

Sodium hydroxide	.. ..	40% solution
Sulphuric acid ..	.. ..	50%
Hydrogen peroxide	.. ..	20 volume

Procedure.—Attack 1000 mg. sample in a tall form 250 ml. beaker with 10 ml. sodium hydroxide.

Warm to complete solution, and cool.

Add sulphuric acid until aluminium hydroxide just precipitates, and then add 14 ml. excess.

Boil for 5 minutes, and filter through a Whatman 540 into a 100 ml. Nessler cylinder.

Allow to cool ; add 4 ml. hydrogen peroxide and dilute to 100 ml.

Mix well and measure on the Spekker absorptiometer using a 4 cm. cell and Ilford Violet Filter No. 601.

As in other photometric methods given it is preferred to prepare the calibration graph from standard alloys, but it may be prepared from a standard titanium solution if desired.

TIN

Tin may be expected in alloys made from mixed remelted scrap. Current specifications covering such alloys usually allow a range of 0·04–0·1%. In certain cases the total impurities of nickel, manganese, lead and tin must together not exceed 1·0%. Occasionally tin is added as a deliberate alloying constituent, e.g. the free cutting alloy B.S.1080 specifies 0·1–0·5%, and there is one aluminium base bearing alloy containing 5·0–5·7%.

Iodate Method (Volumetric)

Principle.—The tin is obtained in solution as stannous chloride by attacking with hydrochloric acid. Complete reduction is ensured

with a nickel spiral, and the strength of the stannous chloride finally determined by titration with potassium iodate in the presence of potassium iodide and starch.

Reagents

Hydrochloric acid	1 : 1
'Cardice'	Solid carbon dioxide
Pure nickel	Wire (approx. 20 S.W.G.)
Potassium iodide	Crystals
Starch solution	
Potassium iodate	Standard solution : 1·8 g pure salt, 20 g potassium iodide, 2 g sodium hydroxide, dissolved in water and made up to 1000 ml.

Procedure.—Weigh 1–2 g. into a 500 ml. conical flask fitted with a bung containing a bunsen valve and a glass rod having a nickel spiral wrapped round its lower end.

Attack with 100 ml. hydrochloric acid; insert the stopper. After solution is complete boil the flask for 10 minutes to ensure complete solution of the tin.

If much elemental silicon is present, filter and return solution to original flask, and boil for further 10 minutes with the nickel spiral immersed in the solution to ensure complete reduction.

Cool in running water; add a small lump of 'Cardice' to cool further, and ensure an atmosphere of carbon dioxide, and titrate with potassium iodate after addition of 2 g of potassium iodide and a little starch solution.

Standardize the potassium iodate against a solution containing a known amount of pure tin dissolved in hydrochloric acid. Place a known amount of this solution in a flask and repeat the procedure as for an analysis.

CHROMIUM

Chromium is added to certain alloys up to a maximum content of 1·0%.

Principle.—The alloy is dissolved in *aqua regia*, fumed with perchloric acid which serves to oxidize most of the chromium. Oxidation is then completed with ammonium persulphate, and the chromate titrated with ferrous ammonium sulphate.

Reagents

Aqua regia	Hydrochloric : nitric = 3 : 1
Sulphuric acid	Concentrated and 1 : 1
Perchloric acid	60%
Silver nitrate	N/10 solution
Ammonium persulphate ..	Pure salt
Hydrochloric acid	1 : 1
Phosphoric acid	Concentrated
Potassium permanganate ..	N/20 solution
Ferrous ammonium sulphate ..	N/20 solution

o-phenanthroline ferrous sulphate indicator (see Note 4)

Procedure.—Attack 1–5 g. sample in a tall-form 500 ml. beaker with sufficient *aqua regia* and 15 ml. perchloric acid.

Cover the beaker with a clock glass and evaporate to the first signs of fuming to remove most of the hydrochloric acid.

Remove from the hot plate and wash the clock glass and sides of the beaker with hot water. Replace the cover glass and evaporate to fuming. Allow to fume for 10 minutes after the orange colour appears when most of the chromium will be oxidized (Note 1).

Cool quickly by standing for half a minute on a metal slab, and then alternately immersing in and removing from cold water. Finally stand about 5 minutes in cold running water (Note 2).

Add 30–50 ml. hot water ; boil for 10 minutes to expel chlorine (if silicon content is high see Note 3). Add 2 ml. 50% sulphuric acid, and dilute to 300 ml. with boiling water.

Add 10 ml. N/10 silver nitrate solution, and 1 g ammonium persulphate and boil steadily for 10 minutes.

Add 2 ml. 50% hydrochloric acid ; boil for further 15 minutes. Cool in running water ; add 2 ml. phosphoric acid and 2 ml. sulphuric acid.

Titration.—Add excess N/20 ferrous ammonium sulphate until the yellow colour is discharged. Add 2 drops of orthophenanthroline ferrous sulphate indicator (Note 3) which colours the solution red. Then add N/20 potassium permanganate until a colourless solution results.

1 ml. N/20 ferrous ammonium sulphate = 0·000866 g Cr.

Notes:

(1) Unless these conditions are rigidly adherred to there is a danger of losing chromium as chromyl chloride.

(2) The rapid cooling at this stage tends to prevent reduction of the chromate.

(3) If silicon content is high filter off SiO_2 at this stage, ignite, treat with hydrochloric acid, fuse residue with sodium bisulphate, extract and add to main bulk.

(4) O-phenanthroline ferrous sulphate indicator; for a 0·025 M. solution, dissolve 0·695 g. of ferrous sulphate in 100 ml. water; add 1·485 g. of o-phenanthroline monohydrate ($C_{12}H_8N_2 . H_2O$) and stir until the latter is dissolved, giving a dark red solution.

LEAD

Lead is sometimes found in minute traces in commercially pure aluminium, probably being derived from impurities present in the natural cryolite used in the reduction process, and may be present as a contamination in remelted scrap aluminium. The usual limit imposed in specifications is 0·05%, but this may occasionally be exceeded in practice.

Electrolytic—Colorimetric Method Using Tetramethyldiaminodiphenylmethane[51]

Principle.—The alloy is dissolved in hydrochloric acid, with a little nitric acid added towards the end of the reaction. The sulphides of lead, copper and zinc are precipitated with hydrogen sulphide in formate-buffered ammoniacal tartrate solution. Lead is then electrolytically deposited at the anode at low current density as lead dioxide. This is then dissolved from the anode and determined colorimetrically by means of tetramethyldiaminodiphenylmethane.

Reagents

Hydrochloric acid	1 : 1
Nitric acid	Concentrated
Tartaric acid	25% solution
Ammonium hydroxide	0·880 S.G.
Formate mixture	As for zinc, Method A
Formate wash	As for zinc, Method A
Tetramethyldiaminodiphenylmethane	Freshly prepared 2% solution in glacial acetic acid
Standard lead solution	0·01 g. pure lead foil dissolved in dilute nitric acid and diluted to 250 ml.

1 ml. = 0·008% lead on 0·5 g. sample.

Procedure.—Carefully attack 0·5 g. sample in a 150 ml. beaker with 1 : 1 hydrochloric acid; add 1 ml. nitric acid towards the end of the reaction.

Boil to complete the solution of the copper, and to expel oxides of nitrogen.

Dilute to 100 ml. with warm water, and filter on a Whatman 541 containing a pulped-up accelerator; wash with hot 1% hydrochloric acid.

To the filtrate add 12·5 ml. of tartaric acid solution, and neutralize with ammonia using methyl red as an indicator.

Add 25 ml. formate buffer solution, and dilute to about 600 ml. with hot water, and bring to boiling point.

Pass a rapid stream of hydrogen sulphide for 15 minutes. Stir in some pulped filter paper, stand in a warm place for 15 minutes and filter off the sulphides of lead, copper and zinc on a Whatman 540. Wash 8 times with cold formate wash.

Ignite the precipitate in a good quality silica crucible at 500° C. Dissolve the residue in 10 ml. of warm 1 : 1 nitric acid (see Note). Evaporate to about 2 ml., dilute to about 150 ml. and electrolyse for 15 minutes at 4 amps. using a small gauze platinum cathode, and a spiral platinum wire anode.

When electrolysis is complete remove the anode on which the lead is deposited as lead dioxide. Wash by dipping into two successive beakers of distilled water, and then immerse in a test tube containing 5 ml. of a solution of tetramethyldiaminodiphenylmethane $CH_2[(C_6H_4)N.(CH_3)_2]_2$ and shake for 2 to 3 minutes until a blue colour as distinct from the greenish colour of the reagent is produced.

Transfer to an Eggertz tube and compare with a standard solution of lead in nitric acid which has been electrolysed and treated in the same way, dilute the darker solution with glacial acetic acid until the colours match.

Calculate the percentage of lead present from the amount of lead in the standard, and the relative volumes in the Eggertz tubes.

Note: If silicon content is high (greater than 1%), ignite the residue at 500° C. Cool, and volatilize the silicon with hydrofluoric acid, nitric acid and oxalic acid, finally ignite at 500° C. to decompose the oxalic acid; extract with 1 : 1 nitric acid and add to main bulk.

MAGNESIUM AND ITS ALLOYS

(A) The Assay of Commercially Pure Magnesium[35, 36, 37]

Commercially pure magnesium always contains very small

amounts of silicon, copper, aluminium, iron and manganese, but the total impurities rarely exceed 0·10–0·15%. Magnesium is obtained by difference after the total impurities have been determined. Blank determinations should be run on all elements.

SILICON

Attack 5–10 g. millings according to expected purity in a covered beaker with concentrated nitric acid added cautiously (Note 1 overleaf).

When solution is complete, add concentrated sulphuric acid (6 ml. per 1 g. metal) and evaporate to fumes.

Cool; digest with hot water, and filter off silicic acid on a Whatman 540.

Wash with hot water, and ignite to SiO_2.

Cool, weigh, treat with one drop of sulphuric acid and 2 ml. hydrofluoric acid. Evaporate and heat to 1100–1150° C. Cool and weigh.

$$SiO_2 \times 0{\cdot}4672 = Si.$$

COPPER

Gas the filtrate from the silicon determination with hydrogen sulphide to precipitate the copper.

Filter copper sulphide on Whatman 541; wash with hot water saturated with hydrogen sulphide.

Finally determine the copper gravimetrically by ignition to CuO; by volumetric determination with standard sodium thiosulphate; or colorimetrically with sodium diethyldithiocarbamate.

ALUMINIUM AND IRON

Boil the filtrate from the copper to remove hydrogen sulphide.

Oxidize with a few drops of concentrated nitric acid.

Add 5 g. ammonium chloride, and then ammonium hydroxide (sp. gr. 0·880) dropwise until neutral to bromo-cresol purple.

The precipitate consists of $Al(OH)_3 + Fe(OH)_3$ and traces of $Mg(OH)_2$. Bring just to boil and filter on Whatman 541.

Dissolve precipitate in 10–15 ml. hot 50% hydrochloric acid, and reprecipitate with ammonium hydroxide.

Filter; wash with hot 5% ammonium nitrate solution.

Ignite and weigh as $Al_2O_3 + Fe_2O_3$.

Fuse the ignited oxides with a small amount of potassium bisulphate in a silica crucible, and extract the melt with water.

Determine the iron colorimetrically with potassium thiocyanate, or volumetrically with potassium dichromate.

Calculate the iron to Fe_2O_3 and subtract from the weight of the original joint oxides to obtain the weight of Al_2O_3.

$$Al_2O_3 \times 0{\cdot}5291 = Al.$$

MANGANESE

This is determined on a separate sample, by the bismuthate method as described below for the analysis of magnesium alloys.

If preferred the persulphate[37] volumetric, or the periodate colorimetric methods may be used.

Notes:

(1) As silicon is present as magnesium silicide, it is important to treat only with concentrated nitric acid, otherwise losses will occur due to the volatilization of silicon hydride.

(2) The hydroxide method has proved rather more satisfactory than any other for the determination of the small amounts of aluminium present in commercially pure magnesium.

THE ANALYSIS OF MAGNESIUM ALLOYS[35, 36, 37, 38]

The elements commonly alloyed with magnesium are aluminium, zinc and manganese. The impurities usually determined are silicon, copper and iron, for which the methods described for commercially pure magnesium are satisfactory.

ALUMINIUM[35, 36, 37, 38, 39, 40, 41, 42]

This may be expected up to 11%.

Modified Basic Succinate Method[40]

Principle.—Aluminium is separated directly from acid solution by means of succinate reagent, any iron being reduced by means of ammonium bisulphite and phenylhydrazine. The resulting precipitate which is dense and readily filterable is ignited, and weighed as aluminium oxide.

Reagents

Hydrochloric acid	20%
Ammonium bisulphite	10%
Phenylhydrazine	
Succinate reagent	10 g. urea, 5 g. ammonium chloride, 5 g. succinic acid, dissolved in 300 ml. water.
Methyl orange	
Ammonium hydroxide	1 : 1
Wash solution	1% ammonium chloride

Procedure.—Cautiously dissolve 1 g. sample in 50 ml. of hydrochloric acid (if the reaction becomes too violent, immerse the beaker in running water).

Filter to remove any copper. Add a few drops of ammonium bisulphite, and 2 ml. of phenylhydrazine to the hot filtrate (Note 1) followed by 300 ml. succinate reagent; boil gently.

Make the solution just alkaline to methyl orange with freshly filtered ammonium hydroxide and boil gently for 90 minutes (no bumping occurs with this precipitate).

Filter on a Whatman 541 (Note 2).

Wash the precipitate 6 times with ammonium chloride.

Ignite for 1 hour at 1200° C. in an unglazed porcelain or platinum crucible, and weigh as Al_2O_3 (Notes 3 and 4).

$$Al_2O_3 \times 0{\cdot}5291 = Al.$$

Notes:

(1) This prevents interference from ferric iron.

(2) The original method[40] recommends that if any precipitate adheres to the sides of the beaker, it should be removed by dissolving in 20 ml. of 1 : 1 hydrochloric acid, reprecipitating with ammonia, boiling for 1 minute, and pouring through the filter. In practice it has been found rarely necessary, as the succinate precipitate usually comes away quite freely from the beaker.

(3) If silicon content exceeds 0·2%, dissolve the sample in perchloric acid, evaporate to fumes, cool, dilute and filter before proceeding with the basic succinate precipitation.

(4) This method is recommended as combining reasonable speed and convenience with high precision.

ZINC[46, 47, 48]

This does not usually exceed a maximum content of 3·5%.

Hydrogen Sulphide Method

Principle.—Zinc is precipitated by hydrogen sulphide in buffered formate solution, and is subsequently converted to oxide in which form it is determined gravimetrically.

Reagents

Hydrochloric acid	1 : 1
Hydrogen sulphide	
Ammonium chloride	'Analar' reagent
Tartaric acid	35% solution
Ammonium hydroxide	Sp. gr. 0·880
Methyl red indicator	
Formate mixture	500 g. ammonium sulphate 400 ml. formic acid (1·2 sp. gr.), 60 ml. ammonium hydroxide. Make up to 2000 ml. with water.
Formate wash	25 ml. of above solution made up to 1000 ml. with water and saturate with hydrogen sulphide

Procedure.—Attack 1–2 g. magnesium alloy with 1 : 1 hydrochloric acid in a 600 ml. beaker. Warm until clear.

Pass hydrogen sulphide, and filter to remove silicon and copper. Boil off excess hydrogen sulphide.

Add 10 g. ammonium chloride, followed by 10 ml. tartaric acid solution.

Make just alkaline to methyl red with ammonium hydroxide and add 25 ml. formate mixture.

Volume should be about 200–250 ml.

Heat to boiling and pass rapid stream of hydrogen sulphide for 15 minutes.

Allow to stand 30 minutes at 60° C., then 90 minutes at room temperature.

Filter on Whatman 40 containing macerated pulp; wash thoroughly 6 times with formate wash solution.

Filter, wash and ignite to ZnO (Note 1).

$$ZnO = 0{\cdot}8034 = Zn.$$

Notes:

(1) The ignition should be started at the front of the muffle to avoid reduction of ZnO to metallic zinc which may be volatilized.

(2) Volumetric methods based on the titration of zinc in sulphuric acid solution using ammonium molybdate as an external

indicator[35] or diphenyl benzidine as an internal indicator[36] have been described, but in order to be reliable these require separation of interfering elements.

An electrolytic method has been described by Osborn.[47]

Investigation of a polarographic determination is being carried out.

MANGANESE

This is present in practically all magnesium alloys in amounts varying from 0·1 to 1·0%.

Volumetric Bismuthate Method

Principle.—Oxidation of manganese to permanganate with sodium bismuthate followed by titration with ferrous ammonium sulphate.

Reagents

Sulphuric acid	1 : 4
Nitric acid	S.G. 1·42
Nitric acid wash solution ..	3%
Potassium permanganate ..	N/10 standard solution
Ferrous ammonium sulphate ..	N/10 standard solution

Procedure.—Attack 1·1 g. millings with sulphuric acid, and when solution is complete add 8 to 10 ml. concentrated nitric acid.

Boil for 2 minutes, cool, add 0·5 g. sodium bismuthate, and agitate for 3 minutes.

Allow to settle for 2 minutes.

Filter on asbestos using suction (if filtrate is not crystal clear it must be re-filtered).

Titrate immediately with N/10 ferrous ammonium sulphate. Add 1 ml. excess ferrous ammonium sulphate.

Back titrate with N/10 potassium permanganate to a pink end-point.

For sample weight of 1·1 g., 1 ml. N/10 ferrous ammonium sulphate = 0·10% Mn.

REFERENCES

THE ANALYSIS OF ALUMINIUM AND ITS ALLOYS

[1] *Analysis of Aluminium and its Alloys*, The British Aluminium Company Limited, Publication Number 399, London, 1941.

[2] *Chemical Analysis of Aluminum*, Aluminum Company of America, New Kensington, Pennsylvania, Second Edition, 1941.

[3] *Analytical Methods for Aluminium and its Alloys (Arbitration Methods)*, Bureau International de l'Aluminium, Translation published by the British Aluminium Company Limited, London, 1938.
[4] *Standard Methods for the Sampling and Analysing of Aluminum and Certain Aluminum Alloys*, Aluminum Research Institute, Chicago, 1939.
[5] *A.S.T.M. Methods of Chemical Analysis of Metals*. American Society for Testing Materials, Philadelphia, Pa., 1943, 130–47.
[6] N. H. Furman, *Scott's Standard Methods of Chemical Analysis*, D. Van Nostrand Company Inc., New York, Fifth Edition, 1939. **1.** 37–52.
[7] Routine Analysis of Aluminium Alloys: *Light Metals*, 1943. **6.** 175–9, based on an article in *Schweiz, Techn. Z.*, April 1942.
[8] E. J. Vaughan, *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis*, Monograph, The Royal Institute of Chemistry, London, 1941.
[9] E. J. Vaughan, *Further Advances in the Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis*, Monograph, The Royal Institute of Chemistry, London, 1942.
[10] F. W. Haywood and A. A. R. Wood, *Metallurgical Analysis by means of the Spekker Photo-electric Absorptiometer*, Adam Hilger Limited, London, 1944. 92–109.
[11] D. F. Phillips and L. L. Edwards, 'Photometric Analysis, Routine Determination of Copper and Nickel in Aluminium Alloys', *Metal Industry*, 1945. **66.** 409–10.
[12] D. F. Phillips, 'The Routine Analysis of Aluminium Alloys by Colorimetric Methods', *Ind. Chem.*, July 1945, 365–71.
[13] W. Stross, 'Rapid Photometric Determination of Copper, Nickel, Manganese and Iron in Aluminium Alloys', *Metallurgia*, 1945. **32.** 257–61.
[14] G. S. Smith, 'Determination of Magnesium in Duralumin', *Analyst*, 1935. **60.** 812–4.
[15] W. Stross, 'Rapid Photometric Determination of Magnesium in Aluminium Alloys', ibid., 1942. **67.** 317–20.
[16] F. Pitts, 'The Determination of Magnesium in Aluminium Alloys', ibid., 1943. **68.** 133–9.
[17] W. H. Hadley, 'The Determination of Silicon in Aluminium and its Alloys', I. ibid., 1941. **66.** 486–9.
[18] W. H. Hadley, 'The Determination of Silicon in Aluminium and its Alloys', II. ibid., 1942. **67.** 5–8.
[19] A. Staples, 'Discrepancies observed in the Colorimetric Estimation of Silicon in Hiduminium R.R. Series of Aluminium Alloys', ibid., 1942. **67.** 287.
[20] B. A. Scott, 'Colorimetric Determination of Silicon in Aluminium Alloys', ibid, 1942. **67.** 389.
[21] W. Stross, 'Photometric Determination of Silicon in Aluminium Alloys: Observations on Hadley's Method', ibid, 1944. **69.** 44–5.
[22] W. H. Hadley, 'Photometric Determination of Silicon in Aluminium and its Alloys', ibid., 1945. **70.** 43.
[23] H. Cox, 'The Photometric Determination of Silicon in Aluminium Alloys', *Metallurgia*, 1946. **33.** 121–3.
[24] A. C. Coates and R. Smart, 'Polarographic Analysis. Application of the Method to Aluminium and its Alloys', *J. Soc. Chem. Ind.*, 1941. **60.** 249–51.
[25] *Spectrographic and Polarographic Analysis of Aluminium and its Alloys*, The British Aluminium Company Limited, Publication Number 401, London, 1943.
[26] W. Stross and G. H. Osborn, 'Determination of Zinc in Aluminium Alloys', *Light Metals*, 1944. **7.** 323–7.
[27] J. H. Bartram and P. J. C. Kent, 'Estimation of Zinc in Aluminium Alloys by means of Quinaldinic Acid, *Metallurgia*, 1946. **33.** 179–81.
[28] G. H. Osborn, 'The Electrolytic Determination of Zinc in Aluminium Alloys', *J. Soc. Chem. Ind.*, 1943. **62.** 58–60.
[29] G. H. Osborn and W. Stross, 'Determination of Manganese in Aluminium Alloys', *Light Metals*, 1943. **6.** 402–6.

[30] J. H. Bartram and P. J. C. Kent, 'Estimation of Bismuth in Aluminium Alloys', *Light Metals*, 1946. **9.**
[31] R. Smart, 'The Determination of Sodium in Aluminium and its Alloys', *J. Soc. Chem. Ind.*, 1943. **42.** 213–6.
[32] G. H. Osborn, 'The Determination of Sodium in Aluminium Alloys by a modified "Scheuer" Method, with particular reference to Alloys containing Magnesium', ibid., 1943. **62.** 216–9.
[33] W. Stross and G. H. Osborn, 'The Photometric Determination of Beryllia in presence of Alumina with p-nitrobenzeneazoorginol, with particular reference to the Determination of Beryllium in Aluminium and its Alloys', *J. Soc. Chem. Ind.*, 1944. **63.** 249–51.
[34] E. C. Pigott, 'Metallurgical Microchemistry (Aluminium Alloys)', *Metal Treatment*, 1943. **10.** 239–48, 272.

THE ANALYSIS OF MAGNESIUM AND ITS ALLOYS

[35] A. Beck, *The Technology of Magnesium and its Alloys*, F. A. Hughes and Company Limited, London, 1940. 482–9.
[36] 'Dow Metal Laboratory Methods', The Dow Chemical Company, *Bulletin Number DM41a*, Midland, Michigan, 1943. 15–37.
[37] *A.S.T.M. Methods of Chemical Analysis of Metals*, American Society for Testing Materials, Philadelphia, Pa., 1943. 148–64.
[38] N. H. Furman, *Scott's Standard Methods of Chemical Analysis*, D. Van Nostrand Company Inc., New York, Fifth Edition, Vol. 1, 1939. 539–53.
[39] V. A. Stenger, W. R. Kramer, and A. W. Beshgetoor, 'Gravimetric Determination of Aluminium in Magnesium Alloys: Benzoate-Oxine Method', *Ind. Eng. Chem.* Anal. Ed., 1942. **14.** 797–8.
[40] A. J. Boyle and D. F. Musser, 'Modified Basic Succinate Estimation of Aluminium in Magnesium Alloys', *Ind. Eng. Chem.*, Anal. Ed., 1943. **15.** 621–2.
[41] F. W. Haywood, F. Harrison and A. A. R. Wood, 'The Rapid Photometric Determination of Aluminium in Magnesium Alloys', *J. Soc. Chem. Ind.*, 1943. **62.** 187–9.
[42] C. H. Wood, 'The Volumetric Determination of Aluminium in Magnesium Alloys, *J. Soc. Chem. Ind.*, 1944. **63.** 317–20.
[43] F. W. Haywood and A. A. R. Wood, *Metallurgical Analysis by means of the Spekker Photo-electric Absorptiometer*, Adam Hilger Limited, London, 1944. 110–24.
[44] A. J. Boyle and V. V. Hughey, 'Photometric Estimation of Silicon in Magnesium and Magnesium Alloys, *Ind. Eng. Chem.* Anal. Ed., 1943. **15.** 618–9.
[45] V. A. Stenger, 'Colorimetric Methods for the Analysis of Magnesium-Base Alloys' *Proc. Amer. Soc. Test. Mat.*, 1944. **44.** 751–61; also *Metal Treatment*, 1944. **11.** 229–34, 258.
[46] E. Q. Laws, 'The Determination of Zinc in Magnesium Alloys and Nickel Alloys', *Analyst*, 1941. **66.** 54–7.
[47] G. H. Osborn, 'The Determination of Zinc in Magnesium Alloys', ibid., 1941. **66.** 412–4.
[48] L. G. Miller, A. J. Boyle and R. B. Neill, 'Routine Determination of Zinc in Magnesium Alloy, Volumetric Methods', *Ind. Eng. Chem.* Anal. Ed., 1944. **16.** 256–7.
[49] W. H. Withey, 'The Analysis of Magnesium Alloys (Conte Calcium and Rare Earths'), *J. Soc. Chem. Ind.*, 1936. **55.** 357–9.

OTHER REFERENCES

[50] R. C. Chirnside, L. A. Dauncey and P. M. C. Proffitt, 'The Separation of Metals by Means of the Mercury Cathode', *Analyst*, 1943. **68.** 176.
[51] Snell, *Colorimetric Methods of Analysis*, D. Van Nostrand Company Inc., New York, 1939. 43–4.

Section II

COMMERCIAL COPPER-BASE ALLOYS

Methods are given for determining major constituents, and the impurities usually encountered.

A list of the usual elements encountered in copper alloys, together with the approximate quantity and alloy type in which they are found, is given below, where 'm.const.' indicates a major or desired constituent and 'imp.' an impurity.

Aluminium.—Aluminium bronze, m.const. 6–11%. Manganese bronze, high tensile brass, m.const. 1–5%.

Antimony.—Tin and lead-bearing bronze, imp. 0·01–1·0%.

Arsenic.—Arsenical copper, m.const. 0·1–1·0%. Tin and lead-bearing bronze, imp. 0·01–0·1%.

Beryllium.—Copper-beryllium, m.const. 6%.

Bismuth.—All alloy types, imp. 0·001–0·1%.

Cadmium.—Copper-cadmium, m.const. 1%.

Chromium.—Copper-chromium, m.const. 1%.

Cobalt.—Copper-beryllium, m.const. 1%.

Iron.—Aluminium-bronze, manganese bronze, high tensile brass m.const. 1–5%. Tin bronze and other alloys, imp. 0·1%.

Lead.—Leaded tin-bronze, leaded brass, free-cutting brass m.const. 1–10%. High-stress alloys, imp. 0·01–0·5%.

Magnesium.—All types of bronze, imp. 0·1%.

Manganese.—Aluminium bronze, manganese bronze, high tensile brass, m.const. 0·1–2·0%.

Nickel.—All alloys m.const. 1·0–30·0%.

Oxygen.—All alloys, imp. 0·01–0·5%.

Phosphorus.—Tin-bronze, phosphor bronze, gunmetal, m.const 0·01–1·0%.

Silicon.—Silicon-bronze, m.const. 0·1–1·0%. Other alloys, imp 0·01–0·1%.

Tellurium.—Copper-tellurium, m.const. 0·1–1·0%.

Tin.—Tin-bronze, m.const. 5–15%. Other alloys, imp. 0·01–0·1%.

Titanium.—Silicon-bronze, aluminium-bronze, m.const. 0·01–0·5%.

Zinc.—Manganese-bronze, brass, nickel silver, m.const. 20–50% Copper-cadmium, m.const. 0·1–5%. Gunmetal, tin-bronze m.const. 0·5–5·0%. Other alloys imp. 0·1%–1·0%.

The methods given are not necessarily the only reliable methods available, but are methods that have been well tried and are known to give satisfactory results.

Electrolytic Deposition and Apparatus

As copper is an element particularly suited to electrolytic deposition, it will be assumed that, for the analysis of copper-base alloys, an electrolytic apparatus is available. In this respect, and from consideration of the principles involved, it will be seen that the electrodes used should have the maximum surface area available, i.e. for deposition a gauze electrode should always be used, as the current which can be passed through the electrolyte and thus the speed of deposition varies directly, all other factors being equal, with the electrode area. It is recommended that for regular use the Fischer type electrodes of Pt/Rh alloy be used as stationary electrodes and that independent stirring be supplied by means of a glass stirrer. Magnetic stirring* can be used if desired but in this case the control is not so flexible and this type of stirring is only suitable under rigidly controlled conditions. As far as apparatus is concerned for large scale determinations, the multiple set layout is best with independent control for each set and in general, as there is always a certain amount of gassing and therefore danger through loss by spray during the course of an electrolysis, it is always advisable to use a spray arrestor. The best type is an ordinary cover glass with a quarter-inch slit-to-centre cut in it, the diameter of the cover glass being just sufficient to cover the beaker used for the electrolysis. In general, as the action of the electrolysis tends to set up a cell, with the resulting back E.M.F., when an electrolytic determination is finished, it is always advisable to remove the electrolyte from contact with the electrode before switching off the current, otherwise of course the cell would tend to deposit back and give incomplete deposition and low results. When weighing platinum gauze electrodes that have been heated for drying purposes, time should be allowed for the electrode weight to settle down before a final weight is recorded.

Determination of Copper

Although the determination of copper in pure copper gives no reliable check on the amount of the impurities present, its determination gives a useful cross-check on the probable total amount of impurities present. Electrolysis is a reliable method for the determination of copper in copper rich alloys.

* Ref. 'Magnetic Stirring', Webb, *Analyst*. 70. 301.

Electrolytic Method

Weigh 0·5–1 g of drillings into a 150 ml. tall type beaker and dissolve in 25 ml. of 'electrolytic' acid mixture. Boil off excess brown fumes, make up to 100 ml. with cold water and electrolyse, using platinum electrodes, of which the cathode has been previously dried and weighed, at a suitable current until all the copper has been removed. With Fischer type electrodes a current of 4 amps can be used and the electrolysis takes approximately three-quarters of an hour. With other types of electrodes the P.D. across the electrodes with the current running should be adjusted to between 2·5–3·0 volts and electrolysis carried on approximately twice as long as it takes for the blue copper colour to go from the solution. When the deposition is complete, test the solution by removing a spot with a glass rod on to a spotting-plate and adding a drop of H_2S water to it. When no black CuS is deposited, indicating complete deposition, add 1 g urea to neutralize any trace of nitrous acid and continue the electrolysis for a further 5 minutes. Remove the electrolyte away from the electrodes, giving the electrodes a preliminary wash from a wash bottle, without switching off the current. Remove the cathode from the electrolysis machine, wash in water and alcohol, allow the excess alcohol to drain off and ignite the remainder. Dry the cathode in an oven at 120° C. for 2 minutes, remove from the oven and allow it to cool for a further 4 minutes before weighing. The difference in weight of the cathode represents the amount of copper in the sample taken.

$$\frac{\text{Difference in weight} \times 100}{\text{weight taken}} = \% \text{ copper.}$$

Notes:

(1) *Electrolytic acid* consists of a mixture of 3 parts each of sulphuric and nitric acid with 10 parts of water.

(2) The colour of the deposit should be salmon pink, of bright matt appearance. A bright coppery appearance generally indicates too high acidity and tends to low results. A flaky, dull brown appearance generally indicates too high current density and also tends to low results through non-adherence of the deposit. The deposit should be so adherent that it is not removed by rubbing with the finger.

(3) Sands, *Electro-chemistry and Electro-chemical Analysis*, Vols. I, II and III.

BRONZES, PHOSPHOR-BRONZE, GUNMETAL

(A) **Copper** (Electrolytic method)

Weigh 0·5 g of drillings into a 250 ml. beaker and proceed as for

the determination of tin (gravimetrically) collecting the filtrate and washings in a 500 ml. conical flask. Evaporate the filtrate to low bulk (about 1–2 ml.), transfer to a 150 ml. beaker and make up to 100 ml. with water. Electrolyse as for the determination of copper at a potential 2·5–3·0 volts until the blue colour fades, then if no appreciable quantity of lead dioxide is visible on the anode, add 4 drops 50% sulphuric acid and complete the electrolysis in the normal way. If there is an appreciable amount of lead present do not add sulphuric acid.

(Wt. of cathode + Cu) − Wt. of cathode = copper.

Note: Lead may also be determined electrolytically by this method in which case the anode as well as the cathode should be weighed before the electrolysis (for copper), which should be carried out in a warm solution with a P.D. of 3·5 volts. The lead in the anode is finally weighed as lead dioxide (see the determination of lead electrolytically).

(B) **Nickel**

Transfer the copper-free electrolyte to a 400 ml. beaker, add 5 g tartaric acid and make alkaline with 50% ammonia solution avoiding undue excess. Bring to the boil and whilst at approx. 70° C. precipitate the nickel with 20 ml. 1% dimethylglyoxime solution in alcohol. Allow the precipitate to settle in a warm place, filter and proceed as for the determination of nickel in aluminium bronze.

The determination may be completed gravimetrically or volumetrically; if, however, the amount present is very small, it is best to filter on to a Whatman No. 41 paper, wash with hot water and incinerate the precipitate and paper in a weighed silica or porcelain crucible at a dull red heat, to nickel oxide.

$$NiO \times 0{\cdot}7858 = \text{nickel.}$$

(C) **Zinc**

Collect the filtrate from the nickel determination into a 500 ml. conical flask, make acid with nitric acid adding 5 ml. in excess, and evaporate down to low bulk (about 5–10 ml.), transfer to a 250 ml. beaker and make up to 50 ml. with water. Make just alkaline with 50% ammonia using litmus paper as an indicator, then just acid, 1 drop, with 20% hydrochloric acid. Warm the solution, add 1 g microcosmic salt, stir to dissolve, and allow the precipitated zinc phosphate to settle in a warm place for about half an hour. Filter on to a Whatman No. 40 paper and wash with warm water. Place the filter paper and precipitate into a weighed silica or porcelain crucible and burn off carefully at a dull red heat, i.e. 550–600° C. Finish burning off at bright red heat, cool the

crucible and contents in a desiccator and weigh the remaining zinc pyrophosphate.

$$Zn_2P_2O_7 \times 0{\cdot}4289 = \text{zinc.}$$

Note: Nickel and copper must be removed completely before proceeding to determine the zinc; if, however, nickel is not present, the glyoxime stage may be omitted. The neutralization prior to precipitate of zinc is critical and the final solution should be very weakly acid.

(D) **Tin** (Gravimetric method)

Weigh 0·5 g of drillings into a 250 ml. beaker and dissolve with 15 ml. nitric acid (sp. gr. 1·2). Evaporate down carefully to a pasty condition, i.e. until just before the appearance of black copper oxide, take up the copper salts with 100 ml. boiling water and bring to the boil, boiling the solution for about half a minute. Allow the precipitate of meta-stannic acid to settle in a warm place until the solution is clear, then filter, using either a double Whatman No. 40 paper or a fairly thick pulp pad. Wash until free from copper with hot 2% nitric acid, then transfer the paper with precipitate to a previously ignited and weighed silica or porcelain crucible, incinerate the paper very carefully at a dull red heat, and finally, when all the paper has burnt, at a bright red heat. Cool in a desiccator and weigh quickly.

$$SnO_2 \times 0{\cdot}7877 = \text{tin.}$$

Notes: If the evaporation has gone too far, the residue may be taken up with a few drops of conc. nitric acid.

If the iron content is over 0·3% this method is not suitable and the volumetric method should be used.

Arsenic, antimony and phosphorus are precipitated along with the tin and whilst the arsenic and antimony can generally be ignored, the phosphorus if over 0·05% should be allowed for by converting the phosphorus, previously determined, to P_2O_5 calculating the weight present on the sample taken, and subtracting this weight from the total weight of $SnO_2 + P_2O_5$.

E.g.: P content — 0·2%. Combined oxide weight = 0·5786 g

$$\text{Weight of P as } P_2O_5 \text{ present in } 0{\cdot}5 \text{ g} = \frac{0{\cdot}2}{200} \times 2{\cdot}29$$

$$= 0{\cdot}0023 \text{ g}$$

$$0{\cdot}5786 - 0{\cdot}0023 = 0{\cdot}5763 = \text{wt. of } SnO_2.$$

The colour of the precipitate should be a pale cream, any black particles indicating copper oxide and insufficient washing.

(E) **Tin** (Volumetric method)*

Weigh 1 g of fine drillings into a 400 ml. conical beaker and dissolve in a mixture of 15 ml. 50% sulphuric acid plus 15 ml. hydrogen peroxide (90–100 vol.). Warm slightly, not exceeding 50° C., until dissolved and then boil for a few minutes to boil off excess hydrogen peroxide. Dilute with 20 ml. of 25% hydrochloric acid, warm until a clear solution is obtained and then add 100 ml. 8% oxalic acid, bring to the boil and boil for 10–15 mins. Cool the solution, make up to 250 ml. in a standard flask and return to the original beaker. Allow the precipitate to settle, then decant the clear layer through a dry Whatman No. 40 paper into a dry 250 ml. beaker. Pipette 50 ml. of the clear solution into a 500 ml. conical flask, add 50 ml. conc. hydrochloric acid, 150 ml. water and 8 g sodium chloride and boil briskly with a nickel spiral for about 20 minutes. Add a small piece of marble, remove the flask from the heat and cool under a stream of carbon dioxide. Add 10–20 ml. freshly made starch solution and titrate quickly with standard iodate/iodide solution until the appearance of a permanent blue colour.

1 ml. std. iodate solution ≡ 0·001 g tin.

Notes: The drillings should be as fine as possible; if they are at all coarse, trouble in dissolving may be experienced which may be overcome by adding a few drops of conc. nitric acid. This must be subsequently eliminated by fuming down to fumes of SO_3.

Stannous chloride is easily oxidized in the air so that care should be taken always to maintain an inert atmosphere in the flask prior to titration.

The nickel spiral before use must have an etched surface which is achieved by boiling in 20% hydrochloric acid solution plus 10 g of sodium chloride.

Std. Iodate Solution.—Make a stock solution containing 3 g potassium iodate, 33 g potassium iodide and about 3 g of potassium hydroxide per litre. Dilute to one-fifth strength for use. The starch solution is made in the normal way but should be fresh each day.

(F) **Phosphorus** (Volumetric method)

Weigh 2 g of drillings into a 250 ml. conical beaker and dissolve in a mixture of 20 ml. nitric acid (sp. gr. 1·2) and 10 ml. hydrochloric acid conc. Digest on the hot plate for about 1 hour, to oxidize the phosphorus, evaporate the bulk to about 10 ml., then

* Edwards & Gailer, *Analyst.* **69.** 169.

add 20 g ammonium chloride and 100 ml. boiling water. Precipitate the phospho-molybdate complex by quickly adding to the solution with vigorous stirring 50 ml. nitro-molybdate solution, the solution should be at approx. 70–80° C. Allow the precipitate to settle in a warm place for about half an hour, filter on to a pulp pad using suction, and wash well, firstly with 3% cold nitric acid solution until copper free, and then with 3% cold potassium nitrate solution until acid free. Transfer the pad and precipitate to the original beaker and pipette into the beaker sufficient N/5 sodium hydroxide solution to dissolve the precipitate (10 ml. caustic solution for each 0·1% phosphorus present). Add 50 ml. cold water, shake well to disperse the pad, and back titrate the excess caustic solution with N/5 hydrochloric acid solution using 1% phenolphthalein solution in alcohol as an indicator.

Then

(ml. caustic solution − ml. acid) × 0·00027 = grams phosphorus.

Notes: N/5 std. hydrochloric.—Take 20 ml. conc. acid and dilute to 1 litre with water. Standardize against N/5 sodium carbonate solution made up accurately, using methyl orange as an indicator.

N/5 std. sodium hydroxide.—Take approx. 9 g sodium hydroxide and dissolve in 1 litre of water. Standardize against the std. acid using 1% phenolphthalein as an indicator.

Nitro-molybdate solution.—For the preparation of this reagent, see Appendix.

(G) **Lead** (Gravimetric method)

Weigh 2 g of drillings into a 250 ml. beaker and dissolve in a mixture of 20 ml. nitric acid (sp. gr. 1·2) and 10 ml. conc. hydrochloric acid. Evaporate to dryness, do not bake, add 10 ml. conc. sulphuric acid, running the acid down the side of the beaker, and fume well for 10 minutes to expel the other acid ions. Cool and dissolve the copper salts by adding 200 ml. water, allow the precipitated lead sulphate to settle by standing in a cool place overnight. Filter on to a Whatman No. 1 paper, wash out the copper salts with cold 4% sulphuric acid finishing with two washes of cold water to remove the acid. Place approximately 10 g ammonium acetate into the filter paper with the lead sulphate and wash through with boiling water into a 400 ml. conical beaker. After all the ammonium acetate has dissolved through the paper, give two additional washings with boiling water and make the filtrate up to 100 ml. with water. Bring the solution to the boil, add 2 drops of acetic acid and slowly add 25 ml. of a·10% ammonium molybdate solution, allow the precipitate of lead molybdate to settle for half

an hour on a warm plate and then filter through a pulp pad or a Whatman No. 40 paper. Wash with hot water, place the paper and precipitate into a porcelain or silica crucible, previously ignited and weighed, and carefully burn off the paper, never allowing the temperature to rise above a dull red heat, i.e. 600° C. When the paper has completely burned, cool the crucible and contents in a desiccator, and re-weigh.

Lead molybdate × 0·5643 = lead.

Notes:

(1) The lead molybdate should be a cream-coloured precipitate before weighing.

(2) The ignition of the paper should not be hurried as there is a chance of the precipitate being reduced or fused if the temperature gets too high.

(3) The filtrate after removal of $PbSO_4$ may be used for the determination of Fe, Ni, Zn, etc.

(H) **Antimony** (Volumetric method)

Weigh 3 g of drillings into a 400 ml. conical beaker and dissolve in 50 ml. nitric acid (sp. gr. 1·2) evaporating down as for the determination of tin. Dilute with boiling water to 200 ml., allow the precipitate to settle, filter on to a double Whatman No. 40 paper, washing free from copper with 3% nitric acid solution and return the paper and precipitate back into the original beaker. To the paper and precipitate add 25 ml. conc. nitric acid, 5 g ammonium persulphate and 20 ml. conc. sulphuric acid, boil to strong fumes of SO_3. If the solution is still brown, cool, add a little more ammonium persulphate (1 g) and 5 ml. nitric acid and again evaporate to strong fumes of SO_3. When the solution is colourless, cool, add 100 ml. water, 1 g sodium sulphite and 20 ml. conc. hydrochloric acid. Add a piece of porous tile and boil steadily for about half an hour until the excess SO_2 is completely expelled, and keeping the total bulk to 100 ml. by additions of hot water. Dilute to 200 ml. with cold water, cool to 10–12° C. and titrate with N/100 potassium permanganate to a permanent pink colour.

1 ml. N/100 potassium permanganate ≡ 0·0006 g antimony.

Notes: If the alloy does not contain tin add 0·1 g of pure tin before dissolving.

N/100 potassium permanganate.—Dissolve 0·316 g potassium permanganate in water and dilute to 1 litre. This may be standardized against a std. antimony solution containing 0·1 g Sb/litre.

Pipette 20 ml. std. antimony solution into a beaker containing 15 ml. conc. sulphuric acid and proceed with reduction, etc.

Arsenic if present will reduce permanganate and allowance should be made, i.e. $As_2O_3 \rightarrow As_2O_5$.

(I) **Iron**

The method as described for the determination of iron in aluminium-bronze may be used. Where the iron content is small, i.e. about 0·1%, the colorimetric method is better and should be used.

(J) **Manganese**

The method as described for the determination of manganese in aluminium-bronze may be used.

BRASS, CUPRONICKEL, ALUMINIUM BRONZE, MANGANESE BRONZE, HIGH TENSILE BRASS, SILICON BRONZE

(K) **Copper** (Iodimetric method)

Weigh 0·5 g of sample into a 400 ml. conical beaker and dissolve in 15 ml. nitric acid (sp. gr. 1·2). Boil off the excess brown fumes and then evaporate the solution down to a pasty condition. Take up with approx. 50 ml. distilled water, make alkaline with 50% ammonia, adding it a drop at a time, until the white copper hydroxide precipitate is just permanent, and redissolve this precipitate by adding drop by drop 50% glacial acetic acid until the solution is clear. When cold add 3 g approx. potassium iodide and titrate the liberated iodine with standard thiosulphate solution using starch solution as an indicator and not adding the starch until the solution is a light straw colour.

1 ml. standard thiosulphate ≡ 0·01 g copper approx.

Notes: The presence of any appreciable quantity of iron or any metal capable of readily existing in an oxidized and reduced form will interfere and give a false figure although iron can be complexed with a small amount of sodium fluoride.

An economy in potassium iodide may be effected by the following procedure: When the solution is ready for titration add 1 g of potassium iodide and titrate as quickly as possible, adding starch solution as before, until the blue colour is just discharged for the first time by one drop of thiosulphate, ignore the reappearance of the blue colour. Now add 1 g of potassium or ammonium thiocyanate, preferably in solution form, and quickly

continue the titration until the blue colour is permanently discharged. This method gives a very clear end-point, at the same time effecting a very considerable economy in potassium iodide.

Solutions:

Standard Thiosulphate.—Dissolve approx. 40 g sodium thiosulphate in water and make up to 1 litre. Standardize against pure electrolytic copper foil, using the above method.

(L) **Copper** (Electrolytic method)

Weigh 0·5 g drillings into a 150 ml. beaker and dissolve in 20 ml. electro-acid mixture. Boil off excess brown fumes and dilute to 100 ml. with cold water. Electrolyse, using platinum electrodes, at a potential of 2·5 volts until all the copper has been removed from the solution, confirming this by removing a drop on to a spotting plate and testing with potassium ferrocyanide solution. Add 1 g urea and electrolyse for a further 5 minutes. Weigh the copper deposit as previously described in the analysis of pure copper.

$$\frac{\text{Weight of copper}}{0{\cdot}5} \times 100 = \% \text{ Cu.}$$

Notes:

(*a*) Electro-acid mixture = 3 vols. HNO_3 conc.
3 vols. H_2SO_4 conc.
10 vols. Water

Ferrocyanide Test.—Take a drop of the solution on to a spotting place, add 1 drop 50% ammonia and 1 drop of 50% glacial acetic acid. Next add 1 drop of a 5% potassium ferrocyanide solution; the appearance of a brown precipitate or the colour of the solution changing to a reddish-brown indicates the presence of copper. This test is very delicate.

(M) **Aluminium**† (Gravimetric or Volumetric methods) in Aluminium Bronze

Weigh 0·5 g drillings into a 150 ml. beaker and proceed as for the determination of copper. Transfer the copper-free electrolyte to a 500 ml. flask and add 3 g tartaric acid and 10 g of ammonium chloride. Make just alkaline with 50% ammonia, add 5 g potassium cyanide and 0·5 g sodium sulphite. Bring to the boil and boil for approx. 2 mins., allow the precipitated ferrocyanides* to

* The ferrocyanide precipitate is manganese and/or zinc ferrocyanide from the manganese or zinc and iron in the alloy. If these are absent and there is no precipitate, then the filtering stage may be omitted. If manganese or zinc are present without iron, then a few drops of a 10% ferric chloride solution should be added after electrolysis to ensure that sufficient iron is present to enable Mn and Zn to be later precipitated as ferrocyanides.

† Ref. *Analyst* 73, 556.

settle for 10 minutes and then filter on to a fairly thick pulp pad into a 500 ml. conical beaker and wash with 10% ammonium chloride solution. Add a further 20 ml. 50% ammonia to the filtrate, bring to the boil and while just off boiling slowly add with constant stirring 75 ml. of a 2% solution of 8-hydroxyquinoline solution. Allow the precipitated Al-oxinate to settle, then filter on to a previously dried and weighed sintered glass filter crucible (Grade 3 porosity), washing with boiling water and using suction. Dry in an oven at 140–150° C. for 2 hours and re-weigh.

$$\text{Al-oxinate} \times 0{\cdot}05787 = \text{Al.}$$

Alternatively the oxinate precipitate may be filtered on to a Whatman No. 4 fluted paper, washed with boiling water and then re-dissolved with 50% hot hydrochloric acid into the original beaker. Make the solution of the oxinate up to 100 ml. with 20% hydrochloric acid and cool to 15° C. Brominate by adding an excess of standard bromate/bromide (N/2·248 solution) using methyl red as an indicator to indicate the excess of bromate/bromide, and add approx. 2 ml. in excess. Add 0·5 g potassium iodide and titrate the iodine liberated by the excess bromate/bromide with standard N/4·5 sodium thiosulphate solution using starch solution as an indicator.

$$1 \text{ ml. N/2·248 bromate/bromide} = 0{\cdot}001 \text{ g Al.}$$

Notes: When adding the 8-hydroxyquinoline solution the reagent should be allowed to run down the side of the beaker so that it is gradually introduced into the hot solution with the consequent production of many precipitating nuclei.

The filtering and washing of the aluminium precipitate on to the sintered glass crucible should be carried through continuously so that the precipitate is never consolidated.

Solutions.—2% 8-hydroxyquinoline—dissolve 20 g of the reagent in 114 ml. acetic acid and make up to 900 ml. with water. Bring to the boil and neutralize with ammonia until the precipitate formed dissolves with difficulty, make up to 1 litre and cool. Filter before use if necessary.

N/2·248 bromate/bromide.—Weigh accurately 12·382 g potassium bromate and 70 g potassium bromide into a 600 ml. beaker, dissolve in cold water and when solution is complete make up to 1 litre in a standard flask. This solution can be taken as a standard.

N/4·5 thiosulphate.—Dissolve 55·15 g sodium thiosulphate crystals in 1 litre of water and standardize the solution against the bromate/bromide solution or against N/10 potassium dichromate solution.

(N) **Iron**

Weigh 0·5–2 g of drillings into a 150 ml. beaker and proceed as for the determination of copper.

Transfer the copper-free electrolyte to a 500 ml. conical beaker, add 10 g ammonium chloride and bring to the boil. Whilst boiling oxidize with a 10% bromine in hydrochloric acid solution until a permanent bromine colour persists, then make ammoniacal with 50% ammonia and boil for half a minute longer. Filter on to a Whatman No. 4 fluted paper and wash with hot water, then redissolve the precipitate back into the original beaker with hot 50% hydrochloric acid, breaking the point of the filter paper if the precipitate sticks unduly. Bring the filtrate to the boil and reduce the iron with a 3% solution of stannous chloride (the yellow colour fades to white), add 2 drops in excess and allow to cool. When cold add 20 ml. of a saturated mercuric chloride solution and 25 ml. of sulphuric-phosphoric acid mixture and titrate with standard potassium dichromate solution to a permanent blue colour, using a 1% solution of diphenylamine in sulphuric acid as an indicator.

1 ml. std. dichromate solution = 0·001 g iron.

Notes: The copper need not be removed unless its determination is required, in which case miss out the electrolysis stage but wash the precipitated iron more thoroughly with hot water and diluted ammonia to free from copper.

As an alternative to diphenylamine as an indicator, a solution of o-phenanthroline can be used. This gives a much sharper end-point.

Sulphuric-phosphoric mixture.—Mix together 1 part by vol. conc. sulphuric, 1 part by vol. syrupy phosphoric acid and 8 parts by vol. water.

Standard dichromate solution.—Dissolve 0·878 g potassium dichromate in water and make up to 1 litre. Standardize against pure iron.

O-phenanthroline solution.—Dissolve 0·695 g ferrous sulphate crystals in 100 ml. water and add 1·485 g o-phenanthroline. Stir until dissolved and use 3 drops for each determination. [Colour change: orange (reduced)—colourless (oxidized).]

(O) **Manganese** (Volumetric method)

Weigh 1 g of drillings into a 500 ml. conical beaker and dissolve in 30 ml. acid mixture. Boil off the brown fumes, make the bulk up to 130 ml. with boiling water, add 0·1 g silver nitrate in solution or solid form, and 2·5–4 g ammonium persulphate. Simmer for

1 minute, timed, at boiling point, cool to 15° C. and titrate with N/10 sodium arsenite solution until the permanganate colour is discharged.

1 ml. N/10 sodium arsenite ≡ 0·001099 g Mn.

Solution

Acid mixture :

Mix together 1335 ml. water
250 ml. conc. sulphuric acid
315 ml. syrupy phosphoric acid
600 ml. conc. nitric acid

N/10 sodium arsenite.—Dissolve approx. 7 g sodium arsenite and 15 g powdered ammonium carbonate in water and make up to 1 litre. Standardize against a standard steel containing a known amount of manganese and treated according to the above method.

Notes :

(1) The times and quantities should be strictly adhered to and the titration carried out as quickly as possible since manganese tends to reoxidize in air under these conditions.

(2) As an alternative finish, the ferrous ammonium sulphate—$KMnO_4$ titration may be used in which case sodium bismuthate should be used for the oxidation.

(P) **Nickel** (Gravimetric method)

For less than 1% Ni take 1 g of sample.

For more than 1% Ni take 0·5 g of sample, or an amount which contains not more than 0·05 g Ni.

Weigh the drillings into a 150 ml. beaker and proceed as for the determination of copper.

Transfer the copper-free electrolyte to a 400 ml. beaker, add 5 g tartaric acid and make alkaline with 50% ammonia avoiding any undue excess. Warm the solution to approx. 70° C. and add 20 ml. of a 1% dimethylglyoxime solution in alcohol, stir well and allow the precipitated nickel glyoxime compound to settle in a warm place. Filter on to a Whatman No. 4 fluted paper and wash with hot water, test the filtrate for nickel with 1 ml. of the glyoxime solution, and re-dissolve the precipitate back into the original beaker with boiling 50% HCl. Bring the solution to the boil and boil for approx. 2 minutes, dilute to 150 ml., add 2 g tartaric acid and again make alkaline with 50% ammonia. With the solution at approx. 70° C. again precipitate the nickel with 20 ml. dimethylglyoxime solution, stir well and allow the precipitate to settle in a warm place. Filter on to a sintered glass crucible (Grade 3

porosity), or a prepared Gooch crucible, previously dried and weighed at 110° C., and wash with hot water. Dry in an oven at 110° C. for 2 hours or to constant weight, cool and re-weigh.

Weight of nickel glyoxime × 0·2032 = grams nickel.

The presence of much copper tends to oxidise the precipitate and give low results.

(Q) **Zinc**

Weigh 2 g of sample into a 250 ml. beaker, dissolve in 40 ml. electro-acid mixture and electrolyse as in the determination of copper until the copper is removed.

Dilute to 200 ml. and gas the heated copper-free electrolyte with H_2S for 5 minutes allowing the precipitate to settle for half an hour. Filter any Group II sulphide on to a Whatman No. 1 paper and wash with cold water, collecting the filtrate into a 400 ml. conical beaker. Add 10 g ammonium chloride to the filtrate, 3 ml. approx of bromine water and carefully neutralize with 50% ammonia adding 5 ml. excess. Bring to the boil, boil for approx. 1 min. and filter the combined hydroxides and manganese salt on to a Whatman No. 4 fluted paper, washing with hot water and collecting the filtrate in a 500 ml. conical beaker. Test the filtrate for nickel by taking out approx. 1 ml. and adding 0·2 ml of 1% di-methyl gloxime solution (if the solution contains nickel add 40 ml. glyoxime solution), heat to 70° C., allow the precipitate to settle and filter, collecting the filtrate in a 500 ml. beaker ; if the solution does not contain nickel this step may be omitted. To the nickel free solution add 25 ml. ammonium polysulphide solution and slowly add, drop by drop, with constant stirring, 50% glacial acetic acid until the solution is a light straw colour, boil for 10–15 minutes, i.e. until the precipitate of sulphur, and any zinc sulphide, has coagulated. Filter on to a Whatman No. 40 paper and wash well with hot water. Place the filter paper and precipitate into a previously ignited and weighed silica or porcelain crucible and carefully burn off the paper, keeping the temperature to a dull red heat. Raise the temperature to a bright red heat, cool in a desiccator and reweigh the crucible and contents (zinc oxide).

$$ZnO \times 0{\cdot}8034 = Zn.$$

Note: This method is accurate up to about 2% zinc, over that amount absorption losses are inclined to be heavy and it would be necessary to re-precipitate the hydroxide and nickel precipitates, combining the second filtrates with the main filtrate.

Solution

Ammonium polysulphide.—Weigh 10 g of flowers of sulphur into a 600 ml. beaker, add 500 ml. 50% ammonia and gas with H_2S until the sulphur has dissolved. Make up to 1 litre with 50% ammonia and store for use.

(R) **Aluminium** 1–5%

Weigh 0·5 g of drillings into a 150 ml. beaker and proceed as for the determination of copper electrolytically.

Transfer the copper-free electrolyte to a 500 ml. conical beaker, add 10 g ammonium chloride, bring to the boil, and whilst boiling oxidize with a 10% bromine in hydrochloric acid solution added dropwise, until a permanent bromine colour persists. Cool a little and make alkaline with 50% ammonia solution, using litmus as an indicator and adding 2 or 3 drops in excess. Bring the solution to the boil, boil for a very short time (10–20 secs.). Filter the combined hydroxide precipitate on to a Whatman No. 4 fluted paper, washing with hot water. The filtrate may be retained for the determination of nickel (gravimetrically). Dissolve back the precipitate into the original beaker with boiling 50% hydrochloric acid solution, breaking the filter paper if necessary to remove the last traces of hydroxide precipitate.

Bring the solution to the boil and again precipitate the combined hydroxides as before, with a slight excess of 50% ammonia. Filter on to a Whatman No. 41 paper and wash with hot water. Transfer the precipitate and paper to a weighed silica or porcelain crucible and burn off first at a low heat and then for 15 minutes at the maximum temperature of the muffle (about 1000° C.). Cool in a desiccator and weigh the combined ferric and aluminium oxide precipitates quickly.

Then having previously determined the iron content, convert it to weight of Fe_2O_3 in 0·5 g sample and subtract this from the combined oxide weight, the difference being Al_2O_3.

$$Al_2O_3 \times 0{\cdot}5303 = \text{grams Al.}$$

Notes: If the copper figure is not wanted, the electrolysis may be omitted, in which case the first combined hydroxide precipitate should be washed free from copper.

After weighing the combined oxides the precipitate may be returned to a porcelain or platinum crucible and fused with approx. 10 g fused potassium bisulphate at a bright red until all the oxides have dissolved. Allow the final mass to cool and dissolve out into a 50 ml. beaker with 100 ml. 10% hydrochloric acid

solution. From this stage the iron may be determined volumetrically by stannous chloride reduction (see previous section (N) 'Iron in Aluminium Bronze').

(S) **Silicon**

Weigh 2 g of drillings into a 600 ml. conical beaker and dissolve in 40 ml. electro acid mixture. Evaporate down to fumes of SO_3 and fume well for 10 minutes. Cool, add 10 ml. conc. hydrochloric acid and 200 ml. boiling water, bring to the boil, boil until all copper salts are in solution, and filter quickly on to a Whatman 541 paper, washing well with 5% hydrochloric acid and hot water. Incinerate the paper in a previously dried and weighed platinum crucible and ignite to red heat. Cool in a desiccator and reweigh. Add 2 ml. 25% sulphuric acid to the crucible and 2 ml. approx. hydrofluoric acid and carefully evaporate to dryness and then heat to redness. Cool and weigh again. The loss in weight after the second ignition is due to SiO_2 from the sample.

$$SiO_2 \times 0{\cdot}4672 = \text{grams Si.}$$

Note: If the ash after the first incineration is white, without showing specks of metallic oxides, the fuming with hydrofluoric acid may be omitted and the weight of ash taken as SiO_2.

COPPER CADMIUM

Determination of Cadmium

Weigh 1 g of sample into a 150 ml. beaker, dissolve in 20 ml. nitric acid (sp. gr. 1·2) and evaporate down to a pasty condition. Take up the copper solution with approx. 100 ml. of 2% sulphuric acid solution warming if necessary, and extract the copper electrolytically. The copper at this stage may be determined (see 'The Determination of Copper (Electrolytically)).

Transfer the copper-free electrolyte to a 400 ml. beaker and dilute to 200 ml. with warm water. Gas with H_2S for 20 minutes of until the cadmium sulphide precipitate begins to coagulate. Allow to settle for a few minutes with a cover glass on the beaker and filter through a Whatman No. 1 paper, washing the precipitate with cold water. Dissolve out the cadmium sulphide by washing with warm 20% hydrochloric acid solution, collecting the filtrate into a 150 ml. beaker, add 2–3 ml. conc. sulphuric acid and evaporate down carefully to fumes of SO_3. Cool, dilute to 50 ml. with water, add a drop of phenolphthalein indicator and make just alkaline with 10% sodium hydroxide solution. Add dropwise

with constant stirring 10% potassium cyanide solution until the precipitate formed dissolves with difficulty, avoiding any excess, then electrolyse using a coppered platinum cathode and a P.D. of approx. 3 volts and approx. 1½–2 amps, until all the cadmium is removed (approx. 1 hour). Dry and weigh the cathode as in the determination of copper.

Wt. of cadmium deposit × 100 = % cadmium.

Note: When precipitating with H_2S it may be necessary to add a drop or two of dilute ammonia to start the precipitation, although if the solution approaches neutrality zinc will be precipitated along with cadmium and will subsequently interfere.

A coppered cathode is prepared by electrolysing for 2–3 minutes in a 10% solution of copper sulphate acidified with a few drops of nitric acid, approx. 0·1 g copper should be deposited on the electrode and the deposit should extend well up the stem of the electrode and be a bright and adherent film.

Section III

WHITE METALS (BEARING METALS, ANTIFRICTION METALS)

These alloys are usually classified into tin base and lead base alloys, the normal constituents being, in addition to the above parent metals, antimony, copper, cadmium, silver, nickel, and occasionally zinc, arsenic and bismuth. Another class of antifriction metal are those composed of lead containing small amounts of the alkaline earths. Other alloys which can be used as bearing metals are the copper-lead alloys, certain bronzes, and aluminium alloys containing tin.

Standardisation of Solutions

The following are recommended methods of standardisation for use in the determination of the usual constituents found in these alloys.

Antimony

1st method.—Dissolve 0·21 g of ferrous ammonium sulphate in 200 ml. of water to which is added 5 ml. of concentrated sulphuric acid. When perfectly cold titrate with N/10 potassium permanganate to the usual end-point.

Amount of iron in the salt taken is one-seventh of 0·21 = 0·03 g

$$\frac{0{\cdot}03 \times 1{\cdot}0901}{\text{ml. used}} = \text{grams of antimony per ml. of solution.}$$

Note: When using $KMnO_4$, the iron value/ml. × 1·0901 gives he equivalent antimony value.

2nd method.—Dissolve 0·2 g of sodium oxalate in 200 ml. of vater to which is added 5 ml. of concentrated sulphuric acid. Heat to near boiling point and titrate fairly slowly with the standard permanganate.

Calculation.—0·2 g sodium oxalate is equivalent to 0·18171 g of ntimony.

$$\frac{0{\cdot}18171}{\text{ml. used}} = \text{grams of antimony per ml. of solution.}$$

Tin

Pure metallic tin may be used and the standardisation carried ɔut precisely as is given for determination of tin in white metal (q.v.) by which means a direct determination of the value of the odine solution used can be ascertained.

A quicker method is to weigh out 0·2 g of arsenious oxide and digest this carefully on a warm plate in a 50% solution of sodium hydroxide. Cool, add a few drops of phenolphthalein, acidify with dilute hydrochloric acid and add 5 g of sodium bi-carbonate. Add 5 ml. of freshly prepared starch solution and titrate to a permanent blue colour with N/10 iodine solution.

The iodine solution is prepared by dissolving 25·4 g of pure iodine and 45 g of potassium iodide in water and making up to 2000 ml.

The approximate strength will be 1 ml. = 0·005935 g tin.

Calculation.—0·2 g arsenic trioxide = 0·2399 g of tin.

$$\frac{0{\cdot}2399}{\text{ml. used}} = \text{grams of tin per 1 ml. of iodine solution.}$$

Copper

Dissolve 0·2 g of copper foil in the minimum quantity of 50% nitric acid and evaporate to syrupy consistency after boiling off all nitrous fumes. Take up with a little water and dilute to 50 ml. Add sufficient sodium carbonate to precipitate basic copper carbonate and redissolve this in the smallest quantity of dilute acetic acid. Add 2 g of potassium iodide crystals and allow to stand for a few minutes. Add 5 ml. of starch solution and titrate with N/10 sodium thiosulphate solution which is made by dissolving 62·05 g of the salt in water and making up to 2500 ml.

When the end-point is approached add 1 g of potassium thiocyanate and quickly complete the titration of the darkened solution until all colour is discharged. If the colour has a tendency to return it is probable that the solution is too dilute or that the nitrous fumes were not completely driven off. In this case it is best to repeat the titration.

Calculation

$$\frac{0{\cdot}2}{\text{ml. used}} = \text{grams of copper per 1 ml. of solution.}$$

Silver

Attack a flattened pellet of silver about 0·1 g in weight with 25 ml. of 50% nitric acid. Boil off red fumes, evaporate to 5 ml. and then dilute to 75 ml. Cool, and add 5 ml. of a saturated solution of ferric alum. Titrate with N/50 potassium thiocyanate to a reddish brown end-point. The potassium thiocyanate solution is made by dissolving 5 g of the salt in water and making up to 2500 ml.

1 ml. of solution = 0·002158 g of silver.

Calcium

The solution used in the assay is N/10 potassium permanganate. Its value in terms of calcium can be calculated as follows :

1 ml. of the permanganate solution = 0·00200 g calcium.

Iron

The solution used for titration is again N/10 potassium permanganate, in which case 1 ml. = 0·00558 g Fe.

Cadmium

The titrating solution is N/10 iodine.

Since the tin/cadmium factor = 0·949, therefore 1 ml. N/10 iodine solution = 0·00562 g Cd.

Sampling of White Metals

These alloys have a tendency for gravity segregation. It is therefore best to sample by a 'dip' method from the molten alloy after stirring. The metal thus withdrawn should be cast into a thin mould and immediately chilled.

The test ingot thus produced, which should be of thin section, is sampled by sawing completely through and the sawings well mixed together.

If the above method is not practicable the alloy ingot should be sampled by drilling or sawing completely through the section.

Determination of Tin

(A) *When tin content is less than* 15%.—After the determination of antimony (q.v.) transfer the solution to a 500 ml. round-bottom boiling flask, add 50 ml. of hydrochloric acid and 1 g of finely powdered antimony. Place into the solution a small piece of iron rod. Fit a bunsen valve and bring to the boil and maintain at boiling temperature for 30 minutes. Close valve and place in cooling box. As an alternative to the valve a small piece of marble may be introduced into the solution. When cold, remove valve and iron rod, add a piece of marble, add starch solution and titrate with N/10 iodine solution in the normal manner.

(B) *When tin content is greater than* 15%. Place 0·25 g of sample in a 100 ml. beaker and add 25 ml. of hydrochloric acid. If the antimony content is below 3% add a few ml. of antimony chloride solution. Heat on hot plate or sand bath without boiling to effect solution. Add potassium chlorate crystals until any black particles of copper and antimony have been redissolved. Make up volume to 80 ml. Introduce a small piece of iron rod and reduce for 30 to 45 minutes on hot plate. Remove the iron rod, wash rod and sides of beaker, add a piece of marble or bubble carbon dioxide through the solution during the cooling stage which is effected by placing in a cooling box. When cold add starch and titrate with N/10 iodine.

Iodine solution.—See standardisation.

Antimony trichloride solution.—Dissolve 120 g of the salt in 500 ml. hydrochloric acid. Transfer to storage bottle and add a further 300 ml. of acid. Make up to 2500 ml. with water.

Starch solution.—Make a thin paste of 2 g of soluble starch with water and pour into 100 ml. of boiling water with stirring. Make up to 500 ml. Add 7 ml. of formaldehyde.

Determination of Copper

Direct determination.—Attack 1 g of sample in a 500 ml. beaker with 10 ml. of hydrobromic acid-bromine mixture. This mixture is made by adding 225 ml. of hydrobromic acid to 25 ml. of bromine with caution. Evaporate to dryness the contents of beaker, add 20 ml. of 50% nitric acid and again evaporate to dryness. Take up with 20 ml. of water and a few mls. of hydrochloric acid. Add sodium carbonate until a precipitate forms. Redissolve in dilute acetic acid adding 5 ml. excess. Add 2 g of potassium iodide and a little starch solution. Titrate with N/10 sodium thiosulphate exactly as is described previously in the standardization of thiosulphate solution for copper determinations.

Alternative methods

(1) *When lead is absent.*—Dissolve 0·2 g of sample in 20 ml. of *aqua regia*, boil off excess acid and add an equal volume of water. Add 2 g of tartaric acid. Add solid sodium hydroxide until the solution is blue in colour and then add a hot saturated solution of sodium sulphide. Filter hot and dissolve the precipitate from the filter with warm 50% nitric acid. Evaporate the solution to remove excess acid, dilute and proceed to the titration as in the previous method.

(2) *When lead is present.*—Proceed as above until the alkaline solution has been obtained. Heat the solution on a hot plate and then pour into it a hot alkaline solution of hydrazine hydrochloride. This solution is prepared by dissolving 10 g of sodium hydroxide in 150 ml. of water and adding 1·5 g of hydrazine hydrochloride. Stir the assay solution well and allow to settle. Filter hot through sintered glass or asbestos and after washing dissolve the precipitated metallic copper from the filter with hot 50% nitric acid. Proceed with the assay as above.

(3) In all the above methods the final determination of the copper can be made by the electrolytic method instead of by means of a thiosulphate titration.

Determination of Antimony

Direct volumetric method.—Dissolve a 1 g sample in 20 ml. of concentrated sulphuric acid in a 500 ml. flask with agitation over a bunsen flame until copious fumes are evolved. Cool and cautiously add 100 ml. of water and, after again cooling, add 15 ml. of concentrated hydrochloric acid. Boil for a few seconds and add a further 100 ml. of water. Titrate when cold with N/10 potassium permanganate as described under standardization of permanganate for determination of antimony.

1 ml. of N/10 potassium permanganate = 0·00609 g antimony.

Note: Arsenic, in the alloy, will be titrated as antimony and therefore allowance must be made if present in any appreciable quantity.

Determination of Silver

Dissolve 2 g of sample in 25 ml. of 50% nitric acid in a 250 ml. beaker. Boil off nitrous fumes. Wash cover and sides of beaker with water and dilute to 100 ml. Add 5 ml. of ferric alum as indicator. Titrate with N/50 potassium thiocyanate until a reddish brown coloration appears.

1 ml. of N/50 potassium thiocyanate = 0·002158 g silver.

Potassium thiocyanate solution.—5 g of salt to 2500 ml. of water; standardise against pure silver.

Determination of Lead

Direct gravimetric method.—In the case of a tin base alloy take 5 g and for a lead base alloy take 0·5 g of the sample. Dissolve in 50 ml. of hydrobromic acid-bromine mixture the composition of which has been given under 'Copper'. Evaporate to dryness and repeat the attack. Cool and add 20 ml. of nitric acid. Boil to expel excess bromine, cool and filter off any residue of silver bromide or insoluble matter. Wash well with hot 2% nitric acid. Add 10 ml. of 60% sulphuric acid and evaporate to fumes. Continue the fuming until a very low volume remains in beaker. Cool and take up with 50 ml. of dilute sulphuric acid, boil to dissolve any copper sulphate and allow to stand. Filter through a sintered glass filter. Wash the lead sulphate with 1 : 6 sulphuric acid and finally with alcohol. Dry at 105° C. for 30 minutes and ignite at 500° C. to a constant weight. Extract the lead sulphate with 30% ammonium acetate solution, wash well with hot water and alcohol. Dry and ignite as before. Loss in weight × 0·6833 = lead.

Alternative methods of completing the determination are by means of the ammonium molybdate titration and by electrolytic deposition on anode but the method given above is recommended especially for small amounts of lead such as occur in a tin base white metal.

Determination of Iron

The colorimetric method is recommended.

The solution in which iron is to be determined must be free from most of the usual constituents and should be approximately of a 10% acidity with sulphuric acid.

Tin, antimony, and lead are removed as described under the 'Separation Method' (q.v.) and the procedure is then as follows :

Add 5 ml. of nitric acid, 5 g of ammonium chloride, and ammonium hydroxide in excess. Add a little pulp, boil, cool and filter through a Whatman No. 40 paper. Wash three times with 3% ammonium nitrate solution until all traces of copper have been removed from the solution. Dissolve the precipitated ferric hydroxide in 20 ml. of 1 : 1 hydrochloric acid and transfer to a Nessler colour tube washing several times with hot water. Cool, add 10 ml. of the potassium thiocyanate solution. In another colour tube run 20 ml. of 1 : 1 hydrochloric acid and 10 ml. of the potassium thiocyanate and sufficient standardized ferric chloride

solution to match the colour of the assay. A 'blank' assay should be run of the reagents used.

Potassium thiocyanate solution.—60 g per litre.

Ferric chloride solution.—Dissolve 0·28 g of ferrous ammonium sulphate in 10 ml. of hydrochloric acid, dilute to 50 ml., add N/10 potassium permanganate until a faint permanent pink colour is produced and make up to 1 litre.

1 ml. of solution = 0·0004 g of iron.

Determination of Arsenic

Distillation-volumetric method.—Weigh 1 g of sample into a 300 ml. flask, add 40 ml. of the ferric chloride-calcium chloride solution. Connect up to a condenser or attach a delivery tube and lead same into a beaker containing 300 ml. of distilled water. Distil for 15 minutes. Rinse out delivery tube or condenser into the receiver containing the distillate. Add a few drops of methyl orange and titrate with N/50 potassium bromate. A 'blank' assay should be run to check freedom from arsenic of the reagents.

Ferric chloride—calcium chloride solution

300 g ferric chloride
400 g calcium chloride

Dissolve in 600 ml. of hydrochloric acid and make up to 1 litre.

Potassium bromate (N/50).—Dissolve 0·5566 g of potassium bromate in water and dilute to 100 ml.

1 ml. = 0·00075 g arsenic.

Determination of Zinc

(A) *In Absence of cadmium, direct gravimetric method.*—Proceed as in the 'Separation Method' (q.v.) up to the removal of lead, copper, iron, nickel. To the filtrate from the estimation of nickel add 10 ml. of a saturated solution of sodium sulphide and allow to stand on hot plate for 10 minutes. Filter off the zinc sulphide through a Whatman No. 40 paper, wash well, dry, and ignite precipitate carefully at not more than 700° C. in a muffle furnace. Weigh as zinc oxide. (Factor to convert to zinc is 0·8034.)

(B) *In presence of cadmium.*—In this case the precipitate produced by the sodium sulphide consists of zinc and cadmium sulphides. These are not filtered off but the solution and precipitates are treated as follows. Add a solution of potassium cyanide, filter and wash well with 2% ammonium nitrate solution. Wash precipitate back into original beaker and add 60 ml. of water. If it is desired to determine the cadmium this precipitate, which contains the cadmium present, is attacked with 60 ml. of hydrochloric

acid and titrated with iodine as usual. The filtrate contains the zinc present and is treated as follows :

Make the solution just acid with hydrochloric acid and add 2–3 g of potassium chlorate. Boil and make ammoniacal. Add a few mls. of sodium sulphide solution to precipitate zinc sulphide. Dissolve by means of hydrochloric acid, add a little in excess and titrate hot with standard potassium ferrocyanide solution using uranium acetate as an external indicator.

Potassium ferrocyanide.—Dissolve 12·93 g in water and make up to 1 litre.

1 ml. = 0·003 g zinc.

Uranium acetate.—Dissolve 1 g in 30 ml. of water.

Separation Method for the Determination of Lead, Copper, Iron, Nickel, Zinc and Cadmium

Take 1 to 5 g of sample and attack with 10–50 ml. of hydrobromic acid-bromine mixture. Evaporate down and take up as usual with 50% nitric acid, using 20 ml. if lead contents are less than 5% and 40 ml. if higher. Boil off excess of bromine, cool, filter off any bromide of silver or insoluble matter. Transfer to a tall 150 ml. beaker and make up volume to 100 ml. Electrolyse at 2·5 amps and determine copper and lead in the usual manner.

Make the electrolyte ammoniacal and heat to boiling. Filter off any ferric hydroxide precipitate and determine iron in the usual manner by a colorimetric method.

To the filtrate add 10 ml. of an alcoholic solution of diemthylglyoxime and, after standing, filter off nickel precipitate. This precipitate is treated in the usual manner for the determination of nickel.

To the filtrate add 10 ml. of a saturated solution of sodium sulphide and the precipitated sulphides of zinc and cadmium are allowed to stand for some minutes on a hot plate. Filter and wash.

If cadmium only is present.—Transfer precipitate and paper to a 400 ml. beaker. Add 60 ml. of water and 40 ml. of hydrochloric acid, stir well and titrate with N/10 iodine using starch as indicator.

If zinc only is present.—Transfer as before and after making slightly acid with hydrochloric acid titrate hot with potassium ferrocyanide solution using uranium acetate as external indicator.

If both zinc and cadmium are present.—Proceed as in Paragraph (B) of the previous determination.

The preparation of the standard solutions required has been described previously.

1 ml. of N/10 iodine = 0·00562 g cadmium.
1 ml. of Standard potassium ferrocyanide = 0·003 g zinc.

Determination of Nickel

Direct gravimetric method.—Dissolve 1 g in a mixture of 10 ml. of hydrochloric acid, 2·5 ml. of nitric acid and 10 ml. of water. Add 1 to 2 g of tartaric acid, add a slight excess of ammonium hydroxide and warm. Add 10 ml. of an alcoholic solution of dimethylglyoxime and allow to stand on a warm plate for some minutes. Filter through a tared Gooch or sintered glass crucible and wash well with warm dilute solution of ammonium nitrate. Dry at 100° C. and weigh. Factor for conversion to nickel is 0·2032.

It is preferable to filter through an ordinary paper and, after drying, ignite at 800° C. and weigh as the oxide. Factor is 0·7858.

Determination of Tin and Antimony in White Metal Drosses

Attack 1 g of sample in 100 ml. beaker with 20 ml. of hydrochloric acid. Heat gently and when reaction ceases add a few crystals of potassium chlorate until the solution is an orange-yellow colour. Allow to cool and filter. Wash well with hot water and reserve filtrate for determination of tin.

Transfer the residue and paper to an iron crucible and cover with powdered sodium hydroxide. Heat gently over a bunsen burner and then raise temperature to red heat. Dissolve out the cold melt with 20 ml. of hydrochloric acid, add an equal volume of water and the reserved filtrate. Introduce an iron rod and reduce until all antimony has been precipitated. Filter and wash. The filtrate contains the tin present and this is estimated in the usual manner by reduction with iron and titration with iodine.

The precipitated antimony is transferred to a conical beaker, 15 ml. of sulphuric acid added and the mixture heated until all antimony is dissolved. Allow to cool, add 15 ml. of water and an equal volume of hydrochloric acid. Now add 300 ml. of water and determine the antimony present by titration with potassium permanganate as usual.

ANALYSIS OF CALCIUM HARDENED LEAD BASE BEARING METAL

Tin and Antimony (Antimony present only as an impurity)

Weigh 5 g of sample into a 450 ml. conical beaker and add 50 ml. 50% HNO_3. Heat gently until action ceases and then boil. Add Whatman accelerator and bring to boil again. Allow to settle for 10 minutes and then filter on a Whatman No. 30 paper. Wash well with hot water. Reserve filtrate for Al determination,

To original beaker add 20 ml. H_2SO_4 and then precipitate and paper. Add 5 g of sodium sulphate and cover with watchglass. Heat gently at first and then boil until organic matter has been destroyed. Allow to cool and add 15 ml. water and 15 ml. HCl. Bring to boil for 1 minute and add a further 150 ml. water. Allow to cool and titrate with N/10 potassium permanganate to determine Sb content. After titration transfer to 500 ml. round-bottom boiling flask and add 50 ml. HCl, 1 g powdered Sb and 1 g pure Fe rod. Fit bunsen valve and reduce gently for 30 minutes. Close valve and cool. When cold remove iron rod and titrate with N/10 iodine to determine Sn content.

Aluminium (present only in small amounts)

Filtrate.—Make first alkaline with NH_4OH and then just acid to litmus with 50% acetic acid. Pass a rapid stream of H_2S through solution for 30 minutes and filter, receiving filtrate in a 600 ml. beaker. Wash sulphides with hot water and discard. Evaporate filtrate down to approx. 100 ml., cool and add 5 g ammonium chloride and (1 : 1) ammonium hydroxide until just alkaline adding slight excess. Boil for a minute and filter on Whatman No. 541 paper. Wash well with hot 2% ammonium chloride solution. Reserve filtrate for Ca and Mg determination. Redissolve precipitate through paper with (1 : 1) HCl and reprecipitate with NH_4OH and filter again washing well with hot water. Discard filtrate and dissolve precipitate with HCl as before, reprecipitate and filter once again. Wash well and transfer precipitate and paper to crucible and ignite. When cold weigh as Al_2O_3. (Factor = 0·5921.)

Calcium and Magnesium (Magnesium present in small amounts)

Acidify filtrate from aluminium separation with HCl and heat to boiling. Remove and add 30 ml. of saturated ammonium oxalate solution, stir and then add enough NH_4OH to have 5% present. Set aside and allow precipitated calcium oxalate to settle for one hour. Filter on a fine texture paper and wash well with hot water. Remove paper and transfer precipitate to original beaker by washing. Dissolve it in 50 ml. (1 : 4) H_2SO_4 and dilute to approx. 200 ml. with hot water, heat to almost boiling and titrate with N/10 potassium permanganate to determine Ca content.

$$1 \text{ ml. } N/10/KMnO_4 = 0{\cdot}002 \text{ g Ca.}$$

Reserve filtrate for magnesium determination.

Make filtrate from calcium separation feebly acid with HCl and

heat to approx. 60° C. Add 10 ml. 8-hydroxyquinoline solution and stir. Now add NH_4OH slowly until distinctly alkaline and allow to settle for 1 hour. Filter precipitate on fine texture paper and wash well with hot water. Discard filtrate and dissolve precipitate in hot 25 ml. (1 : 1) HCl in stoppered bottle. Wash with dilute HCl (90 ml. water and 35 ml. (1 : 1) HCl) so as to give an acid concentration of 20% at a volume of approx. 150 ml. Add a few drops of methyl orange and titrate with N/10 potassium bromate solution until solution is colourless and there is an excess. Add 1 g of potassium iodide and starch and back titrate with N/10 sodium thiosulphate.

1 ml. N/10 potassium bromate = 0·000304 g Mg.

Determination of Mercury (present in small amounts)

Weigh 5 g sample into 400 ml. beaker and add 200 ml. water and 25 ml. HNO_3. Heat gently until sample is decomposed. Cool, dilute with cold water to approx. 300 ml. Add $KMnO_4$ until pink colour persists for 5 minutes to ensure absence of nitrous acid and monovalent mercury. Destroy the excess by careful addition of fine crystals of ferrous sulphate, or a solution of the salt (chlorine free). Add ferric alum solution and titrate with N/50 potassium thiocyanate solution to determine Mg content.

1 ml. N/50 KCNS = 0·002 g Hg

$$\text{or } \frac{\text{Ag Factor}}{1{\cdot}0756} = \text{Hg factor.}$$

Note: Pb, Cu, Bi, Cd, Sn, As, Sb, Fe, Mn, Ni and Co do not interfere. The method fails if hydrochloric acid or chlorides are present.

Section IV

ZINC BASE ALLOYS

Tin

Weigh 10 g of sample into a 450 ml. conical beaker and add in small portions at a time 100 ml. of 50% HNO_3. Heat gently until action ceases and then add a Whatman accelerator and boil for 20 minutes. Allow to stand for 10 minutes on warm plate and then filter on a Whatman No. 30 paper. Wash well with hot water. Reserve filtrate for Cu and Pb.

Add 15 ml. H_2SO_4 to original beaker and then add precipitate and paper. When paper has been dissolved add 5 g of sodium

sulphate and heat gently at first and then boil until all organic matter has been destroyed. Allow to cool.

When cold add 15 ml. water and 15 ml. HCl. Bring to boil for 1 minute and add further 150 ml. water. Transfer to a 500 ml. round-bottom boiling flask and add 50 ml. HCl. Add approx. 1 g powdered Sb and 1 g of pure iron rod. Fit bunsen valve and reduce gently for 30 minutes over burner.

Close valve and place in cooling box.

When cold, remove valve, add starch and titrate with N/10 iodine to determine Sn content.

Copper and Lead

Filtrate.—Electrolyse at 2·5 amps until all Cu has been deposited and then remove and wash electrodes in usual way and, when dry, weigh to determine Cu and Pb contents. Reserve electrolyte.

Aluminium

Make electrolyte up to 250 ml. in measuring flask and pipette out 25 ml. into a 250 ml. beaker. Make up to approx. 150 ml. This is equivalent to 1 g.

Make just ammoniacal and boil for 1 minute. Filter on Whatman No. 541 paper while hot. Wash with ammonium nitrate solution.

Dissolve precipitate from paper with hot HCl (1 : 4) into original beaker. Wash well with hot water and finally with 10% ammonium hydroxide. Reserve paper.

Add 25 ml. HCl and reprecipitate with ammonium hydroxide as before. Boil and filter as before. Discard filtrate and repeat once more.

Transfer final precipitate and paper to crucible and ignite carefully at first. Weigh as Al_2O_3. (Factor = 0·5921.)

Iron

Transfer remainder of solution to colour-matching beaker. To a similar beaker add 40 ml. HNO_3 and make up with water to almost same volume as assay. To both add 10 ml. potassium thiocyanate and then run in standard iron solution until colour match is obtained to determine Fe content. Amount taken is equivalent to 9 g sample.

1 ml. of standard iron solution = 0·0004 g Fe.

Magnesium

1. Weigh 10 g of sample into an 800 ml. beaker, add 200 ml.

water and 50 ml. nitric acid in small portions at a time. Boil for 20 minutes. Cool.

2. Add 30 ml. tartaric acid solution and 450 ml. ammonium hydroxide and cool.

Note: Tartaric acid—100 g dissolved in 1000 ml. water. The Mg precipitates much more easily from a well-cooled solution.

3. Add 25 ml. of microcosmic salt solution and precipitate magnesium ammonium phosphate with vigorous stirring. Allow to stand in a cooling bath overnight.

4. Filter through a Whatman No. 42 filter paper, washing with 1 : 10 ammonium hydroxide. Discard filtrate and washings.

5. Dissolve the precipitate with hot 1 : 4 hydrochloric acid into the original beaker and wash the paper well with hot water. Discard the paper. Add 5 ml. of sulphuric acid and evaporate to fumes. Destroy organic matter by small additions of nitric acid while heating with the beaker covered.

6. Cool, add 50 ml. water and heat to boiling. Filter through a small Whatman No. 42 filter paper and wash well with hot 1 : 4 hydrochloric acid and hot water, catching the filtrate in a 400 ml. beaker.

7. Dilute to 125 ml., add 10 ml. tartaric acid solution and neutralize with ammonium hydroxide. Then make just acid with hydrochloric acid and cool. Add 5 ml. of microcosmic salt solution and precipitate the magnesium by adding a 50 ml. excess of ammonium hydroxide with stirring.

8. Allow to stand in cooling trough for 3 hours, filter through a Whatman No. 42 filter paper and wash the precipitate 5 times with 1 : 10 ammonium hydroxide. Discard the filtrate.

Transfer the precipitate and paper to a crucible and ignite in a muffle at 850° C. for 1 hour. Cool and weigh.

$$\frac{\text{Wt. of residue} \times 0{\cdot}2184 \times 100}{10} = \% \text{ Mg.}$$

Cadmium

1. Weigh a 200 g sample into 3000 ml. beaker containing 1000 ml. water and add 1 : 1 sulphuric acid in small quantities until 400 ml. have been added. When the action slows down, heat the solution until almost all soluble metallics have been dissolved.

Note: The acid should be added so that the solution of the metal will be as rapid as possible without having the action become too violent. With alloys which contain no copper, 23·5 g $CuSO_4 \cdot 5H_2O$ (cadmium free) should be added before adding the acid, to aid in the solution of the sample.

2. Filter through a Whatman No. 2 15-cm. paper into a 3000 ml. beaker transferring all metallics to the paper and reserve the filtrate.

3. Dissolve the metallics from the paper in 50 ml. 1 : 1 nitric acid and catch the solution in a 600 ml. beaker.

Note: Most of the metallic (spongy) copper should be washed from the paper into the beaker before dissolving the adhering particles from the 3000 ml. beaker with HNO_3. Care should be taken to prevent the HNO_3 from becoming excessive.

4. Boil the copper solution to remove nitrous fumes. Cool, dilute to 300 ml. and electrolyse until most of the copper has been removed.

Note: It is only necessary to remove the bulk of the copper at this point as the remaining amount will be eliminated in the H_2S separations.

5. Add 50 ml. of 1 : 1 sulphuric acid to the electrolyte and evaporate to strong fumes of sulphuric acid. Cool, and take up in water and transfer the solution to the 3000 ml. beaker above. Dilute to 2000 ml. and pass a rapid stream of hydrogen sulphide through the solution for 20 minutes. Filter. Transfer the precipitate to the paper, but do not police beaker. Discard the filtrate.

Note: If the acid strength of the solution is right, a dense easily filtered precipitate of ZnS containing CdS will result. If no precipitate of ZnS appears in 5 minutes, add NH_4OH a few drops at a time untilZnS appears throughout the solution. Use Whatman No. 2 15-cm. filter paper for filtering.

6. Dissolve the precipitate from the sides of the beaker and on the paper with cold 3% hydrochloric acid, and catch the solution in a 400 ml. beaker. Wash the paper with cold water. Add 15 ml. 1 : 1 sulphuric acid and evaporate to fumes.

Note: Do not evaporate too much of the excess H_2SO_4.

7. Cool. Dissolve in 200 ml. of water, re-precipitate with hydrogen sulphide and filter as above. Discard the filtrate.

8. Dissolve the precipitate with 3 : 7 hydrochloric acid into the beaker in which the precipitation was made and wash the paper well with hot water. Add 15 ml. 1 : 1 sulphuric acid and evaporate to fumes.

9. Make two more precipitations in the same manner.

Note : The filtrate from the last precipitation should contain no zinc.

10. Dissolve the last precipitate from the paper with 3 : 7 hydrochloric acid and wash the paper well with hot water. Add 10 ml. 1 : 1 sulphuric acid and evaporate to dense fumes of SO_3.

11. Add 50 ml. of water and warm to effect solution. Cool,

filter through a Whatman No. 42 11 cm. filter paper into a tall-form 200 ml. beaker. Wash the paper well with 10% sulphuric acid. Add 2 drops of methyl orange to the filtrate and neutralize with ammonium hydroxide. Make the solution just acid with 10% sulphuric acid and add 3 ml. in excess. Dilute to 150 ml., mix thoroughly and electrolyse for 3 hours with a current of 1 amp.

12. Wash the cathode with water and alcohol and dry at 110° C. Cool and weigh.

Note: The current must be left on until the last washing is finished. The first washing of the electrode must be carried out as soon as possible after the beaker of electrolyte has been removed, since the film of the solution which remains on the electrode tends to redissolve the deposit. Drying should be as short as possible to avoid oxidation of the deposit.

Section V

THE PLATINUM GROUP METALS AND ALLOYS

Introduction

Pt metals' analyses are rather different to that of other non-ferrous metals in that no one scheme of analysis can be laid down but rather a series of methods of attack and chemical separation is necessary depending on the presence or absence of certain Pt group metals.

This chapter is an attempt to present such schemes of attack and separation, with notes on modifications where necessary, when dealing with the more common alloys or solutions of the Pt metals. For a more complete treatment of analytical procedure, consult the excellent section on these metals in *Analysis of Minerals and Ores of the Rarer Elements* (Schoeller and Powell).

Forward Note

Ammonium chloride precipitation of Pt metals and Pt in particular is common practice, but suffers from the defect of co-precipitating other metals* of the group which should remain in solution. This difficulty is largely overcome by two or more re-precipitations.

In the following chapter a method devised by Gilchrist and Wichers (U.S. Bureau of Standards) dispenses with the use of

* NH_4Cl precipitates Pt, Pd and Ir from their hexachloro acids to give respectively yellow, red and black precipitates.

ammonium chloride entirely, but some analysts object to this method on the grounds that this scheme is very suitable for separation of the six platinum metals in solution alone, but is less reliable in the presence of base metals such as will be found in the analysis of commercial minerals, alloys, etc.

Methods of Attack

(1) *Aqua Regia* (3 vol. HCl : 1 vol. HNO_3) only dissolves Pt, Pd and Au giving the chloro-acids, viz.

H_2PtCl_6 yellow, H_2PdCl_6 red, $HAuCl_4$ yellow.

(2) *Fusion with Pb or Zn* (20 × wt. of sample) at 1000° C. in a carbon or graphite crucible with lid (in a clay pot with lump charcoal packing) to render Pt metals more acid soluble (in *aqua regia*).

Pt, Pd, Rh rendered acid soluble
Ru, Os, Ir remain acid insoluble.

(3) *Fusion with alkali and alkaline oxidant* (*nitrate or peroxide*) gives solution of the Pt metals particularly Ir, Os, Ru. Fusion done in Ni or Ag crucible with 20 g Na_2O_2 + 2 g NaOH preferably on powdered or pulverized alloy from a Pb or Zn fusion (as above).

No one method of attack is usually sufficient but rather a combination of two or more of the above.

Suggested lines of attack on an alloy likely to have all Pt group present.—Fuse with Pb to divide six Pt metals into two groups as above, follow with caustic fusion to get all into solution. Follow with distillation to volatilize Ru and Os leaving Rh, Pd, Ir and Pt behind. Pd is next precipitated by dimethylglyoxime followed by separation of Ir and Rh as hydrated oxides and finally Pt determined by precipitation with NH_4Cl.

Standard Methods Involving NH_4Cl Precipitation of Pt

Pb fusion of the alloy is followed by Na_2O_2 + NaOH fusion. The alkaline melt is dissolved in water and transferred to the distillation flask which in turn is connected to the Ru and/or Os train.

Ru train.—4 flasks; 3 of 500 ml. capacity, 1st containing 50 ml. 50% HCl; 2nd and 3rd, 50 ml. 33% HCl; 4th, 20 ml. 25% HCl.

Os train.—2 flasks; 1st 1 litre capacity containing 500 ml. 5% NaOH + 25 ml. alcohol; 2nd 250 ml. capacity containing 50 ml. 5% NaOH + 25 ml. alcohol.

Ru and Os

Either: Distil off OsO_4 only, with HNO_3,* but collect in the Os part of the aforementioned train and follow with the bromate distillation of Ru,* and collect in the Ru part of the aforementioned train.

Or: Carry out combined distillation of Ru and Os oxides† by treating the solution from alkali fusion with 50 ml. saturated sodium hypochlorite in the distillation flask (overnight) then adding 20 ml. HCl and 20 ml. 25% sodium chlorate solution and distilling off both metal oxides. When reaction is near completion add 20 ml. 40% sodium bromate solution to distillation flask and redistil for 15 minutes until evolution of bromine has ceased. Gas burners are lit under the four absorption flasks in the Ru train towards the end of the distillation and air is drawn through the complete train (set up in the order Ru + Os) to carry over OsO_4 to absorption flasks 5 and 6 (i.e. the Os train).

RuO_4 collected as the chloride ($RuCl_3$)

OsO_4 collected as sodium osmate (mauve solution).

Residual solution after distillation of Os and Ru is treated with 10 g NaOH + 2 ml. alcohol and boil for 5 minutes → Pt metals hydroxides. Take up precipitate with *aqua regia* and evaporate to dryness then take up with dilute HCl, filter off any SiO_2 (from alkali attack on the glass flask) and remove by treatment with HF and HCl. The HCl filtrate containing Pt, Ir, Pd, Rh is treated with excess NH_4Cl to precipitate Pt, Ir, (Pd + Rh) partially. This is completed by filtering and treating filtrate with zinc powder to precipitate remaining Pd and Rh.

Combined precipitates are ignited and reduced to metal in H_2, then fused with Pb and dissolved in 15% HNO_3 followed by H_2SO_4 treatment to remove Pb as $PbSO_4$. Then add solid $(NH_4)_2SO_4$ and boil. This gives sulphate solution of Pd, Rh (and any Ag, Cu, etc.) and a residue of Pt, Au, Ir and Ru (traces). Treat this with dilute *aqua regia* to give chloro-acids of Pt and Au and a residue of Ir (and traces of Ru).

Pd.—Sulphate solutions of Pd and Rh. Zn precipitation of metals from sulphate solution (Zn precipitation should be done in chloride or sulphate solution at 80° C.) is followed by *aqua regia* solution of Pd. Pd then estimated by precipitation by dimethylglyoxime from moderate HCl solution by using a slight excess of 1% solution of reagent in 2% HCl or acetone. (Use 0·1 g reagent

* See Gilchrist and Wichers' method for sketch of train.

† Schoeller and Powell, *Analysis of Ores of the Rarer Elements.*

for each 0·2 g Pd.) Stand half an hour and collect orange precipitate of Pd complex (and Au if present) *or* precipitate Pd and Rh with hydrazine hydrochloride (10% solution) after making alkaline with Na_2CO_3 then take up in dilute *aqua regia* (25% solution) precipitate Pd with dimethylglyoxime and retreat filtrate with hydrazine.

Note: Any Au is prevented from being co-precipitated by having HNO_3 present in solution before precipitation.

Pt may be co-precipitated if alcoholic solution of reagent is used since Pt may be reduced to platinous state and reacts like Pd.

Rh.—Precipitation by Zn, hydrazine hydrochloride solution (as above) or bromate hydrolysis—all followed by ignition in porcelain crucible, reduction in H_2 and cooling in CO_2 or by difference from weighed precipitate of the metallic Pd and Rh (by Zn or hydrazine and followed by ignition, etc.).

Chloro-acid solution of Au, Pt and Ir is treated thus :

Au.—Precipitation from $AuCl_3$ by means of $FeCl_2$ solution, or 2% hydrazine hydrochloride from HCl solution or by SO_2.

For determination of Pt and Ir either estimate Pt by precipitation as metal with hydrazine, fusing with Pb and dissolving out Pt with 50% *aqua regia* followed by precipitation with NH_4Cl and decomposing by ignition. Ir by difference.

Or: Change scheme of attack. Thus :

Pb fusion + *aqua regia* solution or alkali fusion { Alkali fusion followed by distillation if Os present in large quantities followed by Pb fusion on distillation residue }

Ru, Os	Ir	Rh	Pd	and	Pt
↓	↓	↓	↓		↓
distil	residue	bromate hydrolysis Rh only as hydroxide ignite and reduce in H_2	by dimethylglyoxime precipitation		filtrate from Rh has Pt precipitated by NH_4Cl

Alternative attack is :

Open up alloy with Pb fusion and follow by

(1) Fusion with Na_2O_2 + NaOH.
(2) Distil Os and Ru.
(3) Precipitate Pt metals (Pt, Pd, Rh, Ir) as hydroxides in residual solution by NaOH and alcohol.

(4) Take up in *aqua regia* (filter off SiO_2, HF treat and any residue is traces of Ir).
(5) Precipitate Pt, Pd, Ir with NH_4Cl.
(6) Precipitate (from filtrate) Rh, Au, etc., with Zn.
(7) Ignite and reduce all precipitates to metals.
(8) Fuse with Pb—Ir remains acid insoluble.
(9) Filtrate contains Pd, Pt, Rh.
(10) Remove Pd with dimethylglyoxime.
(11) Bromate hydrolysis on filtrate to remove Rh.
(12) Pt in filtrate precipitated by NH_4Cl.

Notes:

(1) Ignition of NH_4 compounds, sulphides and hydroxides of all Pt metals except Pt gives the oxide. Pt is the exception and gives the metal. The oxides have to be reduced by H_2 and cooled in CO_2 (to prevent reaction of absorbed H_2 with air giving water vapour absorbed).

(2) Base metals not precipitated by Zn can be conveniently removed by treating the acid chloride solution (nitrate free) with pure Zn at 80° C. when Rh, Pd, Pt, Ru and Ir (partially) are precipitated. (Zinc separation.)

A more reliable separation is effected by treating a hot *slightly acid* solution of the Pt and base metals with 5 g $NaNO_2$ and simmer for 1 hour. Treat with NaOH solution dropwise until precipitation of base metal hydroxides flocculates. This method will separate Rh, Ir, Pt and Ru from Pb, Bi, Cu, Fe, Ni, etc., but Pd is less susceptible to this treatment and may be found in the precipitate. This should therefore be dissolved in HCl and treated with dimethylglyoxime to recover Pd. Re-precipitation of nitrite-hydroxide precipitate is recommended. (Nitrite separation.)

SUMMARY OF PT METAL GROUP SEPARATION

Fusion with Pb and fusion with Na_2O_2 + NaOH gives solution of all Pt metals, followed by distillation of Os and Ru tetroxides are usual lines of attack.

Pb fusion	Insoluble in acid (*aqua regia*)	: Ru, Os, Ir
	Soluble in acid	: Rh, Pd, Pt
Distillation	Volatile	: Ru, Os
	Fixed	: Rh, Pd, Ir, Pt

Therefore according to nature of alloy, use first one then the other method to separate the six metals into sub-groups, e.g. alloys with

high % Os should first have caustic fusion otherwise start with Pb fusion. Further separation makes use of the following features :

(1) *Os only*, distils as OsO_4 from HNO_3 solution (often produced from HNO_3 treatment of alkaline solution from fusion with NaOH and Na_2O_2) then dissolves in alcoholic NaOH (in the absorption train) and gives a mauve solution of sodium osmate.

For separation of Os, Ru and Ir (large % Os) from Pt, Pd and Rh fuse with alkali and distil *before* Pb fusion.

(2) *Ru* distilled with sodium hypochlorite and chlorine or H_2SO_4 + $NaBrO_3$, and RuO_4 is collected in alcoholic HCl to give $RuCl_3$.

(3) *Pd* precipitated from HCl solution by dimethylglyoxime. (Advisable to have HNO_3 present to prevent co-precipitation of Au.)

(4) *Pd, Rh and Ir separated from Pt*—by bromate hydrolysis of dioxides of the first three.

(5) *Ir from Rh, Pd and Pt*

(*a*) Pb fusion, or

(*b*) $TiSO_4$ reduction of last three to metal but Ir only from quadrivalent state to trivalent state (subsequent removal of Ti necessary).

Note: After Pb fusion dissolve in boiling conc. H_2SO_4 + $(NH_4)_2SO_4$. This precipitates $PbSO_4$ and gives sulphate solution of Rh + Pd leaving Pt, Ru, Ir and Os insoluble. Determine Pd with dimethylglyoxime precipitation, destroy excess reagent with conc. H_2SO_4 (boil) and precipitate Rh with Zn. Pt is dissolved from residue above by *aqua regia* and then precipitated with NH_4Cl. Residue of Ru, Os and Ir is weighed, given a caustic fusion, fumed with H_2SO_4, $NaBrO_3$ added and Ru distilled (Os + Ru distilled with Cl_2 + $NaOCl_2$). Ir remains, neutralize H_2SO_4, make alkaline with NaOH, add 5% alcohol and boil. This precipitates hydrated oxide of Ir. Reduce and weigh.

Other Gravimetric Determinations

Os

(*a*) *Hydroxide.*—Sodium osmate solution from distillation is neutralized carefully with H_2SO_4 (mauve solution turns brown) and boiled until black osmium hydroxide is precipitated. Filter, wash with saturated NH_4Cl, dry, ignite at low temperature (below 200° C.) in H_2 and weigh as Os.

(*b*) *Sulphide* (for small amounts only).—Sodium osmate solution is treated with yellow ammonium polysulphide, acidified with

HCl and boiled for a quarter of an hour. Precipitate collected and treated exactly as hydroxide.

In the above the weight of Os metal should be checked by volatilizing off Os as OsO_4 and getting loss in weight.

Caution: OsO_4 is dangerous to inhale and also causes temporary blindness.

Ru

(*a*) *Sulphide.*—The chloride solution from distillation is evaporated and solution boiled with excess ammonium polysulphide and NH_4OH then acidify with HCl. Ru sulphide and sulphur is filtered off, washed with hot water and treated as described above for osmium sulphide.

For large quantities of Ru (more than 0·25 g) best to distil.

Pt

(*a*) *As metal.*—By treating a neutralised acid chloride solution (HNO_3 free) with an excess of 10% hydrazine hydrochloride, boil to coagulate, filter, wash 1% HCl and ignite. (If bulky, advisable to reduce with H_2 during ignition.)

(*b*) *Sulphide.**—To a dilute 5% HCl hot solution of the metal pass a rapid stream of H_2S. Precipitate washed with 1% HCl, ignited and weighed as metal.

(Likely to be contaminated with S and also Group II base metals which must first be removed, e.g. by nitrite treatment.)

Ir

(*a*) *By precipitation as ammonium chloriridate.*—By addition of NH_4Cl in similar manner to Pt precipitation.

(*b*) *As hydroxide.*—By bromate hydrolysis (see Gilchrist and Wichers method).

(*c*) *As metal.*—By precipitation with 10% hydrazine hydrochloride except that acid chloride solution must be made alkaline with NaOH and not merely neutralized (cf. Pt).

Pd

(*a*) *Precipitation by dimethylglyoxime.*—Details given already. Precipitate may be weighed as the complex after drying at 110° C. (factor 0·3167) or ignite and reduced to metal under H_2.

(*b*) *Sulphide.*—Precipitate by H_2S from acid chloride solution. *Not* recommended since Pd sulphide is likely to fuse on ignition.

* Gilchrist and Wichers.

Rh

(*a*) *As metal.*—By hydrazine hydrochloride from alkaline solution in same manner as for Ir.

(*b*) *Hydroxide.*—By bromate hydrolysis followed by reduction to metal by hydrazine hydrachloride as above.

(*c*) *As metal.*—By precipitate with Zn or Mg from sulphate or chloride solution at 80° C. Wash 5% HCl, ignite and reduce under H_2.

RECOMMENDED PROCEDURE FOR SEPARATION OF THE SIX PT METALS FROM ONE ANOTHER

Gilchrist and Wichers' Method (*Jnl. Amm. Chem. Soc.*, Dec. 1935)

The method avoids ammonium chloride precipitation of Pt as being a possible source of causing contamination of the precipitate with Rh, Ir and Pd (under certain conditions). Also here we absorb both OsO_4 and RuO_4 in HCl solution saturated with SO_2 for it is claimed that this is the best condition for subsequent precipitation of Os and Ru as hydrated dioxides.

Outline

Os.—Distil OsO_4 *only* from HNO_3 solution.

Ru.—Then distil RuO_4 from solution of sulphates in H_2SO_4 and $NaBrO_3$.

Both OsO_4 and RuO_4 are absorbed in 6N HCl saturated with SO_2.

Pt.—Filtrate containing Pt, Pd, Rh and Ir converted to chlorides by *aqua regia*, then $NaBrO_3$ is added to boiling solution and on neutralizing all but Pt precipitate as hydrated oxide.

Pt is eventually recovered as sulphide and ignited to metal.

Pd.—Precipitated by dimethylglyoxime.

Rh.—Precipitated by H_2S, ignited to oxide and reduced to metal by H_2.

Ir.—Precipitated as hydrated oxide, ignited and reduced to metal by H_2.

Detailed Account

1. **Os.**—Distilling flask and train of 2 or 3 absorption flasks (ground glass stoppers with grease absent for this absorbs OsO_4).

Absorption solution 150 ml. 50% HCl freshly saturated with SO_2 in first flask (nearly all absorption here) and 50 ml. similar solution in other flasks.

Pt metals solution in distilling flask, dilute to 400 ml. and add

40 ml. 50% HNO_3. Distil for about 1 hour if Os initially present as alkaline osmate or bromo-osmate but 7–8 hours if as chloro osmate (in this case better to distil with conc. H_2SO_4).

Take solution of osmium from all absorption flasks, evaporate, digest with 10 ml. conc. HCl (twice) to decompose sulphites. Then dissolve residue in 150 ml. water, heat, add 10% $NaHCO_3$ until precipitate appears then few drops bromo-phenol blue indicator (0·04% solution). (Yellow to blue at pH4.) Continue adding $NaHCO_3$ until solution is pale blue. Boil solution for 5 minutes to complete precipitation of hydrated dioxide.

Filter off precipitate (first decant liquid) preferably in a special Munroe Pt crucible but a Gooch may be used, wash with hot 1% NH_4Cl and cover precipitate with solid NH_4Cl. Moisten (or impregnate precipitate with saturated NH_4Cl solution). Put Pt cap on bottom of crucible and quartz lid on top. Heat crucible under H_2 flame until all NH_4Cl is expelled then heat under H_2. Finally cool under H_2 and displace H_2 by CO_2 before removal of lid, weigh residue as Os metal.

2. **Ru.**—Evaporate solution left in distillation flask to dryness. Treat with 10 ml. conc. HCl, evaporate and repeat this twice more until all oxides of N_2 evolved. Dissolve residue in 25 ml. water, add 10 ml. conc. H_2SO_4 and evaporate to fumes of SO_3. Transfer this solution (and any Pt which has separated) to similar distillation flask as that used for Os, dilute to 100 ml. with water, add 100 ml. 10% $NaBrO_3$. Distil for 1½ hours, add further 25 ml. $NaBrO_3$ solution and distil for another hour. Absorb Ru tetroxide in 150 ml. 50% HCl saturated with SO_2 as before. Precipitation of hydrated dioxide is achieved by exactly similar process to Os but here wash with hot 1% $(NH_4)_2SO_4$. Take filter paper and precipitate and ignite first in air then H_2. Cool in H_2 and wash residue with hot water (to remove traces of soluble salts). Repeat ignition in air and H_2, cool in H_2 and weigh metallic Ru.

3. **Pt.**—Solution in distillation flask contains Pt, Pd, Rh and Ir also H_2SO_4, sodium sulphate, bromine and bromate. Transfer this to a beaker, decompose bromate with HCl (*Caution*). Evaporate with HCl on steam bath and dilute to 200 ml. water. Bring to boil, add 20 ml. 10% $NaBrO_3$ followed by 10% $NaHCO_3$ dropwise until faint permanent precipitate. Test acidity of solution during process with rod and bromo-cresol purple (0·01%)—yellow → blue at pH6. Add further 10 ml. bromate solution and boil 5 minutes. Increase pH to 8* by few drops $NaHCO_3$ solution

* pH6 is correct for precipitation of Ir and Rh dioxide but is border line for Pd, therefore make more alkaline. Best done in two stages as stated to see clearly the indicator colour. (Gilchrist and Wichers suggest retreating for highest accuracy.)

(test with 0·01% cresol red) until indicator turns pink. Add another 10 ml. bromate and boil 15 minutes. Precipitate of mixed dioxides of Pd, Rh and Ir are filtered preferably on porous porcelain or glass filters leaving Pt in filtrate. Wash precipitate with hot 1% NaCl solution then dissolve precipitate in 20 ml. conc. HCl on a steam bath (Rh and Pd dioxides dissolve quickly but IrO_2 slowly). Reprecipitate hydrated dioxides twice to ensure complete removal of Pt.

To filtrates digest with HCl to destroy bromates then evaporate with HCl (gives yellow Pt solution). Dilute to 400 ml. with water and adjust acidity to 5% HCl. Pass H_2S into the hot solution

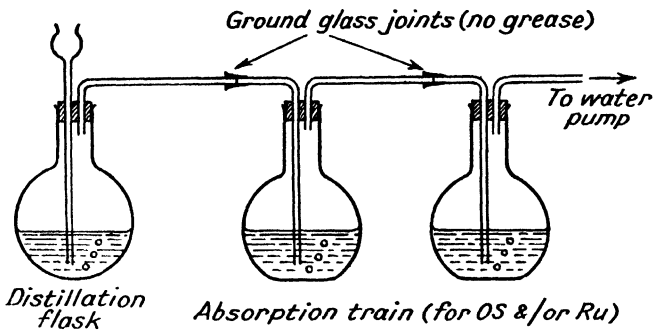


FIGURE 5

using a rapid stream. Filter off sulphide and wash with cold 1% HCl and ignite strongly in air in porcelain crucible to metallic Pt (metal may contain traces of sulphur).

4. **Pd.**—Dissolve mixed dioxides of Pd, Rh and Ir in 20 ml. conc. HCl as before (3), dilute to 400 ml. and add sufficient 1% dimethylglyoxime in 95% ethyl alcohol to precipitate Pd (2¼ g solid reagent per 1 g Pd + 10% excess). Stand 1 hour and filter off orange precipitate, wash hot 1% HCl and hot water (not necessary to re-precipitate but can do by solution in H_2SO_4 + HNO_3, fume to SO_3, dilute and re-precipitate with glyoxime.

(*a*) Pd dimethylglyoxime may be dried for 1 hour at 110° C. and weighed as such (in a porous filter crucible). Factor 0·3167.

or (*b*) To determine Pd as metal, filter on paper and ignite gently in porcelain crucible then strongly in air, then H_2, cool in CO_2 and weigh as metallic Pd.

5. **Rh.**—Take filtrate from above containing Rh and Ir as chlorides with excess glyoxime and destroy latter with 10 ml. H_2SO_4 and 3 ml. HNO_3 and evaporate to fumes of SO_3, dilute with 20 ml. water and re-fume (to destroy nitroso compounds which will interfere with subsequent precipitate of Rh by $TiCl_2$).

Dilute to 200 ml. and heat to boiling. Add dropwise 20% solution of $TiCl_2$ until solution becomes just purple (end-point of precipitation when Rh metal readily coagulates, a few drops excess $TiCl_2$ will now give an orange coloured solution if much Ir is present). Bring solution to boil and filter. Wash with cold 2% H_2SO_4. Redissolve Rh in 10 ml. H_2SO_4 and 5 ml. HNO_3 and fume to SO_3, dilute and reprecipitate as before. Redissolve as before diluting the H_2SO_4 soluting with 20 ml. water and 10 ml. HCl and boil for 15 minutes (colour of solution now rose pink and is suitable condition for precipitation by H_2S). Dilute solution to 500 ml., heat and pass rapid stream of H_2S. Filter sulphide precipitate, wash cold 2% H_2SO_4 and water. Ignite in porcelain crucible carefully in air then strongly and finally in H_2, cool in H_2 and weigh as metal.

6. **Ir.**—Filtrate from above containing mainly Ti and Ir is diluted to 800 ml. and cooled in ice. The Ti must first be removed by precipitation with 6% solution of cupferron ($C_6H_5N.NO.ONH_4$). Filter and wash the titanium precipitate with iced 2% H_2SO_4 containing 1% cupferron. As precipitate may be contaminated by traces of Ir decompose precipitate with 20 ml. conc. HNO_3 and heat. Add 20 ml. conc. H_2SO_4 and fume and precipitate Ti with cupferron as before. Combine filtrates and evaporate if necessary to 200 ml., neutralize most of acid with $NaHCO_3$ and complete as with Pt using bromo cresol purple. Add 20 ml. 10% $NaBrO_3$ and boil half an hour. Filter hydrated dioxide and wash with hot 1% NH_4Cl. Ignite precipitate on filter in a porcelain crucible strongly in air then in H_2, cool in H_2 and weigh as metal.

Alternative method.—Solution containing Rh and Ir can be divided into aliquot parts. In one portion Rh and Ir can be precipitated together as hydrated oxides as described under separation of Pt. The precipitate being washed with hot 1% NH_4Cl carefully ignited first in air and then in H_2. Weigh as mixed metals.

Other portion determine Rh as in (5) and Ir is obtained by difference.

TREATMENT OF ORES

Refining Ores for Pt

Gravity separation and concentration to sp. gr. 14–20, Au and Ag removed by Hg treatment.

Solution of ore in *aqua regia* leaves osmiridium, sand and graphite. On heating with more HCl to 150° C. (to expel HNO_3) Pd is converted to palladous conditions. Pt precipitated as ammonium platinochloride by NH_4Cl, filter, wash and ignite in air and H_2 to metallic Pt.

Less pure Pt given by fusing concentrate with Pb which gives an alloy with Pt (not Os or Ir). Cupel, dissolve Pt in *aqua regia* and treat as above. (Pt contains Rh.)

For full analyses of Pt metals in ores, concentrates, mattes and impurities in commercial Pt metals and special alloys, consult *Analysis of Minerals and Ores of the Rarer Metals* (Schoeller and Powell).

ESTIMATION OF AG, AU AND PT METALS IN STANDARD ALLOYS AND BULLION BARS

Standard Silver Alloys

(*a*) Dissolve alloy in HNO_3 (dilute). Precipitate Ag with HCl, dilute with water, boil, cool for at least twelve hours. Filter, wash with 5% HCl, and water (hot). Remove filtrate and wash AgCl with 1 : 1 NH_4OH. Add 5–10 ml. of NaOH and formaldehyde to precipitate Ag from solution of AgCl in ammonia. Complete precipitation of Ag will be noted when the precipitate becomes dense black in colour, e.g. 20 ml. of formaldehyde would be sufficient for approx. 200–300 mg. of Ag in original alloy. Warm on hot plate (*do not boil*) to coagulate precipitate. Filter off, wash well with hot water to remove soluble salts. Burn off in a small plumbago crucible at low temperature (200–300° C.). *Weigh as Ag*. This method is applicable to low Ag percentages.

(*b*) The volumetric determinations can be found in 'Base Metal Analysis'—e.g. KCNS method using ferric ammonium sulphate as indicator. Method used chiefly for Ag bullion only.

(*c*) *NaCl Method* (Gay-Lussac) for estimation of fine and sterling Ag (92·5% Ag 7·5% Cu.)

Separation of Ag from Pd and Rh.—With HNO_3 parting, Ag, Rh and Pd form nitrate solutions and therefore have to be separated. From Ag beads, separation can be effected by H_2SO_4 or HNO_3

TABLE IV

Treatment of Iridosmine (Osmiridium)

Fuse with excess Zn. Pulverize and heat with Ba_2O_2 then cool, add *aqua regia* and distil to $\frac{1}{4}$ vol.

<table>
<tr><td rowspan="3">Distillate. Contains osmic acid (OsO_4). Redistill and collect in NH_4OH then pass H_2S — precipitates OsS_4 which gives Os on heating in closed crucible.</td><td colspan="3">Undistilled Liquid. Add H_2SO_4, filter off $BaSO_4$. Evaporate to dryness, remove SiO_2. Finally to solution add aqua regia and then strong solution of NH_4Cl.</td></tr>
<tr><td>Precipitate. Ammonium chloriridate ignite to oxide and reduce in H_2 to Ir metal.</td><td colspan="2">Filtrate. Add metallic Zn to precipitate Rh and Ru as powder. Fuse with KOH and KNO_3 and extract melt with water.</td></tr>
<tr><td>Insoluble Rh</td><td>Solution. Potassium ruthenate. Add HNO_3, precipitates ruthenium oxide which on ignition gives Ru.</td></tr>
</table>

TABLE V

Separation of Pt Metals in Ores

Crude ore digested in *aqua regia* for several hours.

<table>
<tr><td rowspan="5">Residue. Osmiridium or iridosmine</td><td colspan="4">Solution. Evaporate to syrup, add HCl and repeat several times. Dilute a little and add NH_4Cl. Stand, filter.</td></tr>
<tr><td rowspan="4">Precipitate. Wash with dil. NH_4Cl, dry and ignite.

PLATINUM</td><td colspan="3">Filtrate. Add Zn, filter precipitated metals, wash boiling water and add aqua regia.</td></tr>
<tr><td colspan="2">Residue. Boil with 10% KOH, wash, mix residue with equal weight of NaCl and heat to 440° C. in Cl_2.
Take up in water, crystallize excess NaCl. Heat liquid with HNO_3 and add saturated NH_4Cl solution.</td><td rowspan="2">Solution. Evaporate, take up in dil. HCl and add solution of $Hg(CN)_2$.

Precipitate. Wash precipitate and ignite.
PALLADIUM</td></tr>
<tr><td>Precipitate. Wash and ignite.
IRIDIUM</td><td>Filtrate. Evaporate to crystallization and ignite the crystals.
RHODIUM</td><td>Filtrate. Add conc. $FeSO_4$ solution. Filter and wash with hot water.
GOLD</td></tr>
</table>

TABLE VI

Quantitative Separation of Metals of Pt Group (for Ores, Sweeps, Residues, etc.)

Treat with *aqua regia* (with or without previous Pb fusion). Any insoluble residue is fused with Na_2O_2 in a nickel crucible. Dissolve melt in HCl. Mix the two solutions, make alkaline and distil in chlorine.

<table>
<tr><td rowspan="4">Volatile Portion. Collected in NaOH solution.
Ru + Os
Acidify and pass H_2S. Sulphides ignited in stream of oxygen. RuO_2 remains and OsO_4 distils over and collected in NaOH and alcohol.</td><td colspan="5">Remaining solution boiled to expel chlorine. Add conc. solution NH_4Cl and 2/3 vol. of alcohol.</td></tr>
<tr><td colspan="3">Precipitate. Pt, Ir, some Rh and traces of Pd. Ignite in H_2 extract with 20% aqua regia.</td><td colspan="2">Filtrate. Rh, Pd, Cu, Fe, Ni and little Pt and Ir. Nearly neutralize with NH_4OH, pass H_2S.</td></tr>
<tr><td>Residue. Rh and Ir. Fuse with $KHSO_4$, extract with water and add dilute H_2SO_4.</td><td>Solution. Pt, traces Pd, Rh, and Ir.</td><td>Precipitate. Sulphides of Au, Cu, Pd, Rh. Ignite and digest with HCl. Repeat.</td><td>Filtrate. Fe, Ni and some Au and Rh. Evaporate to dryness with HNO_3 and ignite. Extract Fe and Ni with HCl. Ignite residue (B) and combine with (A) and (C).</td></tr>
<tr><td>Residue. Ir (trace Rh.)</td><td>Solution. Rh(A) boil with Na_2CO_3 Acidify with HCl. Ignite and combine with Rh from (B) and (C).</td><td>Residue. Rh(C) combine with (A) and (B)</td><td>Filtrate. Cu and Pd. Add KCl and alcohol, Pd precipitated as K_2PdCl_4</td></tr>
<tr><td colspan="5">Residues (A), (B) and (C) contain Rh and Au. Digest in aqua regia which dissolves Au and leaves Rh as residue.</td></tr>
</table>

parting, followed by precipitation of AgCl by HCl and precipitation of Rh with Mg or hydrazine.*

If AgCl precipitate is coloured pink or brown it shows absorption of Pd therefore dissolve in NH_4OH (minimum), warm, just acidify with acetic acid and reprecipitate AgCl (Pd free) with dilute HCl. (Under these conditions Pd is reduced to the palladous tetrammine condition and is not precipitated.)

The filtrate after AgCl removal may be further acidified and Pd precipitated with dimethylglyoxime.

Standard Au Alloys

e.g. (*a*) 90% *Ag*, 10% *Au*.—Dissolve the alloy in nitric parting acids which have varying strengths, 1 : 4, 1 : 1, 2 : 1. (This acid is prepared by adding a small quantity, say 10 g of $AgNO_3$/litre to nitric acid and water in the following ratios by volume :

1 HNO_3 4 H_2O + 10 g $AgNO_3$
1 HNO_3 1 H_2O + 10 g $AgNO_3$
2 HNO_3 1 H_2O + 10 g $AgNO_3$

The alloy is treated first with 1 : 4, warm, let action subside, filter, then treat remainder in 1 : 1 and so on with 2 : 1. Filter, wash with hot water and NH_4OH to remove last traces of silver. Weigh Au residue after ignition.

(b) *Carat golds* (9, 14, 18, 20, 22 carat).—First treat alloys with 1 : 1 HNO_3 acid, warm and let action subside. Then add three times the volume of HCl (1 : 1). This renders all the alloy soluble and also precipitates AgCl. Dilute with water and warm, let stand for 12 hours. Filter off AgCl, wash with hot water. Evaporate filtrate to dryness and heat with 15 ml. of conc. HCl to remove any HNO_3 present. (Meanwhile with AgCl precipitate treat with NH_4OH to dissolve and on the filter paper will often be found a trace of *Au*. Burn off and add to main for *aqua regia* treatment. The $AuCl_3$ solution + $CuCl_2$ + $NiCl_2$ + ($FeCl_3$) is now treated to remove Au by passing in sulphur dioxide which reduces $AuCl_3$ to Au. Filter off, wash with hot water, then with NH_4OH to remove traces of Ag, and with ammonium acetate to remove traces of Pb. Burn off and weigh as Au.

9 carat = 375 parts per 1000
18 carat = 750 parts per 1000

* Alternatively dissolve Ag + Pd + Rh + Pt etc. bead in HNO_3, evaporate to dryness, *fuse* $AgNO_3$ at above 209° C. (this also converts Pt metals to oxides) Cool, leach melt with hot water and filter off Pt metal hydrated oxides and separate as outlined previously.

To calculate parts per 1000

$$\frac{9}{24} \times 1000 = 375$$

24 carat = pure Au.

This method is used also for removal of Au in bullion bars and is the most accurate for estimation of that metal.

To prepare Au powder, $FeSO_4$ is added to a weak solution of $AuCl_3$. This Au is dried after filtering. Care must be taken to wash well with water to render free from contamination by iron.

The $FeSO_4$ method is used for low grade *Au* bullion especially in refining.

Standard Pt Alloys

The Ag and Au are extracted in exactly the same way as carat gold analysis. The filtrate after washing the gold with hot water is removed and evaporated to low volume and hydrogen peroxide added to oxidize $PdCl_2 \rightarrow PdCl_4$, $PtCl_2 \rightarrow PtCl_4$, these chlorides being reduced when SO_2 was added. Boil for 15 minutes, dilute with water, add dimethylglyoxime in acetone to precipitate Pd. Let stand for half an hour. Filter, wash with 5% HCl (acid medium is essential owing to nickel being precipitated, with reagent if alkaline conditions exist). Evaporate filtrate to dryness and destroy dimethylglyoxime with HNO_3 (conc.). Boil until no more brown fumes are evolved, then evaporate to dryness and proceed to destroy HNO_3 with HCl. When complete (after two evaporations with HCl) evaporate HCl to low bulk. Cool, add solid NH_4Cl, stir well and let stand for 12 hours. Dilute with water, dissolve excess NH_4Cl, allow platinum ammonium chloride to settle, filter, wash with 1 : 1 NH_4Cl solution. Dry, burn off, starting decomposition at low temperature rising gradually to 600° C.—Bulk of Pt (80% of total content of Pt) will be extracted in this way. Zinc is added to the filtrate (base metals such as Cu, are also 'zinced' out of solution). Filter, wash with hot water. Burn off. Fuse with $KHSO_4$. Leach with water, all base metals are soluble. Filter. Burn off, heat with HF and HNO_3 to remove SiO_2. Weigh as Pt and add to the main precipitate to give total Pt.

Platinum-Rhodium Alloys

Dissolve alloy in conc. *aqua regia*, evaporate three times with hydrochloric acid and finally to dryness. To the dried $PtCl_4 + RhCl_3$ add 300 ml. of water and 1 ml. of HCl. Add 10 ml. of

sodium bromate and boil. On reaching boiling point, add $NaHCO_3$ solution carefully drop by drop until pH is 6·8 which is determined accurately enough by means of bromo-cresol papers. A precipitate of $Rh(OH)_3$ is formed which is dark-green in colour. This is boiled for at least 15 minutes after adding a further 10 ml. of sodium bromate and the pH is again adjusted to 6·8. Re-boil for 5 minutes. Allow to settle (for 10 minutes). Filter and wash with 1% NaCl solution. The filtrate is evaporated and the excess $NaBrO_3$ destroyed with HCl and the main Pt extracted with NH_4Cl.

The $Rh(OH)_3$ is dissolved through the filter paper with hot dilute HCl. Evaporated to dryness. 200 ml. of water added and sodium nitrite added in reasonable quantities. The solution is then boiled and a colourless rhodium solution is formed. $NaHCO_3$ solution is added and this renders impurities such as Fe, etc., insoluble and are filtered off. The filtrate from the nitrite separation is evaporated and treated with HCl. The above process of bromination is repeated and this results in a pure $Rh(OH)_3$ which is ignited, leached in 5% HNO_3, ignited again and finally cleaned in a Pt dish with HF and 1 : 1 HNO_3. Ignite, reduce and weigh as pure *rhodium*.

Platinum-Iridium Alloys. Standard Alloys. 5%, 10%, 15%, 20% and 25% Ir

Fuse 1 g of alloy with 10 g of Pb in a carbon crucible at 1200° C. for 1 hour. Part button of (Pb + Pt + Ir) in 1 : 4 HNO_3. Precipitate Pb from filtrate as $PbSO_4$ with H_2SO_4 (dilute) and wash with cold water. The insoluble from parting is treated with 1 : 1 *aqua regia* rendering Pt soluble and this is filtered off leaving the insoluble iridium which is washed well with boiling water to remove last traces of $PbSO_4$. The iridium is ignited in a silica crucible, reduced and weighed as Ir. Pt by difference.

Platinum-Ruthenium Alloys (+ possibly Ir)

Any alloy with more than 3% Ru is insoluble in acids and the method used for estimating this metal is exactly the same as that used for *iridium* above.

Ir and Ru may be separated from each other by distillation of Ru. Also insoluble Ru may be checked by this method.

The insoluble (Ir + Ru) from Pb fusion followed by $PbSO_4$ precipitation is washed, dried and weighed and is fused with 3 parts KOH and 1 part KNO_3 in a silver or gold crucible for 1 hour. The melt is cooled, leached with water into a beaker and evaporated to dryness, and then fumed with sulphuric acid. Cool, dilute and

pour into distillation flask. Add 20 ml. of $NaBrO_3$ (10% solution) and heat. Bromine liberated distils off the ruthenium as oxide which is converted to chloride in the receiving flasks containing 50% HCl. Distil for at least 1 hour. The ruthenium chloride is evaporated to dryness once with HCl, diluted with 200 ml. of water, made alkaline with NaOH, some sodium sulphide added together with sodium formate. Boil and make acid with H_2SO_4 (dilute). Reboil, filter, wash with 1% NH_4Cl. Ignite, reduce, clean in HF and HNO_3, burn off, reduce and weigh as *Ru*. Ir by difference.

TABLE VII

Summary

Ag	Au	Pd	Os
Add HCl → AgCl (Estimate with formaldehyde.)	(*a*) Precipitate with SO_2 from $AuCl_3$ solution → Au. (*b*) Precipitate with $FeSO_4$ → Fine Au powder.	Precipitate with dimethylglyoxime in acetone. (This is identical to nickel except there is no need for a buffer and must be in acid solution not alkaline.)	Distil with conc. H_2SO_4 + HNO_3. OsO_4 collected in alcoholic NaOH. (10% alcohol). precipitated as $Os(OH)_3$ at pH 6·8. Filter through a Gooch. This product (OsO_4) is highly volatile on ignition. (DANGER TO HEALTH causes blindness.)

Ru	Rh + Ir	Pt
Distil with conc. H_2SO_4 + $NaBrO_3$. Collect RuO_4 in alcoholic HCl → $RuCl_3$. Precipitate as sulphide, by adding Na_2S + sodium formate. After making alkaline, boil, make acid with H_2SO_4	Oxidize rhodium and iridium chlorides with $NaBrO_3$. Boil and precipitate as hydroxides at pH 6·8. Then separate by alloying with Pb in reducing atmosphere, the Pb-Rh alloy being soluble in conc. H_2SO_4 — Ir insoluble.	Add NH_4Cl to $PtCl_4$ solution → platinum ammonium chloride. Decomposes at 300–400° C. → Pt.

CHAPTER VII

TECHNICAL ANALYSIS OF IRONS, STEELS AND FERRO-ALLOYS

OUTLINES OF RECOMMENDED SCHEMES FOR COMPLETE ANALYSIS OF CAST IRONS AND STEELS

Plain Carbon, Molybdenum, and Nickel Chromium Steels

Carbon.—Combustion method.

Sulphur.—Plain carbon steel containing no molybdenum, evolution method—others barium chloride precipitation, or combustion method.

Manganese.—Steels containing no chromium, sodium bismuthate or persulphate. Steels containing chromium, persulphate method. Zinc oxide or potassium chlorate method.

Silicon.—Filter from the gravimetric sulphur except in plain carbon steels when molybdenum absent.

Nickel.—Dimethylglyoxime precipitation. Direct citrate or ammonium separation if copper absent.

Chromium.—Persulphate or Vignal method.

Molybdenum.—Butyl acetate, lead precipitation or α-benzoin oxime precipitation.

Aluminium.—If low chromium, thiosulphate precipitation as phosphate to remove iron. 8-hydroxyquinoline precipitation. Caustic soda separation if high chromium, precipitation as phosphate or 8-hydroxyquinoline complex.

Copper.—Thiosulphate precipitation in sulphuric acid solution Colorimetric estimation if under 0·5%. Higher amounts finish electrolytically.

Vanadium.—Diphenylamine titration from the chromium solution.

High-Speed Tungsten Steels

Manganese.—Zinc oxide or chlorate after removal of tungsten.

Chromium and Vanadium.—Vignal 1 g sample.

Nickel.—Dimethylglyoxime precipitation.

Cobalt.—Basic acetate or zinc oxide separation. Precipitation

Table VIII

Some Typical Analyses of Steel and Cast Irons

Plain Carbon and Alloy Steels

Spec.	Gr.C.	C.C.	Si	Mn	S	P	Ni	Cr	Mo	V	W	Cu	Co	Ti	
S.70	—	·55	·20	·60	·02	·02	·15	02	—	—	—	—	—	—	Normalized carbon steel
S.14	—	·14	·18	·70	·02	·02	·20	—	—	—	—	—	—	—	Carbon case hardening steel
S.90	—	·14	·20	·30	·018	·02	5·00	·1	·20	—	—	—	—	—	High tensile 5% Ni case hardening
S.65	—	·24	·24	·60	·02	·015	3·20	1·18	·40	.20	—	—	—	—	65 tons Ni-Cr steel
DTD.306	—	·27	·28	·50	·02	·02	·30	3·00	·50	—	—	—	—	—	60–70 tons carbon Cr-Mo
H.S.S.	—	·65	·15	·30	·015	·015	·10	4·40	—	1·50	18 0	—	5·2	—	Tool steel
S.11	—	·30	·25	·65	02	·02	3·50	·70	·20	—	—	—	—	—	55 tons Ni-Cr steel
S.28	—	·30	·25	·40	·02	·02	4·30	1·20	·20	—	—	—	—	—	Air hardening Ni-Cr steel
EN.24	—	·40	·25	·60	·02	·02	1·60	1·10	·25	—	—	—	—	—	1½% Ni-Cr steel bars and billets for forging
DTD.87	—	·40	·25	·60	·02	·02	·30	1 60	·20	—	—	Al 1·00	—	—	55–65 tons Cr-Mo-Al steels for nitriding
S.82	—	·15	·20	·40	·015	·015	4·30	1·20	·20	—	—	—	—	—	Ni-Cr case hardening steel
1% Carbon Steel	—	1·10	·28	·60	—	—	—	1·52	—	—	—	—	—	—	1% carbon steel containing chromium

Stainless Staybrite and High Nickel and Chromium Steels

Spec.	Gr.C.	CC.	Si	Mn	S	P	Ni	Cr	Mo	V	W	Cu	Co	Ti	
DTD.247	—	·65	·40	5·00	·015	·015	12·00	3·4	—	—	—	—	—	—	High thermal expansion steel suitable for valve seats
S.62	—	·25	·40	·30	·02	·02	·20	14·0	—	—	—	—	—	—	High chromium stainless steel
S.80	—	·16	·30	·30	·03	·02	2·50	18·2	—	—	—	—	—	—	High tensile chromium and nickel rust resisting steel
18/8	—	·15	·40	·40	·02	·02	8·00	18·00	—	—	·25	—	—	·80	Staybrite FDP sheet
K.K.K.	—	1·0	·40	·25	·02	·02	1·00	15·3	·70	—	—	—	—	—	High carbon chromium molybdenum steel bars
Inconel	—	·1	·30	·25	·02	·02	80·0	15·31	—	—	—	—	—	—	Nickel chromium iron alloy sheet and strips
DTD.49	—	·40	1·40	·60	·02	·02	14·0	14·0	—	—	2·5	—	—	—	High nickel high chromium steels for valves
H.Ni.Alloy	—	·10	1·00	·35	·02	·02	75·0	20·0	—	—	Al 1·0	..	..	·50	—

Cast Iron

Spec.	Gr.C.	C.C.	Si	Mn	S	P	Ni	Cr	Mo	V	W	Cu	Co	Ti	T.C.	
4.K.6	2·4	·80	2·00	·90	·040	·70	·30	·20	—	·05	—	—	—	—	3·20	Piston & Scraper Rings
Enduron	—	1·60	1·47	·40	—	—	·10	30·0	—	—	—	—	—	—	—	H.R. Rustless Inner Rings
DTD.233	—	·90	2·10	1·00	·040	·60	·30	·30	1·00	·05	—	·30	—	—	—	Outer Rings
SS.931	—	—	2·40	·80	·050	—	—	1·10	nil	—	—	—	Al 1·00	—	3·07	
DTD.277	2·3	·90	2·00	·90	·040	·60	·30	·15	·90	·05	—	·70	—	—	3·20	
Lymalloy	1·9	·90	2·10	·90	·050	·40	·15	1·00	1·00	·05	—	·20	—	—	2·80	

of Co with alpha nitroso beta naphthol. Ignite to Co_3O_4—remove traces of iron and chromium and deduct from Co_3O_4.

High Expansion Steel. DTD. 247

Manganese and chromium.—1 g sample, persulphate method. Add to sample 1 : 7 sulphuric acid, oxidize with nitric acid when the steel will dissolve almost immediately.

Stainless 'Staybrite' High Nickel and Chromium Alloys

Manganese.—Zinc oxide or chlorate method.

Sulphur.—For plain high chromium stainless with low carbon, evolution method—others $BaCl_2$ precipitation or combustion.

Phosphorus.—As in stainless steel.

Nickel.—Dimethylglyoxime precipitation.

Copper.—Electrolytically.

Aluminium and Titanium

Removal of chromium with potassium chlorate also most of nickel and cobalt with ammonium chloride additions. Precipitation with ammonia. Caustic soda precipitation of titanium from hydrochloric acid solutions.

Aluminium in the filtrate.

Precipitation either as phosphate or with 8-hydroxyquinoline from sulphuric acid solutions.

Titanium precipitation as above with iron and aluminium, redissolve in hydrochloric, add sulphuric acid (10 ml.) and take to fumes, finish colorimetrically.

Columbium and Tantalum

Removal of tungsten if present—tannin separation of columbium and tantalum.

Cast Irons

Silicon.—Nitro-sulphuric attack, Ni in filtrate. With austenitic cast irons omit the 4–5 ml. nitric acid (conc.) until the steel is dissolved. Do not bake too strongly on account of high chromium.

Sulphur.—Molybdenum free cast iron, evolution method or combustion.

Carbon and graphite.—On 1 g sample.

Phosphorus.—As in ordinary steels, filter off graphite—austenitic cast iron, as for stainless steels.

Manganese.—Persulphate method after removal of graphitic C. Austenitic cast irons, chlorate method.

Chromium.—0·5 g sample for high chromium cast iron. Others 2 g sample with removal of graphitic C.

Molybdenum.—All types, butyl acetate or α-benzoin oxime. Above 0·8% use 0·05 g sample for the butyl acetate method.

Aluminium.—$AlPO_4$ precipitation after removal of silicon and graphite, or 8-hydroxyquinoline precipitation.

ARSENIC

Determination of Arsenic. Hypophosphite reduction

Weak iodine as used for sulphur estimation

3·959 g iodine and 3 g potassium iodide dissolved in 10–20 ml. cold water make up to 1 litre with cold water.

1 ml. = 0·00116 g As.

Sodium arsenite

1·543 g arsenious oxide and 2 g sodium bicarbonate dissolved in water.

Make up to 1 litre.

If 0·01 N solutions are required :

Weigh out 1·2692 g iodine and 0·4948 g arsenious oxide.

1 ml. = 0·0006 g As.

For samples containing low chromium.—Weigh out 5 g sample into 400 ml. squat beaker and add 0·5 g electrolytic copper, 25 ml. sulphuric acid (30%) and 15 ml. nitric acid (conc.). Digest until all the steel has been dissolved, then dilute and filter, the residue being washed with dilute 2% sulphuric acid, and discarded.

Add 5 ml. potassium permanganate (10 g per litre) and boil the mixture well.

5 ml. saturated sulphurous acid are then added and the solution taken to dryness on the hot plate, heating being continued until all nitric acid is removed. Remove from the plate, cool and add 75 ml. water.

Precipitation of the arsenic.—The contents of the beaker are poured into a 750 ml. conical flask and the beaker rinsed out with 75 ml. hydrochloric acid (conc.). 12 g sodium hypophosphite are added and the mouth of the flask fitted with a cork carrying a reflux condenser.

The flask is then placed on a tripod over a burner and the solution boiled vigorously, to cause steam to issue from the top of the tube, the flask and contents are then cooled under running water. Arsenic is not precipitated unless hydrochloric acid is present in the proportion 1 : 2.

With lesser concentrations copper, bismuth, etc., are precipitated.

Filtration of the precipitate.—Macerate a filter paper with a mixture of 1 part of a saturated solution of bromine in hydrochloric acid (conc.) and 7 parts of water.

When sufficiently disintegrated the mixture is heated on the steam bath for 30 minutes and diluted with an equal volume of water, shaken and bottled.

A filter pad is made of this pulp in the usual way and washed 5 times with water (when it should be quite white).

The arsenic precipitate is filtered on to this pad, washed with 100 ml. hydrochloric acid (30%) followed by 2% ammonium chloride solution.

The filter and arsenic precipitate are transferred to a 800 ml. tall beaker and the funnel well washed.

Add to the filter a little freshly made cold starch solution followed by 100 ml. cold water. Run in from a burette a measured excess of standard iodine solution and allow to stand for a few minutes.

The mixture is then diluted to 250 ml. with cold water, 2 g sodium bicarbonate added and the solution titrated with standard sodium arsenite solution until a fading of the blue colour is observed.

Further additions of sodium arsenite may be made followed by a further 2 g of sodium bicarbonate. (Sodium bicarbonate is necessary to neutralize all the hydriodic acid liberated thus preventing the former reaction taking place in the reverse direction.)

The mixture is well shaken and allowed to stand for a few minutes until the blue colour is discharged.

The titration is completed by the addition of standard iodine with vigorous shaking until a sharp end-point is observed.

The iodine equivalent is obtained by subtracting the volume of sodium arsenite from the standard iodine used.

ALUMINIUM

Determination of Aluminium in Steels and Cast Iron containing up to 1% Aluminium and Low Chromium

Digest 2 to 5 g of drillings in 70 ml. hydrochloric acid (sp. gr. 1 : 16). When completely dissolved oxidize with dropwise addition of nitric acid. Take down to baking on the hot plate to remove nitric acid.

Redissolve in 50 ml. hydrochloric acid. Filter off silicon and ignite in a platinum dish, then add one or two drops of sulphuric acid (conc.) followed by 2 ml. hydrofluoric acid. Evaporate

to fumes, cool, dilute with water to take any salts in solution and add to main filtrate.

Dilute main filtrate to 300 ml., add 1 g ammonium phosphate followed by ammonium hydrate until a faint permanent precipitate appears; faint acidity is restored by 2 or 3 drops 5% sulphuric acid. 15 ml. sulphurous acid are now added together with 10 ml. glacial acetic acid.

The solution is now boiled when 10 g sodium thiosulphate are added, and the boiling continued for 30 minutes keeping bulk up. Allow the precipitate to settle thoroughly, filter through ashless paper pulp (Whatman No. 30) washing thoroughly alternately with hot water and hot 2% ammonium acetate. Ignite in a platinum crucible to constant weight.

Fusion with sodium carbonate.—The ignited residue is fused with 3 g sodium carbonate for about 10 minutes, extracted with hot water, filtered through an ashless pad and well washed with hot water. This will remove any trace of iron. Place on the filter pump and transfer the small precipitate of iron to a crucible and ignite to Fe_2O_3. Deduct this from the weight of aluminium phosphate.

The alkaline filtrate is made acid with hydrochloric acid (sp. gr. 1 : 16) boiled well and a few drops of methyl red added. 0·50 g ammonium phosphate are then added and the solution made alkaline with careful additions of ammonia.

Two or three drops of hydrochloric acid (conc.) are added to restore acidity, the solution is again boiled, and 20 ml. of ammonium acetate added and boiling continued for 15 minutes.

Allow to settle on the edge of the hot plate and filter through an ashless Whatman No. 30 pulp pad, washing well with hot 2% ammonium acetate.

The aluminium phosphate precipitate is ignited slowly at first and finally at 1000° C. to constant weight.

Aluminium phosphate contains 22·11% aluminium.

Interfering elements.—Tungsten. High chromium. High nickel and vanadium, also earth acids.

Tungsten can be removed in the ordinary way after oxidation with nitric acid (sp. gr. 1·42) and digestion—see under that element.

For small amounts of tungsten use cinchonine precipitation.

For high chromium use the caustic soda separation.

Vanadium will be precipitated as phosphate, so redissolve precipitate in hydrochloric acid and add hydrogen peroxide to convert the vanadium to pervanadate. Then continuing the reprecipitation with ammonia and thiosulphate.

Ammonium acetate.—Mix 488 ml. glacial acetic with 500 ml. cold water, add 400 ml. ammonia (sp. gr. 88) make up to 2½ litres.

Determination of Aluminium for Cast Iron and Steels High in Chromium

Weigh out 2 g steel, and digest in 75 ml. hydrochloric acid (sp. gr. 1·16). When completely dissolved oxidize with nitric acid (sp. gr. 1·42) and boil off nitric fumes.

Take slowly to dryness to remove nitric acid, then add 10 ml. hydrochloric acid (sp. gr. 1·16) and take salts into solution. Dilute to 50 ml. and filter washing with hot water.

Ignite the filter paper, transfer to platinum and treat with sulphuric acid 1 drop and 2 or 3 drops hydrofluoric acid.

This residue is then fused with sodium carbonate, extracted with hot water and the iron removed by filtration. The filtrate is added to the main filtrate.

The filtrate after removal of silica is transferred to a separating funnel. This solution is immediately run into hot caustic soda (containing 20 g approx. in about 300 ml. hot water) and the solution continually agitated.

The mixture is then boiled well for a few minutes, allowed to settle and filtered through a hardened filter paper, washing with 1% caustic soda solution. If more than 1% aluminium be present it is usual to dissolve the precipitate in hydrochloric acid, and reprecipitate with sodium hydrate and again filter as before.

The filtrates being then combined, acidify the filtrate with hydrochloric acid (sp. gr. 1·16) using a few drops of methyl red as indicator. Boil well and make faintly alkaline with ammonia (1 : 1).

The pink colour of the solution is restored by the addition of 5% hydrochloric acid added drop by drop. This is then heated to boiling and 20 ml. ammonium acetate added, and boiling continued for 5 minutes.

The precipitate is filtered through ashless paper, Whatman No. 30, and washed with hot water. This is then redissolved through the paper with hot hydrochloric acid (1 : 1) and 20 ml. sodium phosphate (10%) added to the extract, the latter is diluted to 300 ml. with water, adjusted to faint acidity with ammonia and heated to boiling. 10 g of sodium thiosulphate are added and the boiling continued for 20 minutes.

The precipitated aluminium phosphate is filtered through ashless paper, Whatman No. 31, and washed with hot water. It is then ignited to aluminium phosphate containing 22·11% aluminium.

Determination of Aluminium in High Nickel Chromium Iron Alloys, with or without Cobalt

Dissolve 1 g sample in 50 ml. water and 10 ml. H_2SO_4 (conc.). When thoroughly broken up, dilute to 100 ml. and oxidize with 6 g potassium chlorate. Take down to low bulk (about 10 ml.), or until crystals begin to separate out.

Dilute to 300 ml. with hot water and cool slightly to 50° C. and add ammonium hydroxide until precipitate dissolves with difficulty when addition of 10 g ammonium chloride is made. Continue the addition of ammonium hydroxide until a permanent precipitate is formed, or until the solution smells of ammonia. Digest on the corner of the plate for at least one hour.

Cool slightly and filter through a large Whatman No. 31, 18·5 cm. filter paper, washing well with hot water to remove nickel and chromium salts. Discard filtrate. The precipitate is then dissolved through the paper into the original beaker by means of hot dilute hydrochloric acid, the paper being washed thoroughly with hot water. The filter paper is ignited at a low temperature in a platinum crucible, potassium bisulphate added and fused over a burner for a few minutes.

The melt is extracted in the solution of HCl containing the iron aluminium and titanium, 2 or 3 ml. of nitric added, also a few ml. sulphurous acid ; boil for a few minutes, and the whole filtered through a No. 31 paper plug, well wash with hot water and dilute HCl to remove silica.

The HCl solution is boiled down, cooled and 10% sodium hydrate added until almost neutral—this is then transferred to a tap funnel and run in a rapid stream of drops into 100 ml. 10% solution sodium hydrate (hot). Make up to 500 ml. the clear filtrate containing the aluminium from 1 g sample. Acidify the solution with HCl using methyl orange as indicator, add sodium phosphate and acetic acid, and precipitate the aluminium with sodium thiosulphate in the usual manner.

Filter, wash and weigh as $AlPO_4$ containing 22·11% aluminium.

This method can be used with a high nickel, chromium, aluminium titanium standard steel with satisfactory results.

8-Hydroxy-quinoline Precipitation

8-Hydroxy-quinoline 10% alcoholic solution

Dissolve 10 g of reagent in 100 ml. alcohol.

8-Hydroxy-quinoline 2% acetic acid solution

Dissolve 10 g of reagent in 180 ml. of acetic acid, add ammonia to faint turbidity. Filter and dilute to 500 ml.

For nickel-chromium steels and steels containing not more than 1% chromium.

Weigh out 1–2 g sample into a 750 ml. flask and dissolve in 50 ml. sulphuric acid (1 in 7). When completely dissolved, oxidize with nitric acid (conc.) and take down to fumes of sulphur trioxide.

Cool. Dilute with 200 ml. hot water taking all salts into solution—filter and wash 2 or 3 times with hot water. Reserve filtrate. Ignite the filter paper and residue and treat with sulphuric and hydrofluoric acid.

Fuse with 2 g potassium bisulphate and extract in reserve filtrate.

Heat to boiling and add 3 g ammonium persulphate, boil to destroy excess persulphate. Cool the solution, add 20 g tartaric acid, followed by ammonium hydroxide (sp. gr. 0·880) in slight excess, using litmus paper as indicator. After addition of 10/15 g potassium cyanide AR (to keep all the nickel in solution as the double cyanide), heat to boiling, add 0·5 g sodium sulphite, and digest for 20 minutes.

Cool and filter through a paper pad, Whatman No. 31, washing with 5% ammonium chloride solution.

First Precipitation of the Aluminium Complex

To the filtrate add 10/20 ml. of 8-hydroxyquinoline alcoholic solution and stir vigorously. Heat to 60 °C.—allow to stand for 20 minutes. Filter through a Whatman paper No. 31 pad, washing with warm water.

Dissolve the precipitate from the pad with hot hydrochloric acid into the original beaker, again washing with hot 5% hydrochloric acid. Add 7 ml. sulphuric acid (conc.), evaporate to fumes adding nitric acid additions until the solution is clear, again taking to fumes.

Remove from the plate and cool, dissolve salts in 150 ml. of hot water and boil clear.

Second precipitation of aluminium hydroxyquinoline complex

To the cool solution add 20 g tartaric acid and make just alkaline with ammonia (sp. gr. 0·880), adding a slight excess, followed by 3 g potassium cyanide (AR). Heat to boiling, add 2 or 3 drops methyl red and make faintly acid with acetic acid, dilute to 250 ml. reprecipitating the aluminium as before with 25 ml. 8-hydroxyquinoline acetic acid solution (2% strength), followed by 50 ml. ammonium acetate (25%). Stand the flask containing the precipitate on the edge of the hot plate at 60° C. for 20 minutes with stirring.

Filter on a weighed sintered glass crucible of porosity 4 washing with warm water at 50° C. After drying at 110° C. for at least 2 hours, cool and weigh until constant weight is obtained.

$$\text{Aluminium } \% = \frac{\textit{weight of aluminium complex} \times 5{\cdot}87}{\textit{weight of sample}}.$$

Note: The aluminium complex may be collected on an ashless filter paper, washing well with warm water. Transfer to a crucible and dry. Cover with a little oxalic acid and ignite, gently at first and then strongly at 1000° C. Weigh as Al_2O_3 containing 52·91% Al. The ash should be quite white.

Tungsten, if present, must be removed. For this the steel must be dissolved in hydrochloric acid (conc.) and be oxidized with nitric acid (conc.), taken down to 10–15 ml. and diluted with hot water—filter and remove.

7 ml. sulphuric (conc.) should be added to the filtrate and taken to fumes.* Carry on as in above method.

If manganese is precipitated by persulphate addition, clear with drops of 10% HCl or remove by filtering.

* Titanium can be separated by cupferron at this stage from dilute sulphuric acid solution.

CARBON

Estimation of Carbon by Colour

Standard and steel have to be of similar composition and have been subjected to similar heat treatment.

Other points to be noted are :

1. The colour is the darker the more rapidly the sample is dissolved and is bleached by daylight.

2. In hardened steel there exists a form of carbon which produces no colour. The colour varies with the form in which the carbon exists in the steel: annealed steel gives a somewhat different tint from that obtained by the same steel in a normal state, although in both cases the carbon exists in combination with the iron.

Hardened steel in which comparatively little carbide of iron is present, yields a much lighter colour than that obtained from the normal steel.

As example a mild steel of 0·3%C will give in the hardened condition approximately 0·24%.

3. Colour is destroyed by continual heating.

4. Interference of nickel, chromium, copper and molybdenum.

Weigh out into test tubes the same weight of the steel and of a standard of approximately the same carbon content. For ordinary steels usual to take 0·1 g sample but for a high carbon steel 0·05 g sample.

Add nitric acid (sp. gr. 1·2) 3–5 ml. slowly at first to prevent a violent reaction. The reaction is considered to be completed when there are no bubbles present, and the brownish flocculent matter is dissolved.

Place in bath of boiling water with occasional shaking to destroy gas bubbles. Usual time 20–30 minutes. 20 minutes for an ordinary low carbon steel and 30 minutes in the case of a high carbon steel.

Remove from plate and cool.

Sometimes with high carbon steels a slight black residue of graphite is left—this must be filtered off before making the comparison.

The colours are compared in matched Eggertz tubes and the necessary dilutions made so as to match in the ordinary way.

Graphitic Carbon in Cast Iron and Pig Iron

Weigh out carefully 1 g cast iron. Transfer to 350 ml. conical beaker. Dissolve in 50 ml. HNO_3 (sp. gr. 1·2) as quickly as possible, taking care not to boil vigorously, thus allowing the solution to become too concentrated and avoiding the precipitation of gelatinous SiO_2 causing delay in filtering.

When all the iron is taken into solution remove from the plate, rinse down the sides of the beaker with hot water. Filter through an asbestos pad or Gooch crucible, the asbestos being previously ignited and washed before use. The precipitated graphite must be well washed with hot water also hot 10% hydrochloric acid followed by hot water. If graphite tends to filter slowly add 2 or 3 drops of hydrofluoric acid to the solution. Dilute caustic soda (10% strength) is used to remove last traces of silica—the final washings being hot 10% hydrochloric acid to remove iron salts and hot water until acid free.

Dry crucible in air bath at 100° C. until constant weight—cool and weigh.

Ignite in muffle. Loss in weight gives weight of graphite.

It is usual to transfer the thoroughly washed precipitate of graphite to a clean freshly ignited combustion boat. Dry at 100° C. and burn off in a stream of oxygen. The CO_2 is absorbed in soda lime.

$$\text{Weight of } CO_2 \times 0{\cdot}2727 \times 100 = \% \text{ graphitic C.}$$

Wet combustion method. Total carbon

This method is especially useful for very heavy drillings, armour plate clippings, etc., when difficulties would be experienced with direct combustion.

The solution of copper ammonium chloride is made as follows :

250 g cuprous ammonium chloride dissolved in 1 litre of water. Filter for use.

Take 2·727 g of drillings. Cover with 100 ml. of cupric ammonium solution.

Allow to stand for several hours in a warm place at temperature 80–90° C. with frequent agitation.

During the operation metallic copper will be seen to separate, but will gradually pass into solution. Add 20 ml. HCl and heat (the most satisfactory temperature is 80–90° C.), to dissolve any copper. Dilute with hot water and filter through asbestos fibre washing with hot water and weak dilute HCl. Finally twice with hot water.

Transfer to clean freshly ignited combustion boat. Dry at 100° C. and finish by the dry combustion process.

With high carbon austenitic nickel chromium iron and cobalt alloys cover the asbestos containing the carbon mostly in the form of carbide with 2 g preheated red lead.

Total Carbon in Iron and Steel

The recommended method is by direct combustion which is carried out as follows :

The steel is burned in a refractory boat in a current of oxygen and the resultant CO_2 absorbed in a weighed tube containing soda lime, soda asbestos or similar absorbent. The oxygen is passed through a 50% sulphuric acid solution in which chromic acid has been dissolved, and then soda lime or soda asbestos before entering the furnace. As the whole of the carbon may not be burnt to CO_2 and as the sulphur is only burnt to SO_2 the exit end has a plug of platinized asbestos, which acts as a catalyst to complete the oxidation.

The gases are passed through one or two gas-washing bottles containing the sulphuric acid–chromic acid solution before being absorbed in the soda lime. The furnace may be of any type, and containing a single tube open at each end, or a single tube closed at one end, electrically heated running at 100–110 volts and 6–8 amps is found to be most suitable.

Combustion tube of Morgan ($\triangle$H) 26 inches long $\times$ $\frac{7}{8}$ inches internal diameter, capable of withstanding a temperature of 1200° C. and packed at the exit end with a plug of platinized asbestos.

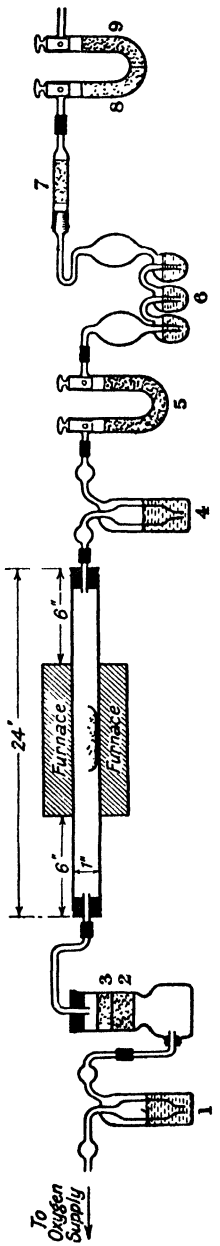


FIGURE 6. Combustion apparatus for total carbon in steel.
1, Concentrated H_2SO_4. 2, Soda asbestos. 3, Dry $CaCl_2$. 4, Saturated CrO_3 in 1 : 1 H_2SO_4. 5, Dry $CaCl_2$.
6, 40 per cent. KOH (or soda asbestos in a Nesbitt bulb) 7, Dry $CaCl_2$ (very fine mesh). 8, Dry $CaCl_2$.
9, Soda asbestos.

With the closed end type of furnace the inner and outer tubes are silica. The life of the combustion tube is impaired by the splashing of the iron and lead oxide, and may be improved by the use of sheet nickel covering in the heating zone.

With the single tube closed and rounded at one end, protection is afforded by burning the sample in a thick walled silica inner tube, thus giving to the outer silica tube considerable increase in life. With this combustion tube temperature should be maintained 900–950° C. and be capable of reaching to 1200° C.

The apparatus should be carefully tested for air leaks. (Fig. 6)

Procedure.—Weigh 2·727 g of the sample into combustion boat (1 g for cast iron previously ground, if necessary). Cover with a little red lead which has been preheated to remove any carbonaceous matter, and place the boat into the hot zone of the furnace.

Connect the weighed soda lime tube and insert the bung. Pass a slow stream of oxygen for 15–30 seconds and then shut the oxygen off. When combustion commences (this is observed by noting the sucking up of the chromic sulphuric acid in the centre tube), the oxygen is turned on and the supply increased to maintain a slow bubbling through the gas bottles.

When the gas flow increases to a rush, the oxygen is gradually diminished until a uniform steady flow.

The rush indicates completion of combustion. Continue passing the oxygen for 18–20 minutes. Disconnect the soda lime tubes

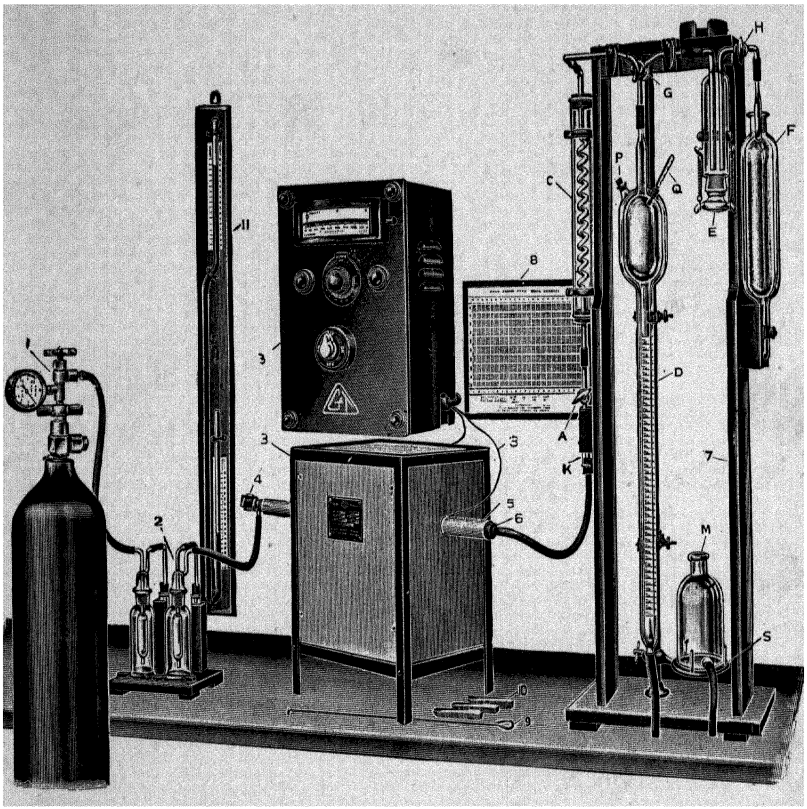


FIGURE 7. Complete combustion and absorption train (Griffin and Tatlock Ltd.).

[*Facing p.* 419

and reweigh. The increase in weight in milligrams × 10 = % carbon.

It is usual to cover the ends of the soda lime tubes with rubber policeman tips for weighing and when not in use.

Notes:

(1) For cast irons and other high carbon irons, use only 1 g of sample and multiply result by 27·27 instead of 10.

(2) The soda lime tube bulb is filled with freshly dried calcium chloride, kept in place with cotton wool plugs.

(3) The soda lime is bought in the 10–14 mesh grade. Add about 0·5 g of phenolphthalein powder to 500 g of soda lime. Grind and mix slowly and thoroughly until the mixture turns pink. This indicates sufficient moisture to ensure perfect absorption. As the tube becomes 'neutralized' the pink colour changes to a dark red.

(4) With 'chunky' samples and some of the high nickel steels, it is advisable to mix a low carbon standard steel to initiate the combustion. The carbon in this standard is deducted from the result.

(5) In some extreme cases note (4) will not suffice. In these cases 2·727 g of steel are digested in a strong solution of copper ammonium chloride. The solution is filtered through a fine, well-ignited asbestos pad. The beaker is well cleared with a policeman and all solids rinsed on to the pad. Wash well with cold dilute HCl and cold water. Transfer the asbestos pad to a combustion boat and thoroughly clear the funnel with asbestos pulp, adding this to the boat. Dry thoroughly and proceed as in ordinary carbon. *It is not necessary* to observe the burning instructions and it is only necessary to keep the steady flow of oxygen, there being no steel to burn and use up oxygen.

Operation of Strohlein Apparatus (Fig. 7)

Furnace temperature range 1000 to 1500° C. by pyrometer (low temperatures have given low results).

Solutions in the absorption apparatus

Levelling bottles.—10% sodium chloride solution, acidified with sulphuric acid and coloured with a little litmus solution to make easy reading. (Does not dissolve CO_2.)

Absorption vessel.—Is filled with potassium hydroxide, *the U tube* is filled with lumps of chromic acid to eliminate any sulphur.

After the apparatus has been filled with oxygen, two taps at the top of the Strohlein are turned on and the gas expelled into the air. The apparatus is then ready for use. The oxygen is left just bubbling through the tube and a boat with one gram sample is

pushed into the tube to about the middle of furnace. The rubber stopper at the end of the tube is quickly inserted and the oxygen turned on again. The rate used is a fast stream of bubbles through the washing bottle and the process of the reaction can be observed from the rate of descent of the liquid in the measuring tube. Reaction generally takes about 2 minutes and it will be noticed that the level in the measuring cylinder starts falling and then slows right up during reaction. When it speeds up again, the reaction is nearly over, and gas is passed until the measuring burette has been nearly filled. The tap at the top of the burette is closed to shut off any further oxygen. Levels are then adjusted in the normal way and the sliding scale adjusted so that the zero mark coincides with the bottom of the meniscus. The tap is then turned to communicate with the absorption vessel and the contents of the measuring cylinder are passed over twice into the absorption burette and then back again. It will be found that the non-return valves at the top of the measuring cylinder and the absorption vessel allow exceptionally quick operation. It is necessary to watch for any bubbles being left in the valve part of the absorption vessel. If there are, a few ml. of gas must be passed backwards and forwards two or three times when the bubbles will automatically clear and pass back into the measuring cylinder again. The levels are adjusted and the percentage of C in the steel is read off directly on to the scale to the third place of decimals.

If there is the slightest doubt as to whether all the carbon has been taken up, the gas in the measuring cylinder may be run off to the open air through the two taps and fresh oxygen passed through the furnace into the measuring cylinder and absorbed and treated in the usual way. Any C which is unoxidized during the previous experiment will be shown up on the figures and the percentage can be added directly to that obtained in the first experiment. This procedure is only necessary when some of the more difficult oxidizable materials are being treated.

A layer of red lead is spread over the sample in the boat to prevent the formation of an inert crust.

A correction table is supplied with the instrument. This gives correction according to the barometric pressures and temperatures of the measured gases. The temperature is taken from the thermometer which is inserted in the top of the measuring cylinder, and it will be found if the instrument is working steadily that the temperature will rise slowly and steadily. With the aid of the correction chart a complete day's working may be put through continuously and the necessary corrections applied.

A complete estimation can be made in about 7 minutes.

The normal burette reads directly from 0 to 1·5% C when 1 g of sample is taken.

For higher carbons a smaller sample is taken. For very low carbons, i.e. 0·05%, etc., a special micro burette can be obtained.

Most suitable for furnace stage work, where time factor is of considerable importance.

For this a rapid ignition at 1050° C. for 6–7 minutes, the volume of CO_2 is then collected and measured.

Life of tube 200–300 determinations.

COBALT

Gravimetric methods

Separation of cobalt from iron. For all steels and amounts of cobalt.

Basic Acetate Separation

2 g steel dissolved in 75 ml. hydrochloric acid. Digest thoroughly until all carbides are broken up, which may take at least one day or even a longer period. Cautiously oxidize with a few drops of conc. nitric acid, adding a few more drops in excess. Keep on the boil with further additions of hydrochloric acid until the separated tungstic oxide is quite yellow. Take down to dryness and redissolve in a little HCl—about 15 ml. (not necessary if silicon is not to be determined). Dilute to 250 ml. with hot water and allow to stand about 3 hours until cold. Filter off tungstic oxide, washing with a little hot water containing a few drops of hydrochloric and nitric acid (*a*).

To the filtrate containing all the iron, nickel,* manganese and cobalt, neutralize with ammonium hydrate finishing with ammonium carbonate until a precipitate is just produced. Clear by adding hydrochloric a few drops at a time, with frequent shaking and allowing to stand 5 minutes after each addition; finally add 6 drops in excess. Add 5 g ammonium chloride, exactly as in the case of manganese and nickel, this will prevent absorption. Bring to the boil. At about 70° C. a precipitate should come down.

Add 3 ml. ammonium acetate to complete hydrolysis (15–20 ml. is permitted in the case of manganese but not in the case of nickel or cobalt).

For nickel and cobalt. The amount of ammonium acetate is important; excess of it should be avoided; it is unnecessary and further, the hydrolysis temperature of nickel and cobalt is about 170° C. The presence of excess of ammonium acetate may thus

* See Mn when V present.

tend to bring down the hydrolysis temperature to the boiling point of water, and some nickel and cobalt would be precipitated.

Make up to the mark in a 500 ml. graduated flask with boiling water, allowing 5 ml. correction for volume of precipitate and temperature. Mix well and filter through dry paper. Collect 250 ml. clear pink cobalt acetate solution containing the cobalt from 1 g steel by filtering into graduated flask.

Note: With steels and alloys containing high nickel contents the clear pink colour of the cobalt acetate will be entirely hidden by the green colour of the nickel.

Zinc Oxide Separation.

Treat as above to (*a*).

Neutralize filtrate with ammonia and cool, finishing with sodium carbonate until a permanent precipitate has just been obtained. Redissolve in a few drops of hydrochloric acid with repeated shaking, adding 4 or 5 drops in excess. Add 5 g ammonium chloride followed by an emulsion of zinc oxide (1 g to 1 g steel). Shake well, to complete precipitation (avoid using excess of zinc oxide), transfer to 500 ml. graduated flask, make up to the mark with cold water, allow 3 ml for precipitate, and filter. Solution will contain cobalt present in 1 g steel.

Note: It is suggested by various authorities that owing to absorption of cobalt by the precipitated iron, two zinc oxide separations are necessary. It should be pointed out that if the preliminary 'neutralization' be carried out to its limit, short of a permanent precipitation and then an addition of 5 to 10 g of ammonium chloride is made before the zinc oxide emulsion is added, a complete separation of the cobalt is possible. A minimum of zinc oxide must be used, however.

The steel could, with advantage, also be dissolved in sulphuric acid oxidized with nitric acid, taken down to about 10 ml. and diluted with 200 ml. hot water.

All tungstic acid, if present, must be filtered off, the solution neutralized with sodium carbonate and carried through as in above method.

After either of the above separations, finish by the following method :

(1) Precipitation in dilute HCl solution with alpha-nitroso-beta naphthol.

To the filtrate containing the cobalt in 1 g steel, add 3 ml. hydrochloric acid and heat to 70° C.

The reagent is made by dissolving 2 g alpha-nitroso-beta naphthol in 75 ml. glacial acid and 75 ml. hot water. Bring to the

boil and filter if necessary. For each milligram of cobalt, add 1·5 ml. of this reagent. Digest at 70° C. for half an hour. The dark red voluminous precipitate composition $Co(C_{10}H_6NO.O)_3$ is filtered off, washed with hot 2% HCl and hot water, ignited at 800–850° C. to black cobalt oxide.

Co_3O_4 contains 73·44% cobalt.

Note: When nickel predominates over cobalt, or a considerable quantity of it is present, the precipitate should be ignited, dissolved in HCl and re-precipitated.

If the filtrate has been taken from the basic acetate separation it is usual to dissolve Co_3O_4 in HCl, and when completely dissolved oxidize with nitric acid.

Precipitate any iron present with ammonium chloride and ammonia. Digest for half an hour and filter off ferric hydrate and any trace of chromium present. Ignite precipitate to Fe_2O_3, and Cr_2O_3, deduct from weight of Co_3O_4. This should not be more than 1 or 2 milligrams.

Colorimetric Estimations of Cobalt

The oxide, after the usual ignition, is dissolved in a few ml. nitric acid (sp. gr. 1·2) and the solution made alkaline with ammonia. 2 or 3 ml. of 1% potassium ferricyanide solution are added, resulting in an intense pink colour due to the formation of the cobalt amine ferricyanide. The intensity of this colour is compared with that obtained by one similarly treated containing a known amount of standard cobalt solution.

[0·6 g cobalt ammonium sulphate/litre : 1 ml. = 0·0001 g Co.]

CHROMIUM

Estimation of Chromium. 'Vignal' Method

For all chromium steels and high-speed steels containing tungsten.

Method.—Dissolve 2 g of drillings (for stainless and high chromium steels above 10% chromium use 0·5 g sample) in 70 ml. 10% sulphuric acid.

When completely dissolved oxidize with nitric acid (sp. gr. 1·42) a few drops at a time until completely oxidized, then boil off the brown fumes (1).

When all carbides have been taken into solution (usually necessary to destroy these by fuming *not* too strongly to avoid the

formation of insoluble chromic sulphate which is difficult to dissolve) dilute with hot water to 300 ml. and bring to the boil, adding 2 or 3 small pieces of broken porcelain to stop bumping.

Oxidize the chromium by adding a 3% solution of potassium permanganate until a permanent pink colour persists, adding further small additions of permanganate if necessary.

Remove from the plate. A few crystals of manganous sulphate are then added and the solution boiled for a further 10 minutes to ensure the complete precipitation of undecomposed potassium permanganate which is converted into hydrated dioxide of manganese, thus :

$$2KMnO_4 + 3MnSO_4 + 7H_2SO_4 = K_2SO_4 + 2H_2SO_4 + 5MnO_2H_2O.$$

Remove from the plate, cool and filter through a No. 31 pulp filter pad, washing 6 or 7 times with cold water.

Titrate by adding an excess of weak ferrous ammonium sulphate from burette. Add 10 ml. syrupy phosphoric acid to decolorize the iron. Titrate excess of ferrous ammonium sulphate with weak potassium permanganate 0·173 N, shaking well, until 1 drop gives permanent pink.

1 ml. = 0·05% Cr on 2 g sample.

Titrate with 0·1 N ferrous ammonium sulphate and permanganate for high chromium steels.

1 ml. = 0·3466 % Cr on 0·5 g sample.

(2) For high-speed tungsten steels on 1 g sample.

1 ml. of 0·1 N standard ferrous ammonium sulphate and permanganate = 0·001733 g Cr

(1) For high chromium steels and alloys, do not oxidize before the steel is thoroughly dissolved, otherwise a coating of silica will be formed round the steel and it will become passive.

(2) With high-speed tungsten steels, on 1 g sample, take down to sulphate fumes and redissolve in 20 ml water 2 or 3 times before oxidation with nitric acid, to break up the carbides.

Tungsten does not interfere and the yellow tungstic oxide can remain in the solution during the oxidation in boiling solution of the chromium with permanganate.

(3) A definite excess of ferrous ammonium sulphate must be used for titration.

If vanadium is present a disappearing end-point will be noticed.

The actual end-point of the chromium titration however is obtained when two drops of the standard permanganate give a permanent pink colour on shaking and standing for one minute.

(4) *With cast irons.*—Graphite must be filtered off before oxidation with permanganate.

Estimation of Chromium

Persulphate Method.—This is a very satisfactory method for most steels, and has the advantage in the ordinary low chromium steels, of the estimation of chromium and manganese together.

With tungsten steels, after oxidation with nitric acid and dilution with hot water, the yellow tungstic oxide is filtered off before proceeding with the above method.

After dilution and before oxidation with persulphate, especially if the manganese is low, add 5 ml. 0·1 N potassium permanganate —bring to the boil and remove any pink colour before addition of ammonium persulphate. This modification is necessary for high chromium steel, because using a smaller weight of sample the manganese content is so small.

Titration should be conducted in exactly the same manner as in the preceding method using weak or 0·1 N ferrous ammonium sulphate with external indicator potassium ferricyanide, or internally with diphenylamine sodium sulphonate as indicator when vanadium is present.

With steels of high carbon and chromium contents, the complete decomposition of carbides must be ensured by evaporation to fumes before oxidation with nitric acid.

For details of the method see under 'Manganese'.

Additions of ammonium persulphate are :

8 g are used for a 15% chromium
12 g are used for a 23% chromium

COLUMBIUM AND TANTALUM

Determination of Columbium and Tantalum in Steel : with or without Tungsten

2–5 g steel dissolved in 50 ml. hydrochloric acid and the mixture thoroughly boiled. Nitric acid (sp. gr. 1·42) is then added a few ml. at a time to complete oxidation. After cooling 25 ml. perchloric acid (sp. gr. 1·12) are added cautiously.

The cover is replaced and the mixture evaporated to fumes, with the beaker covered to avoid any loss in perchloric acid. The residue is leached with hydrochloric acid (sp. gr. 1·16), taken down to 15 ml., diluted with hot water and allowed to stand 2 or 3 hours (preferably overnight).

The solution is then filtered, washing with dilute hydrochloric acid (1 : 9) the precipitate being collected on ashless pulp and after well washing, ignited in a weighed platinum crucible.

The ignited residue is weighed, treated with sulphuric acid and H.F., dried, re-ignited, and again weighed.

Increase in crucible weight gives Cb_2O_5 and/or Ta_2O_5 and WO_3.

For steel containing tungsten

The mixed oxides are fused with 4 g potassium carbonate in a platinum crucible. The fused mass is lixiviated with 200 ml. hot water, care being taken to break down any lumps.

The crucible is rinsed and discarded, and the hot solution treated with a freshly prepared solution containing 1 g crystalline magnesium sulphate, 2 g ammonium chloride, 25 ml. water and 4 drops ammonia (conc.).

The covered beaker is placed in a water bath for one hour. The flocculent precipitate is collected on ashless filter paper and washed with 25% saturated ammonium chloride—the filtrate is taken for W determination and the precipitate taken for columbium.

Determination of columbium

The precipitate is washed back, with the same wash liquor, into the original beaker, and the washed filter paper placed in the platinum crucible intended for the ignition of the tannin precipitate (TP[1]).

The suspension of the magnesia precipitate in a bulk of 150 ml. is acidified with HCl and digested on the water bath for 1 hour.

An equal volume of a saturated solution of ammonium chloride is added and the mixture is adjusted with ammonia to faint acidity to litmus.

The solution is now treated with 2 g ammonium acetate, heated to boiling, and a freshly prepared tannin solution 5% is added until flocculation is complete. The precipitate (TP[1]) is allowed to settle on the water bath, collected with the aid of a gentle suction, washed with 25% saturated ammonium chloride and ignited with the filter from the magnesia precipitate.

If (TP[1]) requires further purification, it is again fused with potassium carbonate, and the operations described above repeated,

yielding a second magnesia precipitate and a filtrate which is added to the first filtrate.

The magnesium precipitate is digested with acid and again treated with tannin as for (TP^1) giving (TP^2) which is ignited, leached as usual and weighed as mixed earths.

The latter may then be separated by the oxalotartrate procedure described later.

Determination of tungsten

The filtrate from the magnesia precipitate is adjusted by dropwise addition of HCl until just colourless to phenolphthalein and is treated with a freshly prepared 5% solution of tannin when flocculation to a white precipitate occurs if much chloride present.

Make just acid with HCl. The liquid is boiled gently for 5 minutes, during which time the precipitate darkens and flocculates; precipitation is completed by the addition of 5 ml. of 5% cinchonine hydrochloride, boiling for a further 5 minutes.

After standing overnight the precipitate is filtered off, washed with 5% ammonium chloride containing a little tannin and ignited to oxide.

Removal of tungsten from the mixed oxides.—Can also be carried through in the following manner.

Transfer the filter and precipitate to a clean (and preferably new) nickel crucible and ignite at a temperature just high enough to burn off carbonaceous matter.

Add approximately 2 g A.R. sodium hydroxide pellets to the ignited residue, then a few drops of water and dry the residue thoroughly on a hotplate. Fuse the mass gently over a small flame until a clear fusion is obtained. A final dull red heat for about 1 minute is all that is necessary. Dissolve the cold melt in 10–15 ml. of half saturated sodium chloride solution, warming gently if necessary, and allow the crucible and contents to stand in the cold for several hours or preferably overnight.

Filter the contents of the crucible on a small, tight, paper pulp pad, and wash with small portions of half saturated sodium chloride solution until the washings do not react alkaline to litmus. Place the pulp and precipitate in a small 250 ml. beaker, stir to a thin paste with water and add a few drops of hydrochloric acid. Digest on the hotplate just short of boiling until all dark particles have disappeared, adding a few more drops of hydrochloric acid if necessary. Allow the beaker to cool, then filter through a Whatman No. 541 12·5 cm. paper washing with hot 10% ammonium chloride solution.

Ignite paper and precipitate in a tared silica crucible and weigh

as mixed tantalum and columbium pentoxides. The tantalum and columbium are then separated by the fractional tannin procedure exactly as described by Schoeller, and is outlined below.

For routine work and for work in which the greatest accuracy is not required, it is sufficient only to re-treat the first mixed fraction of tantalum and columbium oxides into a further two fractions, a pure tantalum portion, the remainder being taken as columbium.

It is not recommended to determine tantalum, columbium, silicon and tungsten on the same sample. It is better to determine tungsten in a separate portion of the samples and to correct the weight of tungstic oxide from the amount of earth acids found previously.

When the two metals are present together, separation of the oxides is effected by a method which depends on the differential hydrolysis of the oxalo-tartrates of the two metals in the presence of tannin.

The principle of the method (due to Schoeller and his collaborators), is operated in the following manner.

An accurately weighed quantity (0·2–0·25 g) of the mixed oxides (5 g sample containing approximately 3% columbium will give the necessary quantity of mixed oxides), is fused with 8 g dehydrated potassium pyrosulphate in a platinum dish, the temperature being slowly raised to a bright red heat and the heat maintained until all the sulphur trioxide is expelled.

The melt is cooled and extracted in a 250 ml. conical beaker containing an aqueous solution of 3% ammonium tartrate and 4% ammonium oxalate. The dish is washed in the same solution so that the total extract is about 150 ml.

The solution is heated to boiling and whilst boiling 25 ml. of 2% aqueous tannin solution added. (A yellow precipitate may form, according to the acidity of the extract from the fusion.)

While still boiling, 50% ammonia solution is added drop by drop until a permanent flocculent yellow (Ta) precipitate forms.

The drops are continued until the reddish formation (due to Cb) produced locally round each drop disappears only slowly. In this way a yellow precipitate containing most of the tantalum is obtained. The solution is kept hot for a few minutes longer and the precipitate filtered off, using ashless filter paper, and washed thoroughly but sparingly, with hot diluted oxalate-tartrate solution.

The precipitate and paper are ignited in a platinum dish at a high temperature ; cool and weigh as Ta_2O_5 = *Residue A*.

The filtrate, which should not exceed 250 ml., is heated to boiling and a further 25 ml. tannin added.

The dropwise addition of (1 : 1) ammonia is repeated in this case

until the reddish coloration is permanent and the whole precipitate is orange red.

This is filtered off, etc., and weighed as remainder of Ta_2O_5 + some of Cb_2O_5 = *Residue B*.

This residue is reserved for further treatment.

The filtrate is again boiled and an excess of tanning solution added.

Ammonia is added until precipitation is complete, the solution then being definitely alkaline.

Tannin decomposes in alkaline solutions so that the precipitate is discoloured to a dirty brown and may even be violet.

The solution is kept hot for 1 or 2 hours on the hot plate and the precipitate then filtered off, washed, etc., as before, and weighed as Cb_2O_5 = *Residue C*.

The residue B is fused with potassium pyrosulphate and extracted in exactly the same manner as the original sample.

The extract is boiled, treated with 25 ml. tannin and then ammonia (1 : 3) added very cautiously in drops until the red (Cb) coloration produced round the drops only disappears after a time.

The precipitate, which should be quite yellow and is precipitated at boiling point, is filtered off, washed with oxalate-tartrate mixture, ignited and weighed as Ta_2O_5 = *Residue* B_1.

Columbium in the filtrate is precipitated completely as in the case of *Residue C*, the precipitate being weighed as Cb_2O_5 = *Residue* B_2.

$$\text{i.e. Total } Ta_2O_5 = (A + B_1) \times 0{\cdot}8193 = Ta$$
$$\text{Total } Cb_2O_5 = (B_2 + C) \times 0{\cdot}7000 = Cb.$$

Note: Pure Ta_2O_5 is white even when hot. Presence of Cb_2O_5 renders it a yellow colour.

Separation of Cb and Ta less difficult when Ta present in larger amounts.

The above method is satisfactory for all steels with the exception of those containing tungsten which interferes.

Cupferron Precipitation

Weigh out 2 g sample into 400 ml. beaker and dissolve in 75 ml. H_2SO_4 (1 : 4). Cool and dilute to 100 ml. Add a little paper pulp, and with constant stirring, make dropwise additions of cupferron solution (6%) until the precipitate begins to turn a reddish brown colour. (The amount of cupferron required is governed by the columbium content. Precipitation of the Cb is complete when

formation of the reddish brown compound appears.) Allow to stand for 5 minutes.

Filter the precipitate on a Whatman No. 41 paper 12·5 cm. containing a little pulp.

Wash with cold dilute sulphuric acid 5% containing 1 ml. of the reagent solution per litre, and finally wash 5 times with cold dilute ammonium hydroxide. (If tungsten molybdenum and copper are known to be absent washing with ammonia may be omitted.)

Transfer the paper and precipitate to a platinum crucible, dry and ignite at 650° C. Cool, add 1 ml. sulphuric acid (1 : 4) and 5 ml. hydrofluoric acid and evaporate to dryness.

Fuse the residue in 2 g potassium bisulphate at a low temperature, cool and extract in 150 ml. of dilute HCl (2%). Boil and allow to digest for 15 minutes. Filter on a paper pad washing with hot dilute hydrochloric acid (2%). Dry and ignite at 950° C. in a weighed platinum crucible.

$$\text{Cb}\% = \frac{\text{Wt. of } Cb_2O_5 \times 69{\cdot}9}{\text{Wt. of sample}}$$

This method is not satisfactory in the presence of tungsten, tantalum and titanium, all of which will contaminate the final residue.

COPPER

Determination of Copper

Thiosulphate precipitations for samples containing no tungsten

Digest 1–10 g of steel (according to the copper content) with 100 ml. water and 20 ml. strong H_2SO_4 and heat quietly until drillings are dissolved and decomposed.

Dilute with hot water to 350 ml. Add 20 g sodium thiosulphate. Cuprous sulphide and free S are precipitated.

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2 + S.$$

The sodium thiosulphate is thus decomposed by the sulphuric acid liberating SO_2.

Now boil until the liquid is almost clear. The residue is filtered off through pulp and thoroughly washed with hot water, dried and ignited at a low temperature (550° C. maximum). The residue contains the copper as a mixture of cupric oxide and cuprous sulphide (Cu_2S) also silicon and Fe_2O_3.

For steel containing tungsten

Transfer 5 g of drillings into a 40 ml. squat beaker. Dissolve

in 75 ml. hydrochloric acid. When completely dissolved add nitric acid (sp. gr. 1·42) in sufficient amount to complete oxidation.

Boil gently until the tungstic acid becomes quite yellow, and evaporate to low bulk.

Dilute to a 100 ml. with hot dilute hydrochloric acid (1 : 4). Allow to stand for 20–30 minutes and filter through a paper pad washing with hot dilute hydrochloric acid—5% strength.

To the filtrate add 25 ml. sulphuric acid (sp. gr. 1·84) and evaporate just to fumes of sulphur trioxide to remove nitric and hydrochloric acid. Remove from the plate and cool. Add 50 ml. of hot water and take all salts into solution, by boiling. Almost neutralize the solution by additions of ammonium hydroxide (1 : 1) to a darkening iron colour, and add 30 ml. saturated sulphurous acid and digest at incipient boiling to reduce ferric iron.

Add 20 ml. sulphuric acid 1 : 1 and dilute to 350 ml. with hot water. Boil and add 20 g sodium thiosulphate.

Boil for 15 minutes and complete the determination as described in the previous method.

Copper is then estimated in one of three ways.

(1) *Electrolytically.*—Brush the ignited residue into a small 350 ml. beaker, and decompose with 10 ml. nitric acid (sp. gr. 1·2).

Dilute to 25 ml. with hot water and filter through a small paper pad (into a 350 ml. beaker) sufficient to retain the silica. Wash well two or three times alternately with nitric acid (sp. gr. 1·2) and hot water.

Add 7 ml. sulphuric acid (conc.) ; make up to 200 ml. with water and electrolyse at 70° C. for 15–20 minutes, with a current 3–4 amps and rotating electrodes.

(2) *Colorimetric estimation.*—Dissolve the precipitate of CuO and Cu_2S in nitric acid—dilute with hot water about 5 ml.—make alkaline with ammonium hydroxide. Iron will be thrown out of solution and can be removed by filtering, through a small 31 pulp filter pad. Make the filtrate just acid again with nitric and boil down to about 15 ml.

Remove from the plate. Cool and add ammonium hydrate in excess when the blue copper salt can be compared with a standard steel or blank solution containing no copper, after additions to this sample have been made using a standard copper solution.

1 g Cu per litre
1 ml. = 0·001 g Cu.

(3) *Iodimetric titration.*—Transfer the residue from the first precipitation after ignition into a 350 ml. flask. Dissolve in

5 ml. nitric acid (sp. gr. 1·2), dilute to 30 ml. with water and add ammonium hydroxide in excess. Boil and filter, washing with hot water. Evaporate to about 5 ml. Add 2 or 3 drops ammonium hydroxide followed by 5 ml. acetic acid and about 1–3 g solid potassium iodide, according to the amount of copper present, shake well and titrate with standard sodium thiosulphate solution, using starch as indicator.

The liberated iodine is at once titrated with standard sodium thiosulphate until the brown colour of the iodine changes to pale yellow.

Starch solution is then added and the titration continued cautiously, with agitation, until the blue colour of the iodide disappears and the mixture has a pale yellowish or cream coloured tint of cuprous iodide.

The blue colour should not return on standing for several minutes.

A rapid return of the colour generally indicates

(*a*) Presence of nitrous acid.

(*b*) Presence of ferric salts.

(*c*) Undue dilation of the solution.

Weak iodine.—Dissolve exactly 1·5296 g pure potassium dichromate in water, add 15 ml. sulphuric acid (1 : 2). Cool and add this to a solution containing 15 g potassium iodide—make up to 1 litre.

Standardize against a solution of thiosulphate of similar strength.

$$1 \text{ ml.} = 0{\cdot}001983 \text{ g Cu.}$$

This is used for standardizing the thiosulphate and also for back titration.

Weak sodium thiosulphate.—Dissolve 7·7422 g pure salt in cold water and make up to 1 litre.

Standardize against electrolytically pure copper.

Note: With cast iron and stainless steels take 1 g sample, digest to completely break up the carbides which will take at least one day. Then proceed as above thiosulphate precipitation without filtering.

Precipitation as sulphide.—All silica must be removed for quantitative work, best conditions for precipitation being from acid solutions of about N or 2N strength at temperature 30–60° C.

The black sulphide of copper is digested on the edge of the plate, filtered, washed free from interfering elements, dried and ignited at a low temperature.

The residue then being redissolved in 5 ml. nitric acid and carried through as (2) or (3) above.

Copper in Mild Steel and Cast Iron

Dissolve 5 g of sample in 100 ml. HCl (50% solution). The residue from the volumetric sulphur may be used.

Boil, add zinc filings to reduce completely. Cool thoroughly, add a little zinc sulphide and shake thoroughly. Stand for 2 hours. Filter, washing with 2% cold hydrochloric acid containing a little H_2S.

Ignite in porcelain or silica crucible. Dissolve ash in a few drops conc. HNO_3 and finish off colorimetrically or by the thiosulphate titration. This is a good routine method for plain carbon steels.

LEAD

Determination of Lead in Steel

For samples of low chromium content. *Sulphate separation*

Steels containing up to 0·5% chromium.

Ammonium acetate

488 ml. glacial acetic acid.
500 ml. water.
400 ml. ammonium hydrate (sp. gr. 0·880).
Make up to 2½ litres.

Sulphuric/alcoholic wash

700 ml. water.
50 ml. sulphuric acid (sp. gr. 1·84).
100 ml. alcohol.
Dilute to 1 litre.

Digest 5 g sample in 500 ml. beaker, with 75 ml. sulphuric acid 1 : 3.

Take down to sulphur tri-oxide fumes, being careful to avoid spitting.

Cool, remove from the plate and add 100 ml. hot water and boil until all soluble salts are taken into solution.

(A) Allow to cool, adding a further 100 ml. water together with 30 ml. industrial alcohol and allow to stand for 2 or 3 hours, preferably overnight.

Filter through a Whatman 30 pulp pad washing with dilute sulphuric/alcohol solution. Dissolve the precipitate on the pad with hot ammonium acetate and wash alternately with hot water and dilute ammonium acetate.

Add 5 g tartaric acid followed by ammonium hydroxide in excess.

Dilute with hot water to 200 ml. and precipitate the lead by addition of 5–8 ml. ammonium molybdate (2% strength).

Bring to the boil and allow to stand on the edge of the hot plate for half an hour.

Filter through a Whatman No. 30 pulp pad washing with a little hot ammonium acetate (2% strength).

Transfer to porcelain crucible and ignite at a temperature not exceeding 650° C.

Cool and weigh as lead molybdate.

$$\text{Lead \%} = \text{Wt. of } \frac{\text{Lead Molybdate} \times 56{\cdot}44}{\text{Wt. of sample}}$$

Estimation of lead as sulphate can be carried through after firstly washing the sulphate of lead free from iron or until no reaction for iron is observed by the use of $K_4Fe(CN)_6$, followed by dissolving the lead sulphate on the pad with hot ammonium acetate solution.

This leaves the silica (the acetate of lead will have passed through into the filtrate). Wash well alternately with hot water and ammonium acetate. Again take to fumes to reprecipitate the lead as sulphate. When cool, add 30 ml. water and 10 ml. absolute alcohol as before.

Allow to settle, collect in a Gooch crucible previously ignited and weighed, thoroughly washing with sulphuric acid (1 : 9) and finally with dilute alcohol. Dry, ignite at a very moderate heat, and weigh as lead sulphate.

$$PbSO_4 \times 0{\cdot}6831 = Pb.$$

The lead molybdate method is preferred to that of lead sulphate, since the precipitate of lead molybdate is more easy to handle.

Samples of High Chromium Content

Weigh out 5 g sample into 650 ml. beaker. Add 50 ml. HCl. Heat until dissolved and take to dryness—avoid baking the residue.

Add 100 ml. warm water, boil clear and filter through paper pad washing well with hot water, dilute filtrate to a bulk of 400 ml.

Cool to 20 °C. and pass a rapid stream of hydrogen sulphide through the solution for 20 minutes.

Filter through a Whatman's 40 pad, washing with dilute hydrogen sulphide solution. Dissolve the precipitate of lead

sulphide into the original beaker with 25 ml. hot nitric acid (sp. gr. 1·2). Pass through the filter pad again and collect in a 250 ml. beaker, washing with hot water.

Add 5 ml. sulphuric acid (conc.) and take down cautiously to fumes of sulphur trioxide.

Proceed from (A) in previous method.

In those cases where contamination of the sulphide residue with iron sulphide is not excessive, conversion to lead sulphate may be omitted.

MANGANESE

Determination of Manganese in Cast Iron and Steel

Sodium bismuthate method

Dissolve 1·1 g of sample in 30 ml. nitric acid (sp. gr. 1·2) in a 350 ml. tall beaker and boil well to expel nitrous fumes. With cast irons, filter off graphitic carbon and siliceous matter through an asbestos plug, washing with sp. gr. 1·2 nitric acid. Cool slightly by the addition of a little cold water and add sodium bismuthate. Although in most cases the addition of 1 g of bismuthate would be satisfactory, there are occasions when a high carbon or a high temperature would cause reduction of the bismuthate before oxidation of all carbonaceous matter. Also all bismuthate is not up to full oxidizing standard. It is therefore considered safer to add small amounts to slight excess.

Boil well and continue with small sodium bismuthate additions until a slight permanent precipitate is obtained showing the complete oxidation to the permanganic salt as indicated by a permanent pink colour.

$$4Mn(NO_3)_2 + 10NaBiO_3 + 28HNO_3 = 4NaMnO_4 + 6NaNO_3 + 10Bi(NO_3)_3 + 14H_2O.$$

Clear the solution by the careful addition of sulphurous acid and expel the excess SO_2 by boiling. (A crystal or two of pure AR salt of ferrous ammonium sulphate may be added instead of the sulphurous acid, if desired.)

Boil well in each case. Remove from the plate and cool. Dilute slightly with cold water and add 0·5 g sodium bismuthate, shake well and allow to stand 5 minutes. Filter through asbestos pad, washing with cold 2% nitric acid until the filtrate washings are colourless.

Titrate with 0·1 N ferrous ammonium sulphate and 0·1 N

potassium permanganate until a permanent pink colour is obtained.

Note: An excess of at least 1 ml. of ferrous ammonium sulphate must be used to ensure that there has been a complete reduction of the manganese.

1 ml. = 0·1% Mn on 1·1 g sample.

This method is not satisfactory in the presence of chromium. All traces of chloride must be absent.

Standardize as nearly as possible under conditions of the assay.

Methods of Separation

The separation of iron, titanium, aluminium and chromium from manganese, zinc, nickel and cobalt is based on the fact that the salts of ferric iron, aluminium, chromium and titanium are much more easily hydrolysed than those of manganese, zinc, nickel and cobalt.

Uranium, vanadium, molybdenum, tungsten and phosphorus all have acid oxides, therefore form salts with iron when ammonia is added to a solution containing iron and these metals.

Titanium and zirconium form hydroxides.

Precipitation with ammonium chloride and ammonia

Ammonium hydroxide precipitates ferric iron, aluminium and chromium as hydroxides insoluble in excess of the reagent. Zinc, nickel and cobalt are also precipitated as hydroxides but the precipitate is soluble in excess of the reagent.

Manganese is also precipitated as hydrate, which is not soluble in excess, but it can be rendered soluble by the previous addition of ammonium chloride before precipitating with ammonia.

The precipitated hydroxides are not quantitative, although all the iron, aluminium and chromium are precipitated.

The precipitated hydroxides absorb some of the salts in solution.

Absorption can be minimized and even be prevented by the following means :

(1) Presence of ammonium salts in the solution previous to precipitation minimizes absorption.

(2) In the case of nickel only, run the ferric iron and nickel solution into a mixture of potassium cyanide and ammonia. The potassium cyanide should only be slightly in excess of the theoretical quantity. Nickel cyanide (single cyanide) is first precipitated, and this dissolves in excess of the potassium cyanide and forms a double cyanide of nickel $K_2Ni(CN)_4$.

In the absence of ammonium salts or potassium cyanide, it is

noticed that the more alkaline the solution from which the ferric iron has been precipitated, the greater is the nickel and cobalt absorbed.

Therefore it is best to finish the precipitation in a neutral or slightly acid solution ; on this depends the basic acetate solution.

The basic acetate separation for the estimation of manganese is very useful in high speed steels and iron ores. It is not so essential now, but is a useful check method in referee cases. In high speed steels one usually uses the zinc oxide separation and takes one fraction of filtrate for manganese and another for cobalt, so there is not wastage of time. In any case a skill in either of these separations is desirable.

Basic Acetate Separation

This depends on the precipitation of the iron in such a way as to leave the solution acid with acetic acid.

Digest 2 g steel in hydrochloric acid, oxidize with nitric acid and simmer until digested, and carbides have been taken into solution.

Dilute with cold water to about 200 ml.

Neutralize all free acid with ammonia, then finish with dilute ammonium carbonate, and shake well until the ferric hydroxide which is at first precipitated, redissolves in the remaining ferric chloride.

The constitution of the solution may be represented by $8Fe(OH)_3 . FeCl_3$.

The solution is now said to be neutralized. Add a few ml. excess ammonium carbonate to give a permanent precipitate. This is then redissolved, adding a few drops of hydrochloric acid (conc.) at a time with continual shaking to take the ferric hydrate into solution. Then add 4 or 5 drops in excess.

Add 5 g ammonium chloride and bring to the boil, and at 70° C. a precipitate should be formed.

This is due to :

1. The reduced solubility of $Fe(OH)_3$ in $FeCl_3$ at a high temperature.

2. The partial hydrolysis of $FeCl_3$ and the first precipitation of $Fe(OH)_3$ which has been held in solution.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl.$$

Now add 10–15 ml. ammonium acetate, this completely precipitates the iron due to :

1. The decomposition of the HCl formed above, and the formation of acetic acid.

$$(NH_4)\,C_2H_3O_2 + HCl = H . C_2H_3O_2 + NH_4Cl.$$

2. The conversion of the remaining ferric chloride to ferric acetate which is readily hydrolysed to an indefinite basic ferric acetate.

Vanadates, molybdates and chromates of iron are also hydrolysed and so are not separated from iron by this method.

Boil for 3–5 minutes, remove from the plate and transfer to 500 ml. graduated flask ; make up to the mark allowing for temperature correction and volume of the precipitate. Shake well. Filter off 250 ml. clear solution. The pH of the solution should be approximately 4·5–5.

Cool, add 5 ml. bromine followed by excess of ammonia. Boil well. Stand for half an hour and filter through ashless pulp, (Whatman's No. 31) washing well with hot water.

Dissolve precipitate in a few ml. sulphurous acid, washing well with alternate washings of hot water and dilute sulphurous acid.

Add 10 ml. nitric acid (sp. gr. 1·2).

Boil off SO_2 and finish as in the sodium bismuthate method.

Notes:

(1) Excess of nitric acid should be avoided on first oxidation.

(2) With nickel and cobalt present, only use 3 ml. ammonium acetate (see under 'Cobalt').

(3) The hydrated oxide of manganese can be transferred to crucible and ignited to Mn_3O_4 containing 71·92% manganese. Usual to have slight contamination by iron.

(4) For high speed steel (high tungsten) remove WO_3 before neutralization.

(5) If decomposition commences below 70° C., the precipitate is collodial, and must be discarded if decomposition does not occur until boiling point is reached. There is a danger of incomplete precipitation of the iron on addition of ammonium acetate.

(6) Convert V if present, to pervanadic acid by H_2O_2 to prevent loss of manganese.

Ammonium Acetate

Mix 488 ml. acetic acid (glacial) with 500 ml. water and add 400 ml. ammonium hydrate (sp. gr. 0·880). Dilute to 2½ litres.

Zinc Oxide Separation.

Suitable for steels high in chromium

Digest 2·2 g steel in 30 ml. HCl or 50 ml. 20% H_2SO_4, oxidize with 5 ml. nitric acid and boil off excess.

Dilute with 200 ml. cold water and add ammonium hydroxide

until a slight turbidity, which dissolves on repeated shaking. Boil and finish the neutralization with sodium carbonate solution until a slight permanent precipitate is obtained.

Redissolve this precipitate with HCl added drop by drop with shaking and standing, using only one or two drops excess of HCl. Then add a further 5–6 drops of acid.

Stand for 10 minutes. Add ammonium chloride (5 g) followed by an emulsion of zinc oxide (1–3 g for each gram of steel), to produce a precipitate and completely hydrolyse the iron. *Avoid excess.*

Dilute to 500 ml. in a graduated flask, making allowance for temperature and volume of precipitate. Shake well. Filter off 250 ml. clear solution. Add bromine and ammonia to precipitate the manganese, bring to boil, filter off, washing well with water. Redissolve in sulphurous acid and nitric acid and proceed as for the bismuthate estimation of manganese.

Notes:

(1) For tungsten steels filter off WO_3 before proceeding to the neutralization.

(2) Phosphate precipitation cannot be used after this method.

(3) With steels high in vanadium, convert vanadium to pervanadic acid by addition of a few ml. H_2O_2 (20 vols.) prior to the addition of the zinc oxide, otherwise there is loss of manganese owing to danger of precipitating manganese as basic manganese vanadate with ferric and chromic hydroxides. It has been suggested that with a 1% vanadium steel as much as 0·25% manganese may be lost.

Determination of Manganese in Steel containing up to 5% Chromium

Arsenite Method

Standard solution. Sodium arsenite

7·61 g arsenious oxide
30·0 g sodium bicarbonate

Add bicarbonate to accurately weighed arsenious oxide. Add hot distilled water and boil gently until all the grey powder is dissolved.

Cool—filter through pulp. Make solution up to 2 litres.

Method.—1·1 g steel dissolved in 15 ml. 1:3 sulphuric acid. Oxidize with 30 ml. nitric acid (sp. gr. 1·2).

Boil off nitrous fumes and oxidize with sodium bismuthate. Reduce with ferrous ammonium sulphate and cool. Reduce chromium with a further crystal of ferrous ammonium sulphate. Add 0·5 g sodium bismuthate and stand for 5 minutes.

Filter and titrate with standard sodium arsenite.

$$\text{Then } \frac{\text{No. of ml. taken}}{10} = \% \text{ manganese.}$$

To standardize.—Take a conical flask containing 30 ml. distilled water. Add 10 ml. H_2SO_4 (20%). Cool.

Run into this solution 10 ml. standard 0·1 N potassium permanganate. Titrate with standard sodium arsenite until all the pink colour is dispelled. 10 ml. 0·1 N $KMnO_4$ should take 10 ml. standard sodium arsenite.

Persulphate Method

2 g drillings are dissolved in 50 ml. water and 7 ml. conc. H_2SO_4 in a 650 ml. conical beaker.

When completely dissolved oxidize with nitric acid to break up any carbides present.

Take down to dryness, swirling to prevent spurting. Dilute with 500 ml. boiling water. When all sulphates in solution (with cast iron filter off graphitic carbon) oxidize with 6 g ammonium persulphate (8 g for stainless 18/8).

$$MnSO_4 + (NH_4)_2S_2O_8 + 3H_2O = MnO_2H_2O + 2H_2SO_4 + (NH_4)_2SO_4$$

Boil gently for 40 minutes keeping volume constant.

Cool and filter through paper pulp, washing the precipitate several times with cold water, until there is no trace of chromium left.

Transfer precipitate to original beaker making sure that all the manganese is cleared from the funnel by wiping with a clean piece of moist paper which is added to the pulp in the beaker.

Dilute to 200 ml. with cold water.

Dissolve precipitate in 10–20 ml. standard ferrous ammonium sulphate and titrate excess with weak standard potassium permanganate.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

1 ml. = 0·0792% Mn on 2 g sample.

Notes:

(1) All trace of chlorides must be absent as this will interfere

with the precipitation of the manganese giving a low manganese figure and a correspondingly high chromium figure.

(2) Not satisfactory for high tungsten high speed steels, owing to the excess of nitric acid required to clean the WO_3.

(3) For steels low in manganese (lower than 0·30%) difficulty is often experienced in obtaining complete precipitation of all the manganese—in such a case advisable to use either the sodium bismuthate method in the absence of chromium or chlorate method in the presence of chromium. When it is desired not to estimate manganese, addition of $KMnO_4$ as for high Cr steels is advisable.

Determination of Manganese in Steel containing over 5% Chromium. Chlorate Method (Ford and Williams).

Dissolve 2·75 g drillings in 50 ml. HCl.

After break-up of carbides take down to dryness to remove HCl. Redissolve in 20 ml. nitric acid (conc.).

Boil down to paste to remove hydrochloric acid, then add 30 ml. of HNO_3. Remove from the plate and cool.

Add 5 g potassium chlorate, washing down the sides of the beaker with warm water.

$$Mn(NO_3)_2 + 2KClO_3 + H_2O =$$
$$MnO_2 . H_2O + 2KNO_3 + 2ClO_2$$

Stand on a cool part of the plate until the crystals of chlorate have dissolved and the MnO_2 begins to precipitate. Then place on hotter part of the plate. Take down to 2–3 ml. when all MnO_2 will be out of solution.

Remove from the plate. Add 30 ml. nitric acid together with a further 5 g potassium chlorate and about 200 ml. hot water.

Keep on the boil 20–30 minutes.

Filter through asbestos pad, washing well with hot water until every trace of chlorate is removed from the precipitate. Transfer the pad to original beaker, removing every trace of manganese precipitate from funnel with a small portion of damp asbestos.

Add enough 0·1 N ferrous ammonium sulphate from a burette to dissolve all MnO_2 and dilute with cold water.

Titrate excess with 0·1 N potassium permanganate until solution just turns pink.

$$\frac{\text{ml. Ferrous Ammonium Sulphate} - \text{ml. } KMnO_4}{10} = \% \text{ Mn.}$$

0·1 N potassium dichromate may be used instead of the 0·1 N permanganate. In this case use potassium ferricyanide as external indicator.

Notes:

(1) This method is of general application.

(2) *Removal of tungsten and silicon.*—With high tungsten and silicon steels, filter through asbestos pad before chlorate addition. Wash well. Hydrofluoric acid will effectively remove silicon.

(3) With steels containing cobalt, care must be taken to wash the manganese precipitate free from cobalt salts.

Manganese in Plain Carbon Steels (Colorimetric)

Weigh exactly 0·1 g of sample into a 1 in. diameter boiling tube. Into another tube weigh 0·1 g of a standard steel with known manganese content. One standard will do for 8–10 samples done at the same time. Into each boiling tube add 10 ml. of sp. gr. 1·2 nitric acid from a burette. When the reaction has stopped, put the tubes into a beaker of boiling water. Boil until all brown fumes are expelled. Shake the tubes to dissolve any salts dried out, and add 15 ml. of 1% silver nitrate solution to each tube. Add to each tube about a grain of moist ammonium persulphate and boil until effervescence ceases.

Cool thoroughly. Transfer the standard to a comparison tube (large Eggertz tube), rinsing the boiling tube well with distilled water. Dilute to a known volume (say 10 ml. for each 0·1% Mn). Transfer the sample into another comparison tube, rinsing well with distilled water. Shake each tube thoroughly. Dilute the sample until the depth of colour exactly matches the colour of the standard. The volume of the sample divided by 100 = % Mn.

Example standard = 0·52% Mn.

Dilute to 52 ml.
Sample = 57·5 ml.
Mn = 0·575%

Notes:

(1) With steel having a chromium content over 0·25% a tint is given which makes comparison difficult.

(2) A colorimetric estimation may be made by oxidizing with lead peroxide in lieu of the silver nitrate–persulphate addition, but in this case the solutions must be boiled over a sandbath.

Colorimetric Manganese (Bismuthate)

Dissolve 0·2 g of sample and 0·2 g of standard steel in 10 ml. sp. gr. 1·2 nitric acid in boiling tubes. When all are completely dissolved, cool slightly and oxidize with a little sodium bismuthate.

Boil, and if no brown precipitate, add a little more bismuthate. Clear with a little sulphurous acid or ferrous sulphate. Boil 2

minutes and cool. Oxidize with a little sodium bismuthate and filter through ignited asbestos pad into 25 ml. stoppered jar and wash with 2% nitric acid until washings are colourless. Dilute each to 25 ml. and shake thoroughly.

Pipette 10 ml. of each into Eggertz tubes and dilute sample and standard until the colours match. The standard is usually diluted to a multiplication of its manganese content and the sample volume is divided by this factor to give percentage of manganese. One standard will satisfy up to ten samples carried through at the same time.

Notes:

(1) Before oxidation the tube must be well shaken to dissolve any brown deposit on the sides.

(2) Before filtering, make sure there is a precipitate to show excess of sodium bismuthate.

(3) This method should not be used for steels containing more than 0·25% chromium.

(4) Owing to the shortage and high price of good quality asbestos fibre, the pads may be salvaged by shaking well with a little hydrochloric acid to dissolve the excess bismuthate. Pour the mass on to a filter disc in a funnel connected to a filter pulp and wash free from chlorides with cold water, followed by 2–3 washes with 2% nitric acid.

MOLYBDENUM

Ammonium acetate

488 ml. glacial acetic acid
500 ml. water
400 ml. ammonium hydrate (sp. gr. 0·880)
Make up to 2½ litres

Determination of Molybdenum

In steel containing chromium with or without vanadium, and containing not more than 2% molybdenum.

Digest 2 g sample in 60 ml. conc. hydrochloric acid in a tall 650 ml. beaker. When thoroughly digested oxidize with nitric acid and take all carbides into solution. Take down to dryness. Redissolve in 30 ml. HCl (dilute) and boil down, dilute and filter. Filter off WO_3 (if present) and SiO_2. Transfer filtrate to separating funnel.

Dissolve 20 g of caustic soda in 250 ml. boiling water in the

beaker used for the estimation, and slowly run in the solution containing the iron and molybdenum from the funnel, with repeated shaking. Wash down the separating funnel with hot water and add to the caustic soda solution. Transfer to 500 ml. graduated flask making up to the mark with boiling water. Shake well and proceed to filter 250 ml. clear caustic soda solution containing all the molybdenum from 1 g of steel.

To solution add methyl orange, then add 8–10 ml. HCl in excess, after making just acid, followed by 2 ml. sulphurous acid and boil well until excess SO_2 is driven off.

Add 75 ml. hot ammonium acetate solution, boil well and add 10 ml. of a 4% lead acetate solution. Digest at boiling point for 1 hour and filter through a Whatman's No. 30 pad washing well alternately with ammonium nitrate solution and hot water.

Ignite gently at the mouth of the muffle to pure lead molybdate.

$$PbMoO_4 \times 26{\cdot}16 = \% \text{ Mo.}$$

In the event of V being present in the steel, proceed as follows :

The caustic soda solution containing the molybdenum and most of the vanadium is acidified with hydrochloric acid—a little methyl orange indicator present—then add about 10 g ammonium chloride. Bring to the boil and add 1 g manganous chloride, boil well and add ammonia drop by drop until the solution is distinctly alkaline.

On boiling a precipitation of brown manganese pyrovanadate will be seen, boil 5 minutes, remove from the plate and make this solution quite cold. Allow to stand one hour, filter washing with cold water containing 5% ammonium chloride and now proceed as if vanadium absent.

With cast irons high in phosphorus it is necessary to have about 10 g ammonium chloride present to keep phosphorus in solution (1).

Notes:

(1) This amount of ammonium chloride is sufficient for cast irons up to about 0·4% P. Above this P content an extra 5 g of ammonium chloride for each additional 0·1% P is advisable, up to a maximum of 35 g ammonium chloride.

(2) To make the lead molybdate more granular reprecipitation is often carried out.

Dissolve the precipitate of lead molybdate by the dropwise addition of hydrochloric acid (conc.). When dissolved, add ammonium hydroxide until the solution is just neutralized then add a further 5 ml. hydrochloric acid in excess.

Precipitation with Alpha Benzoin Oxime, weighing as Molybdic Oxide

Interfering elements: tungsten, palladium, chromium (ic), vanadium and tantalum.

These give precipitates in dilute mineral acid solutions.

Alpha benzoin oxime solution

Dissolve 2 g alpha benzoin oxime in 100 ml. acetone. This should be freshly made before use.

Method.—Dissolve 1–2 g of steel in 50 ml. HCl (sp. gr. 1·16) in a squat 400 ml. beaker. When completely dissolved, oxidize with nitric acid and take down to dryness, baking lightly for 30 minutes.

Dissolve the baked mass in 50 ml. hydrochloric acid (sp. gr. 1·16), evaporate to low bulk (about 10 ml.), and dilute with 200 ml. hot water.

Filter to remove silica and tungstic oxide, washing with dilute 5% hydrochloric acid.

Cool to as low a temperature as possible (in ice) reducing any chromium and vanadium, if present, with a few drops of a saturated ferrous sulphate solution. Next add 2% alpha benzoin oxime, followed by 10 ml. bromine water, and 5 ml. of the reagent solution, stirring well after each addition.

After allowing to stand 10 minutes in a cold water bath, filter through a No. 31 12·5 cm. paper or pulp.

Wash several times with cold dilute sulphuric acid (1% strength) containing a few ml. of the reagent per litre. Transfer to platinum crucible, dry and ignite carefully between 300 and 500° C. for 20 minutes.

$$\text{Molybdenum } \% = \frac{\text{weight of } MoO_3}{\text{weight of sample}} \times 66{\cdot}66$$

Notes:

(1) 5 ml. alpha benzoin oxime should be used for each 0·01 g Mo present. Add an excess of 10 ml.

(2) Any trace of iron can be collected by dissolving the molybdic oxide in ammonia—separating the iron and igniting it and deducting this from the weight of MoO_3.

Colorimetric Method for Steel and Cast Iron using Butyl Acetate

Acid No. 1.—50 ml. conc. HNO_3 + 10 ml. H_2SO_4 (conc.) + 60 ml. water.

Acid No. 2.—150 ml. water + 10 ml. HCl (conc.) + 40 ml. H_2SO_4 (conc.)

Stannous chloride.—25 g stannous chloride dissolved in 20 ml. HCl.

Bring to boil and add 120 ml. water without cooling.

Sodium thiocyanate.—5% solution in water.

Butyl acetate.—Shake 250 ml. butyl acetate in a separating funnel with 5 ml. sodium thiocyanate solution and 25 ml. stannous chloride solution. Discard the aqueous layer.

Method.—Weigh out 0·1 g sample (0·05 g if above 0·8% Mo) into 350 ml. beaker. Dissolve in 10 ml. acid No. 1. (For ordinary steels and cast iron with up to 5% chromium, 10 ml. nitric acid (sp. gr. 1·2) has been found an advantage, one or two additions being necessary, with boiling down, to completely remove carbides, then add Acid No. 1.) Heat until fumes appear.

Add 20 ml. Acid No. 2 and heat until all the salts are in solution, cool to room temperature. Transfer to separating funnel, adding about 10 ml. water. Rinse out beaker with 10 ml. sodium thiocyanate solution adding washings to funnel, then add 15 ml. freshly made stannous chloride also to funnel, swirling slightly.

Add 10 ml. butyl acetate to separating funnel (for over 0·3% Mo add 20 ml.). Shake well for 1 minute, allow to separate out and draw off clear layer. Transfer upper coloured layer to comparison tube, adding a further 2 ml. butyl acetate and shaking again, any further small amount of the butyl acetate containing the molybdenum being added to the solution in the comparison tube.

0·1 g of a standard steel of known molybdenum content, should be treated in exactly the same manner as the assay and compared to find percentage molybdenum. For convenience use a standard steel containing 0·40% molybdenum.

This should then be made up with butyl acetate to 20 ml.

Then 1 ml. = 0·02% Mo.

In a similar manner a 0·42% molybdenum standard should be made up to 21 ml.

The red colour shows the presence of molybdenum thiocyanate, the intensity of this solution being an indication of the molybdenum content.

Notes:

(1) For stainless and tungsten steels dissolve in hydrochloric acid and oxidize with nitric acid (or *aqua regia*), then add Acid No. 1 when all carbides have been taken into solution.

(2) For high chromium steels, do not fume too strongly to avoid formation of insoluble chromic sulphate.

(3) For cast iron use 0·05 g sample and fume strongly, if over 0·8% molybdenum. Graphite carbon will not interfere, the graphite will be seen on the upper portion of the butyl layer.

Careful separation of the first layer, followed by further addition of butyl acetate, should remove all the molybdenum and leave the graphite.

(4) Turbidity is often observed owing to high copper in steel.

NICKEL

Determination of Nickel. Cyanometric

Potassium cyanide

Potassium cyanide 10 g
Potassium hydroxide 10 g
Water up to 2 litres

Silver nitrate

Silver nitrate (pure salt) 5·7907 g
Water up to 1 litre
Standardize KCN against silver nitrate

Ammonium citrate

600 g citric acid
100 ml. water
Dissolve in 380 ml. ammonia (sp. gr. 0·880)
Make up to 1 litre

Then 20 ml. = 12 g citric acid.

For steels and nickel alloys containing under 1% chromium—cobalt and copper absent.

Method.—Dissolve 0·1–1 g steel or alloy in 30 ml. hydrochloric acid (sp. gr. 1·16). When completely dissolved oxidize with dropwise addition of nitric acid (sp. gr. 1·42). When all carbides are attached remove from the plate and cool. Dilute to 100 ml. with cold water and add ammonium citrate—20 ml. for 1 g sample (5 ml. being added for 0·25 g sample).

Cool, carefully neutralize the solution with ammonium hydroxide (sp. gr. 0·880) adding 1 ml. in excess.

Cool and titrate with standard potassium cyanide and silver nitrate, adding 2 or 3 crystals of potassium iodide as indicator and ammonium sulphate to sharpen the end-point.

Assuming 10 KCN = 10 $AgNO_3$
Then 1 ml. = 0·1% Ni on 1 g
$NiCl_2 + 4KCN = K_2Ni(CN)_4 + 2KCl$
$AgNO_3 + 2KCN = KAg(CN)_2 + KNO_3$
$AgI + 2KCN = KAg(CN)_2 + KI$

Standardization.—Take 200 ml. cold water, 3 drops ammonia, and a crystal of KI and ammonium sulphate. Add 1 ml. KCN. Take back to turbidity, then add 20 ml. KCN and reach turbidity again with silver nitrate.

Notes:

(1) The less potassium iodide used the more sensitive the indicator.

(2) Excess ammonia delays and interferes with the formation of potassium nickelo-cyanide.

(3) This method is not suitable for steels and irons containing high chromium. For high nickel steel use 0·1/0·5 g sample.

(4) *Copper* will be converted to the double cyanide thus registering as nickel—so if any appreciable amount of copper present use glyoxime precipitation method for the nickel.

(5) *Cobalt.*—Cyanometric method not suitable owing to the formation of cobalt amines.

(6) After the addition of ammonium citrate do not leave in strong daylight before titrating.

(7) High silicon will cloud the end-point and should be filtered off before neutralization.

Direct Separation of Iron and Chromium

Rapid volumetric estimation of nickel.

When the amount of nickel in a steel is known approximately, a determination can be made very rapidly by a single precipitation of the iron and chromium, followed by a cyanometric estimation of the Ni. Not a suitable method when any copper and cobalt present, but most satisfactory method for stainless and ordinary nickel chromium steels.

Method.—0·1–1 g steel or Ni alloy (0·5 g Staybrite) dissolved in 10 ml. hydrochloric acid. When completely dissolved, oxidize with dropwise addition of nitric acid (sp. gr. 1·42) and digest to break up carbides.

Remove from the plate and cool.

Transfer to 500 ml. graduated flask washing in every trace of the nickel-iron-chromium solution, dilute with cold water.

Neutralize excess of acid with 2N. ammonium hydroxide (1 vol.

NH_4OH, 2 vols. water.) just short of a precipitate and the solution has assumed a deep orange colour. Make quite cold.

Run in carefully, standard potassium cyanide solution from a burette adding 4 or 5 ml. more than the nickel estimated to be present requires.

Shake well and add 35 ml. 2N ammonia. Make up to 500 ml. with cold water adding approximately 2 ml. for the volume of the precipitate and proceed to filter 250 ml. Transfer to conical flask. Add a crystal or two of potassium iodide and ammonium sulphate.

Titrate with standard silver nitrate until a permanent turbidity is obtained.

$$\frac{(\text{ml. KCN} \times \text{Factor}) - (\text{ml. } AgNO_3 \times 2) - 0{\cdot}04}{10} = \text{Nickel \%}$$

Use standard potassium cyanide and silver nitrate as in previous method.

Note: Incorrect results are obtained with the use of excess potassium cyanide.

Solution of Dimethyl Glyoxime 1% Strength

Weigh out 5 g dimethyl glyoxime, transfer to flask and add 500 ml. absolute alcohol. Warm the mixture slightly until dissolved.

Precipitation with Dimethyl Glyoxime

Dissolve 1 g steel in 20 ml. hydrochloric acid, oxidize with nitric acid, dilute with hot water to 150 ml., add 20 ml. ammonium citrate.

Make faintly ammoniacal and add a slight excess 1% alcoholic dimethyl glyoxime.

Heat to 70° C. and allow to stand for 30 minutes in a warm place. Cool and filter.

$$2\left\{\begin{matrix}CH_3C:NOH\\ |\\ CH_3C:NOH\end{matrix}\right\} + NiCl_2 = \begin{matrix}CH_3C:NOH\\ |\\ CH_3C:NO\\ |\\ CH_3C:NO\\ |\\ CH_3C:NOH\end{matrix}\!\!\diagdown\!\!\diagup Ni + 2HCl$$

This precipitate can be treated as follows :

(1) *Dried as nickel glyoxime*

The red precipitate is filtered into a Gooch sintered glass

crucible, previously dried and weighed. Washed free from chlorides, and dried for one hour in an air oven at 100° C. until constant weight is obtained. The composition of the precipitate is $Ni(C_4H_7N_2O_2)_2$ and it contains 20·32% nickel.

(2) *Cyanometric estimation*

Filter through a No. 31 paper, wash with hot water.

Dissolve the precipitate back in the original beaker with 5% hydrochloric acid.

Take to dryness and redissolve in a very small amount of hydrochloric acid, oxidizing with a few drops of nitric acid.

Remove from the plate and cool, add 2 or 3 ml. ammonium citrate, make just ammoniacal, cool and titrate with standard potassium cyanide and silver nitrate using potassium iodide and ammonium sulphate (1 or 2 crystals) as indicator.

Notes:

(1) About 30 ml. dimethyl glyoximes should be used for a 3% nickel steel.

1 ml. = 0·0025 g Ni.

Theoretically 0·01 g Ni are precipitated by 4 ml. dimethyl-glyoxime. 5 g dimethyl-glyoxime per 1 g nickel is necessary to give proper excess.

An excess of 10 ml. per estimation will give the necessary amount. The filtrate must be retained however, again heated to 70° C. and a further addition of dimethyl glyoxime added. If no further precipitate is observed all nickel will have been precipitated from solution.

Avoid using large excess of dimethyl glyoxime. If the content of the solution exceeds 50% some of the red precipitate will be redissolved.

(2) Excessive amounts of ammonium hydroxide, cobalt and copper hinder the precipitation and react with dimethyl glyoxime and so add excess reagent and allow a longer time to precipitate.

(3) With high copper and cobalt it is necessary to reprecipitate the nickel.

Basic Acetate Separation

Carry through in exactly the same way as for manganese with the following modification :

With manganese 15 ml. ammonium acetate are allowed, but for nickel or cobalt *not more than* 3 *ml.* ammonium acetate is permitted.

This in excess will tend to bring down the hydrolysis temperature and some nickel would be precipitated.

To the cold solution add bromine and ammonia to remove manganese and estimate the nickel in the filtrate in the usual way after adjusting the neutrality.

NITROGEN

The Determination of Nitrogen in Ferric Alloys and other Materials by direct Nesslerization without Distillation (W. C. Newell)

Analytical procedure for steels and alloys.

A quantity of 1 g of the steel or alloy is dissolved in 5 ml. sulphuric acid and 20 ml. of water, after which a few drops of 30% hydrogen peroxide are added to clear the solution of carbides.

The solution is then concentrated to fuming for half an hour, 2 g potassium sulphate being added beforehand, if it is known that the steel contains titanium.

The solution is then cooled, diluted and transferred to a graduated 250 ml. flask; 40 ml. of 20% caustic soda are then added, this being sufficient to make the solution appreciably alkaline after the precipitation of most of the metals as hydroxides.

The solution is then made up to 250 ml. with distilled water and allowed to settle. Some of the solution is then decanted through a filter which has previously been well washed with dilute caustic soda to remove ammonia, and a measured 100 ml. are transferred into a Nessler cylinder; 5 ml. of 5% gum arabic are added and mixed, followed by 2 ml. of standard Nessler reagent.

The solution is then mixed and the colour intensity compared in the usual way with the standard ammonium chloride solution added to 100 ml. taken from a similar blank test, in which the same amounts of gum and salts are present. It is inconvenient to filter off the whole of the solution, owing to the bulk of the hydroxide precipitate, and filtration is avoided altogether if the solution can be left long enough so that sufficient clear decantable solution is obtainable.

It is found that two colorimetric comparisons may be made for each test if desired. In accordance with the recommendations of Gotta and Seehof insufficient hydrogen peroxide is added to oxidize the whole of the iron to the ferric state, and the black hydroxide formed on the addition of the alkali settles out readily. If there is a detectable amount of ammonia in the hydrogen peroxide, this can be eliminated by distillation in the presence of sulphuric acid, or, alternatively, 0·1 g of sodium peroxide may be used for the oxidation.

The possible absorption of ammonia by the hydroxide precipitate was studied by adding a known amount of ammonium chloride solution to an acid solution of pure iron of known low nitrogen content. Within the limits of experimental error the recovery of the ammonia from the ammonium chloride, after the separation of the hydroxide precipitate was complete. Thus for example to a sample of pure iron found to contain 0·0016% of nitrogen the equivalent of 0·008% of nitrogen was added as ammonium chloride, and the test gave an apparent nitrogen content of 0·0094%.

It was once accidentally observed, however, that when a portion of the solution had been filtered and the hydroxide precipitate had been allowed to dry in the filter, a large portion of the ammonia contained in a further quantity of solution was absorbed on passing through the hydroxide on the filter. Clearly therefore such conditions must be avoided. The possibility of there being nitrides in steel, which are only hydrolysed to ammonia, by the boiling caustic soda in the normal distillation method, has been suggested by Jordan and Swindells. So far the author has not encountered any steels which confirm this suggestion, though the possibility is appreciated, and the results obtained have been carefully compared with those obtained by the vacuum fusion method, or by the conventional chemical distillation method.

Results obtained by the different methods shows that agreement between the figures is good.

It was found to be well worth while to keep the ammonia blank down to an absolute minimum by the use of redistilled sulphuric acid, well boiled caustic soda, distilled water similarly boiled with a little caustic soda and gum solution made ammonia free by passage through permutit.

With these precautions the blank becomes negligible and, owing to the speed with which the determinations can be made, the significance of ammonia absorption from the laboratory atmosphere becomes of less consequence.

It has been found that the determination of the nitrogen content of steel and other alloy samples by this simple non-distillation method using gum, represents an enormous saving in time, labour, apparatus and laboratory space as compared with the usual distillation method. A further saving in time and an increase in accuracy are possible by eliminating the visual matching of the colour intensities by the use of a photoelectric absorptiometer.

REFERENCES

W. C. Newell (Brown Firth Research Laboratories, Sheffield), *J.I.S.I.*, 1945. **152.** 333–9.
Nessler, 'On the properties of mercuric iodide and the compounds of mercury, particularly with respect to ammonia, and on a new ammonia reaction', Inaugural Dissertation—University of Freiberg, 1856.
Koch and McMeekin, *Jnl. American Chemical Society*, 1924. **46.** 2066.
Wicks, *Jnl. of Laboratory and Clinical Medicine*, 1941. **27.**
Folin and Denis, *Jnl. of Biological Chemistry*, 1916. **26.** 473.
Chiles, *Jnl. American Chemical Society*, 1928. **50.** 217.
Snell and Snell, *Colorimetric Methods of Analysis*, New York, 1943. D. Van Nostrand Co.
Gotta and Seehof, *Zeitschriftfur analytische. Chemic.*, 1942. **124.** 216.
Swinden, Fourth Report of the Oxygen Sub-Committee, Sec. II, Part C, *J.I.S.I.*, 1943. Note p. 302.
Jordan and Swindells, U.S. Bureau of Standards, 1922, *Scientific Paper* 457.

Nitrogen

G. C. Lloyd, Sixth Report, Heterogeneity of Steel Ingots, *J.I.S.I.*, 1935. Sp. Report No. 9, p. 121.
E. C. Pigott, *Metallurgia*, Jan. 1948. 129–32.

OXYGEN

The Determination of Oxygen in Steel

It is unnecessary to emphasize the importance and desirability of establishing a method for the determination of oxygen in steel.

The Seventh Report on Heterogeneity of Steel Ingots deals with the vacuum fusion method and represents co-ordinated work carried out at the National Physical Laboratory, Sheffield University, and the Central Research Department, United Steel Companies Limited, Sheffield.

Detailed descriptions have been given of the apparatus used in each of the three laboratories.

Seventh Report on Heterogeneity of Steel Ingots

W. W. Stevenson and G. E. Speight, *The Vacuum Fusion Method for the Determination of Oxygen in Steel.* 65–81.

Improvement in the Vacuum Fusion Method for the determination of total Oxygen in Steel

H. A. Sloman (National Physical Laboratory), A critical examination of the method.

Fourth Report Oxygen Sub-Committee

T. Raine and J. B. Vickers, *The Vacuum Fusion Method.*
Swinden, Stevenson and Speight, 1943. **2.** 239.
E. C. Pigott, *Metallurgia*, May 1948. 6.

PHOSPHORUS

Estimation of Phosphorus

In plain carbon and low chromium steels.

Dissolve 4 g of steel in 80 ml. nitric acid (sp. gr. 1·2) in a 750 ml. conical flask, when dissolved boil off all brown fumes and add 8 ml. of a 3% solution potassium permanganate and digest for 5 minutes.

Clear the precipitate with 5 ml. hydrochloric acid (conc.). Cool to 70° C. Neutralize with 15 ml. 50% ammonia or until a precipitate of iron persists for a short while, then redissolve by adding 3 ml. of nitric acid to clear. Now add 40 ml. of a clear filtered ammonium nitro molybdate solution. Shake well and allow to stand 1 hour.

The yellow precipitate may be collected and estimated as follows :

Dissolve in 0·1 *N caustic soda and excess NaOH titrated with* 0·1 *N* H_2SO_4, *using phenolphthalein as indicator.*

The precipitate is well washed once with 2% nitric acid and 6 or 7 times with 5% potassium nitrate until free from acid. This is then transferred to the original flask now clean and a measured quantity of 0·1 N caustic soda followed by hot water added. Shake well and stand 10 minutes. Add few drops phenolphthalein, titrate excess caustic soda with 0·1 N sulphuric acid until the pink colour just disappears.

1 ml. 0·1 N caustic soda = 0·00337 % P on 4 g.

It is advisable to standardize the solutions against a standard steel of known P content. Also the standard sulphuric acid must be standardized against standard decinormal sodium carbonate.

In certain low alloy steel containing chromium, decomposition may be facilitated by the addition of 10 ml. hot water to the sample before nitric acid addition.

For steel containing vanadium add 3 ml. saturated solution of sulphurous acid before adding the nitro-molybdate solution.

Use approximately 10 ml. standard caustic soda solution for each 0·025% P.

Ammonium nitro molybdate

Grind 100 g ammonium molybdate and dissolve in 200 ml. boiling water. Cool and add 200 ml. ammonia (sp. gr. 0·880). Mix 750 ml. of water and 500 ml. nitric acid in a Winchester quart. Cool. When both solutions are cool, add the ammonia solution to the nitric acid solution, a few ml. at a time, with continual

shaking, dissolve any molybdic acid as soon as formed, by shaking and cooling.

Precipitation as lead molybdate, igniting and weighing as such

After filtering and washing the yellow precipitate free from acid, it is dissolved in 5 ml. ammonia (conc.) poured in drops over the precipitate, which quickly dissolves. Wash well with hot water and a few drops of ammonia and place the flask containing ammoniacal solution on the hot plate.

Weigh out into another beaker 10 g ammonium chloride and add to this 50 ml. ammonium acetate, filter if necessary, bring to the boil. Add to the ammoniacal solution containing the phosphorus 10 ml. hydrochloric acid, followed by 10 ml. 4% lead acetate. This is immediately poured into the boiling solution containing the ammonium acetate and ammonium chloride, washing in every trace of the lead solution. Pure lead molybdate is precipitated as a granular precipitate—which is allowed to stand for one hour, filtered and washed well and ignited in the cool part of the muffle.

$$\text{If 2 g steel taken } \frac{\text{Weight of } PbMoO_4 \times 0{\cdot}007}{2} \times 100 = \%\ P$$

Ammonium acetate.—Mix 488 ml. glacial acetic acid with 500 ml. water. Add 400 ml. NH_4OH (sp. gr. 0·880). Dilute as required.

Lead acetate.—Dissolve 4 g lead acetate in 100 ml. hot water, add a few ml. glacial acetic and filter if necessary.

Phosphorus in stainless steel and steels containing tungsten.—To 2 g sample add 25 ml. hydrochloric acid and 35 ml. nitric acid (conc.) previously mixed.

Take to dryness but do not bake too strongly. Take up in 30 ml. conc. nitric acid. Evaporate nearly to dryness. Take up in 20 ml. nitric acid, oxidize with 8 ml. 8% potassium permanganate and destroy the brown colour due to the permanganate with sulphurous acid or hydrochloric acid (sp. gr. 1·16). Dilute to about 50 ml. and filter. Make just ammoniacal with ammonia and then add sufficient excess to produce a slight precipitate. Make just acid with conc. nitric acid, adding 5 ml. excess. Precipitate with ammonium nitro-molybdate and carry on in the usual way.

Precipitation with Magnesia Mixture and Ignition to Pyrophosphate

Method suitable for tungsten steel and iron ores.

Magnesia mixture

Dissolve 25 g pure magnesium chloride and 25 g ammonium chloride in hot water. Cool, make up the volume to 200 ml. and add 50 ml ·88 ammonia. Allow to stand for one day and filter off the clear solution.

The ore or alloy is dissolved in HCl + HNO_3. When dissolved, evaporate to just dry and redissolve in small amount of HCl. Filter, washing with dilute HCl. Ignite insoluble. Dissolve ash in HCl and add to previous filtrate. Metals of Group II are removed by H_2S and filtered off. The filtrate is boiled to expel excess of H_2S, oxidized with HNO_3, cooled and made alkaline with ammonia. If enough iron is not present to precipitate all the phosphorus as ferric phosphate, add a little ferric chloride, again acidify with HCl and add a slight excess of ammonia, repeat these operations until a reddish precipitate is formed.

Now add acetic acid until distinctly acid, boil a few minutes, filter, wash once with hot water, redissolve in dilute HCl and reprecipitate with ammonia and acetic acid. Boil filter and wash with hot water. Dissolve the precipitate in warm dilute hydrochloric acid, wash with hot water. Evaporate filtrate nearly to dryness, add 5–10 g citric acid dissolved in water and filtered. Add 5–10 ml. magnesia mixture and ammonia to slight alkalinity. Allow to stand in cold water till quite cold; add one third volume of strong ammonia stirring thoroughly and allow to settle overnight. Filter wash with ammonia (1 : 2) containing 3% ammonium nitrate.

Dry, ignite slowly at first finally at strong heat until quite white. Weigh as $Mg_2P_2O_7$.

$$Mg_2P_2O_7 \times 0{\cdot}2784 = P.$$

The magnesium pyrophosphate should be quite white, if slightly discoloured a reprecipitation is necessary.

Phosphorus by Visual Comparison (Admiralty method)

Quinine molybdate method

Dissolve 1 g of quinine sulphate in 30 ml. HNO_2 (sp. gr. 1·2). Dissolve 40 g ammonium molybdate in water and filter. Add barium oxide to precipitate the sulphate present, and filter. Add 200 ml. of HNO_3 (conc.). Cool and add the quinine solution. Make up to 1 litre.

Method.—Dissolve 1 g sample in 10 ml. HNO_3 (sp. gr. 1·2) in a 50 ml. conical beaker. Digest the solution and add a solution of

potassium permanganate dropwise to a permanent precipitate. Clear with a few drops of H_2SO_3 and cool. Add 3 ml. NH_4OH (1 : 1), cool and add 10 ml. of the quinine molybdate reagent.

Make up to 50 ml. and compare turbidity with a set of standards of suitable range in steps of 0·01% P, put on with each batch of samples.

Preparation of Standards for Visual Phosphorus Methods

Standard solution of diammonium hydrogen phosphate

$$(NH_4)_2\,HPO_4$$

Weigh out 0·085 g of the A.R. salt.

Dissolve in water and make up to 1 litre.

5 ml. = 0·001 g phosphorus.

Range of standards.—0·01; 0·02; 0·03; 0·04; 0·05; 0·06 % P.

Preparation.—Select a piece of bar iron with a phosphorus content not exceeding 0·01%.

Weigh out 5 g of bar iron drillings and dissolve in 500 ml. HNO_3 (sp. gr. 1·2). Boil off nitrous fumes and oxidize with 15 ml. potassium permanganate solution (12 g per litre). Boil for a few minutes, reducing with 15 ml. SO_2. Boil off nitrous fumes, cool and add 150 ml. NH_4OH (1 : 1). Cool and make up to 1 litre.

For use take 20 ml. of this solution. It will contain 0·1 g steel with a P content of 0·01% and be in the same condition as the samples prior to the addition of the quinine molybdate reagent.

To prepare the range of standards, add measured quantities of the standard phosphate, as indicated below to 5 g of the bar iron (after dissolving in HNO_3, sp. gr. 1·2) in order to make up to the P content required and proceed as above.

0·02%	P standard	will	require	25	ml.	standard	$(NH_4)_2HPO_4$	solution	
0·03%	,,	,,	,,	50	,,	,,	,,	,,	
0·04%	,,	,,	,,	75	,,	,,	,,	,,	
0·05%	,,	,,	,,	100	,,	,,	,,	,,	
0·06%	,,	,,	,,	125	,,	,,	,,	,,	

Steels with known phosphorus content can be weighed out with the sample to fit in the range.

The method is suitable for plain carbon steels and used where a quick colour comparison is required.

Perchloric acid method. For high chromium steels containing tungsten and columbium

2 g sample. Transfer to 400 ml. beaker, add cautiously nitric

acid (sp. gr. 1·42) 30 ml. followed by 30 ml. HCl (sp. gr. 1·16) and digest until dissolved.

Rinse down the sides of the beaker, add 20 ml. perchloric acid (sp. gr. 1·54) and evaporate to strong fumes. (With certain grades of perchloric acid a blank is necessary.) Continue fuming for at least 10 minutes after the chromium is completely oxidized. (This degree of fuming is essential to ensure complete conversion of phosphorus to the form which is precipitated by nitro-molybdate. It should be carried out with the beaker covered.) Cool slightly, redissolve by warming with 10 ml. HCl (sp. gr. 1·16) to reduce the chromate, dilute with 20 ml. water and add 10 ml. hydrobromic acid (sp. gr. 1·5), evaporate to fumes with the beaker uncovered until chromium just begins to re-oxidize.

Cool slightly, add 35 ml. water, take all salts into solution and filter through a small paper pad, washing with dilute nitric acid (2% strength), keeping the bulk as low as possible.

Add 5 g ammonium chloride, warm to 75° C. and add 35 ml. nitro-molybdate reagent.

Shake well and allow to stand in a warm place to effect complete precipitation.

Note: Filter and proceed as in one of the previous methods. Hydrobromic acid is a powerful oxidant. The re-oxidation of the chromium is easy to detect by the colour.

REFERENCE

'The Determination of Phosphorus in Austenitic Chromium Nickel Steels' *Jnl. I.S.I.*, 1947. **155**. 375–91.

SELENIUM AND TELLURIUM

Determination of Selenium

2 g steel are dissolved in a mixture of 20 ml. of nitric acid (sp. gr. 1·42) and 30 ml. HCl (sp. gr. 1·16), the solution evaporated to 15 ml., cooled, diluted to 50 ml. and silicic acid filtered off, the filtrate being received in a dropping funnel.

The solution is run in a rapid stream of drops into 200 ml. of 10% caustic soda solution, and, after making up to exactly 500 ml., a 250 ml. portion is filtered off through double folded filter papers.

The fraction is transferred to a large beaker, made slightly acid with hydrochloric acid (using methyl orange as indicator) and boiled down to 200 ml.

About 200 ml. of hydrochloric acid (sp. gr. 1·16) are added to give the test solution an acidity of 50% with hydrochloric acid.

Cool to 20° C. and pass a stream of sulphur dioxide until the solution is saturated (30–40 minutes). Warm the solution to 70° C. and allow to cool for 1 hour, and filter off the precipitated selenium through a Gooch crucible.

Wash with hot hydrochloric acid and with two final washes of cold water, until free from chlorides.

The Gooch crucible is dried at 105° C. for 1 hour and weighed. The precipitate consists of elementary selenium.

Tellurium interferes.

Determination of Tellurium

Not more than 0·2 g tellurium should be present in 50 ml. 25% hydrochloric acid (sp. gr. 1·16). Bring to the boil, add 15 ml. of a freshly prepared saturated solution of sulphur dioxide and follow with 10 ml. of a 15% aqueous solution of hydrazine hydrochloride and again a further 25 ml. saturated sulphur dioxide.

Bring to the boil to allow the precipitate to settle in an easy filterable form (this should not require more than about 5 minutes). Filter through a weighed filter crucible, wash free from chlorides. Finally wash with alcohol (to remove all water and prevent oxidation), dry to constant weight at 110° C. Weigh as tellurium.

Standard Volumetric Method for Stainless Steels

The selenium is separated by SO_2 and titrated with potassium iodide and sodium thiosulphate.

N/20 sodium thiosulphate

Dissolve 12·5 g AR reagent in water, add 0·1 g sodium carbonate and dilute to 1 litre.

N/20 iodine

Dissolve 6·35 g iodine in 100 ml. of potassium iodide (10%) and dilute to 1 litre. *Standardize* the thiosulphate solution against 0·1 N potassium permanganate as follows :

Run 20 ml. of 0·1 N potassium permanganate into 50 ml. of dilute 5% sulphuric acid containing 1 g of potassium iodide. Shake and titrate the liberated iodine against the sodium thiosulphate solution, using starch as indicator.

5 g drillings dissolved in a mixture 30 ml. hydrochloric acid and 25 nitric acid (conc.). When the violent reaction ceases, evaporate down to dryness on a water bath or on a cool part of the plate.

Redissolve by the addition of 50 ml. 1 : 3 hydrochloric acid. Filter through a paper pad, washing 2 or 3 times with dilute hydrochloric acid and hot water. Dilute to 150 ml., adding 100 ml.

hydrochloric acid (conc.) and digest at 70° C. for 10 minutes. Cool to 20° C. and pass a stream of sulphur dioxide gas until the solution is saturated. Again heat to 70° C. and allow to stand for 1 hour. Filter on a Whatman's No. 30 filter pad. The selenium can be estimated gravimetrically as in the previous method. The residue should be red.

Transfer pad and residue to a 250 ml. beaker, adding 10 ml. nitric acid and 10 ml. sulphuric acid (conc.). Heat to destroy organic matter, with further nitric acid additions if necessary.

Cool, dilute to 50 ml. and warm to 70° C. Make faintly ammoniacal, digest for 10 minutes and filter through a small paper pad, washing with hot water (to remove any trace of iron).

Acidify the filtrate with dilute sulphuric acid 50%. Add 20 ml. excess. Heat to 60° C., add 3 g urea (to destroy nitrous acid and nitrites). Stir, allow to stand and cool to room temperature.

Add 3 g potassium iodide, stir for 3 minutes and dilute to 200 ml. Titrate with sodium thiosulphate (N/20) until the iodine colour gradually fades and approximately 5 ml. has been added in excess.

Add 5 ml. starch solution (1%) and titrate with N/20 iodine to a permanent blue colour.

$$\text{Selenium } \% = \frac{(\text{ml. thiosulphate} - \text{ml. iodine}) \times 0{\cdot}0987}{\text{weight taken}}$$

SILICON

Hydrochloric Acid Method. For Plain Carbon Steels and Steels low in Chromium content

Weigh out 4·67 g of sample into a 450 ml. beaker. Add 50 ml. hydrochloric acid (sp. gr. 1·16) and place on the hot plate, covering the beaker with a glass cover.

When completely dissolved* place beaker over the hot part of the plate and boil to dryness. When completely dry half remove the cover and bake until the 'cake' is slightly pink. This should take 15–20 minutes, and will oxidize the iron to the ferric state.

Remove from the plate and cool. Add 30 ml. of hydrochloric acid (sp. gr. 1·16), replace cover and put back on to hot plate. Boil until completely dissolved, and dilute to 200 ml. with hot distilled water. Stand on edge of the hot plate for 10 minutes.

Filter through an ashless paper pad rinsing beaker on to pad

* If complex carbides of chromium, etc., are found, these should be broken up by oxidizing with a few drops of nitric acid before boiling dry.

with a fine jet of hot water, at the same time detaching all traces of silicon from the cover and beaker by means of a policeman, again rinsing on to pad.

Wash the pad three times with hot 5% hydrochloric acid and then with hot water until free from iron. Suck the pad dry on a filter pump, and transfer to a porcelain or vitreosil crucible, cleaning sides of funnel with a little moistened ashless filter paper, which is added to the pad in the crucible.

Ignite at 1000° C. (approx.), cool and weigh.

$$\text{Wt. of ash} \times 10 = \% \text{ silicon.}$$

If baking is done as described in method, oxidation of the iron without the nitric acid is achieved.

Notes:

(1) For steels containing over 1% silicon use half weight and multiply by 20.

(2) If the residue after ignition is not white showing contamination, this may be due to yellow tungstic oxide, titanium or vanadium. Transfer ash to weighed platinum crucible, add a few drops of strong sulphuric acid followed by a few drops of hydrofluoric acid.

Evaporate to dryness on the hot plate, finally igniting in the muffle furnace at about 800° C.

Loss in weight is silica which has been volatilized (as silicon tetra fluoride).

Nitro-Sulphuric Acid Method

Use 4·67 g for steel and 1 g for cast iron. Dissolve in 50 ml. water + (4·5 ml. HNO_3 + 2·5 ml. H_2SO_4 for each gram of sample).

When dissolved place over the hottest part of the plate and take down to fumes.

Remove from the plate. Cool and add 100 ml. hot water. When cake is dissolved bring to the boil and add 10 ml. HCl, and filter immediately. Ignite and weigh as SiO_2

$$\text{Wt.} \times 10 = \% \text{ silicon}$$
$$\text{For cast iron wt.} \times 46{\cdot}7 = \% \text{ Si.}$$

Note: When filtering wash three times with hot dilute HCl and three times with cold water.

High chromium steels should not be baked too strongly. With high chromium cast irons (austenitic cast irons) it is recommended

to dissolve the 1 g sample in 50 ml. water + 2·5 ml. H_2SO_4 and not until completely dissolved is the nitric acid added, then digest to remove carbide and carry on as above. If necessary treat with HF. Do not bake too strongly.

Perchloric Acid Method

For steels containing columbium and tantalum.

Weigh out 2·336 g steel into a 400 ml. squat beaker, dissolving in 30 ml. hydrochloric acid (sp. gr. 1·16). When completely dissolved, oxidize with nitric acid (sp. gr. 1·42).

Add 25 ml. perchloric acid (sp. gr. 1·54) and evaporate to fumes with the beaker covered to avoid loss of perchloric acid.

Boil for 2–5 minutes, do not allow the contents of the vessel to become pasty or solid.

Remove from the plate, allow to cool, add 30 ml. hydrochloric acid (sp. gr. 1·16) and heat to boiling, dilute with 200 ml. hot water.

Filter off the precipitated silicon together with the earth acids and tungsten if present on an ashless filter pad, washing well with hot 2% nitric acid and hot water.

Transfer to weighed platinum crucible and ignite at 800° C. Weigh. Treat with a few drops of sulphuric acid (sp. gr. 1·42) and hydrofluoric acid 3 to 4 drops. Evaporate to dryness, ignite as before until constant weight is obtained.

Loss in weight will give weight of silicon.

$$\text{Silicon } \% = \text{wt. of } SiO_2 \times 20.$$

Note: This method is of general application.

SULPHUR

Solutions required

Stock ammoniacal cadmium chloride

Sp. gr. 0·88 ammonia 500 ml.
6·25 g cadmium chloride
Water 1000 ml.

Sodium thiosulphate

Dissolve 7·7422 g sodium thiosulphate in water.
Add 0·5 g sodium bicarbonate.
Make up to 1 litre.

Iodine

This solution is calculated to liberate iodine in solution so that 1 ml. = 0·0005 g S.

Dissolve exactly 1·5296 g pure potassium dichromate. Add 15 ml. sulphuric acid (1 : 2), cool and add to this a solution containing 15 g potassium iodide and make up to 1 litre.

1 ml. = 0·010% S on 5 g sample
= 0·001983 g copper.

Evolution Method

This process depends on the fact that when hydrochloric acid is added to steel, the iron and manganese sulphides are decomposed and an equivalent amount of H_2S evolved as gas.

The evolved gas can be absorbed in various ways and estimated thereby.

Weigh out 5 g of drillings into a 750 ml. conical flask, fitted with a rubber bung holding a thistle funnel and delivery tube. The thistle funnel should have a bulb trap or be inserted so that it almost reaches the bottom of the flask.

Immerse the end of the delivery tube in 200 ml. of dilute ammoniacal cadmium chloride. (Made up with 40 ml. of stock solution and 160 ml. water) in a 350 ml. conical beaker.

Now add 100 ml. boiling 50% hydrochloric acid through the thistle funnel, and keep hot until all vigorous effervescence ceases, being careful not to boil before the sample is thoroughly dissolved, otherwise ferric chloride will pass into the absorbent solution and a high result would be obtained.

When completely dissolved bring to the boil to expel any remaining H_2S gas. Detach delivery tube from flask.

Make solution quite cold and add 30 ml. hydrochloric acid (sp. gr. 1·16) and standard iodine solution until a faint yellow colour appears showing excess of iodine. Titrate excess of iodine with standard thiosulphate solution using starch as indicator. If these conditions are observed high results should not be obtained. Satisfactory results can also be obtained by the addition of 30 ml. hydrochloric acid (1·16) followed by a few drops of fresh starch solution and standard iodine until a faint blue colour appears showing excess of iodine. Add a little (2–3 ml.) of starch solution and titrate the excess of iodine with thiosulphate solution.

Notes:

(1) All oxidizing agents must be absent.

(2) This method cannot be used for steels and irons containing molybdenum.

Gravimetric Method. Precipitation as Barium Sulphate

Weigh 5 g of steel into a 600 ml. squat beaker, adding

a pinch of potassium chlorate or nitrate. Add 30 ml. of nitric acid. Then add slowly 30 ml. of hydrochloric acid. A violent action takes place. After all the hydrochloric acid has been added and the reaction subsides, place on hot plate. When completely dissolved boil to dryness, taking care to avoid spitting. Cool and add 30 ml. of hydrochloric acid and again boil to dryness.

Take up in 30 ml. hydrochloric acid and boil down to 15 ml. Remove from the plate and add a further 5 ml. of hydrochloric acid.

Dilute with hot water, filter through pulp and wash twice with hot water.

Dilute to about 200 ml. Add 20 ml. barium chloride solution (20%). Bring to the boil and allow to stand overnight in a warm place.

Filter cold through No. 40 pulp, washing once with a cold 5% solution of hydrochloric and two or three times with cold water. Dry on the pump, transfer to crucible and ignite in the muffle.

$$\frac{\text{Wt. of } BaSO_4 \times 13{\cdot}73}{5} = \% \text{ S.}$$

Notes:

(1) Perfectly clean utensils should be used in carrying through estimation.

(2) A blank estimation must be carried through and the weight subtracted from weight of $BaSO_4$.

(3) With high carbon high chromium alloys, chromium carbide is formed which is difficult to take into solution, sometimes passing through the pulp filter into filtrates if water is used for washing. To prevent this wash with a little dilute hydrochloric acid. Baking at too high a temperature should be avoided, otherwise the barium sulphate will be contaminated with chromium.

(4) With tungsten steels, after baking for the second time, take up in 30 ml. HCl. Boil down to 20 ml. Remove from the plate and add 200 ml. hot water. Stand 2 hours to enable the tungstic oxide to settle. Filter and precipitate with barium chloride in the usual way.

(5) In steels and irons of sulphur content below 0·02% add a known quantity of 0·01 N sulphuric acid, carrying out a blank under similar conditions.

(6) With steels containing vanadium, precipitate in 20% HCl to prevent formation of barium vanadate.

Combustion Method

Weigh out 1·6 g into unglazed porcelain boat, 3 in. long × ½ in.

wide × ⅜ in. deep, and spread evenly over the boat, cover the drillings with 0·5 g pure tin foil. (The addition of tin is necessary with all alloyed steels—with plain C steels tin may be omitted.)

Place into combustion furnace (at 1300° C.) and pass oxygen at a moderate rate of flow until ignition is completed (1½–2 min.). The escaping gas passes through delivery tube into absorbent (see below) contained in a 250 ml. conical flask.

Wait until absorption solution turns pink and to avoid sucking back, supply a fairly fast stream of oxygen. Seven minutes after commencement of experiment remove absorption flask and titrate with 0·1 N NaOH until pink just disappears.

Calculate the percentage sulphur from the factor obtained by the standard which must be carried out with each batch.

If back titration is needed use 0·01 N HNO_3. The silver nitrate is decomposed by the SO_2 and small amounts of SO_3 to form HNO_3.

Example. 0·05% S. standard required 4 ml. NaOH.

Then 1 ml. = 0·0125% S
Sample required 1·6 ml. NaOH
% S = 0·0125 × 1·6 = 0·02% S

Solutions required

Silver nitrate—4 g per litre.

Methyl red—Indicator (1 g in 60 ml. ethyl alcohol + 40 ml. water. Stand 12 hours and filter.)

0·01 N caustic soda.

Freshly boiled and cooled distilled water.

For absorption use 100 ml. of the distilled water + 10 ml. $AgNO_3$ solution + 5 drops of indicator.

Note: The furnace used must maintain a temperature of 1300° C. and the temperature must be taken by pyrometer before work commences.

Silit rods are used for the heating element, being generally the most satisfactory type, and are easily replaceable when they fail. The tube must be pythagoras type to remain gas-tight at elevated temperatures.

By using 1·6 g sample at least 200 estimations can be done on one tube before it is discarded. With S contents 0·05—0·1% use 1 g sample; with 0·1–0·25% use 0·5 samples.

Fine drillings should be used whenever possible.

Advantages

(1) *General application.*

(2) *Slightly better figures with Staybrite and high chrome steels than obtainable with the gravimetric method.*
(3) *Rapid method.*

Disadvantages
(1) High temperature necessary for combustion.
(2) Only 90% yield.
(3) Comparative short life of combustion tube.
(4) Possibility of low figures with lumpy drillings.

The combustion method for sulphur determination, is generally regarded as a sound and practical method. Little interference is occasioned, and considerable time can be saved by using this method.

TIN

Decinormal Sodium Thiosulphate
Dissolve 24·8202 g pure salt in water and make up to 1 litre. Standardize against copper sulphate or preferably electrolytic copper.

Decinormal Iodine
Dissolve 12·692 g resublimed iodine together with 30 g potassium iodide and make up to 1 litre. Standardize against 0·1 N sodium thiosulphate.

1 ml. = 0·005935 g Sn.

Tin in Carbon Steel
Dissolve 5 g of sample in 100 ml. of 50% HCl in flask fitted with thistle funnel and delivery tubes. When dissolved add two 2 in. wire nails and 0·2–0·3 g of powdered antimony. Boil gently until nails are completely dissolved. Cool under tap, having the end of the delivery tube dipping into a 10% solution of sodium carbonate. This solution is sucked spasmodically into the flask and creates an atmosphere of CO_2.
When thoroughly cooled remove fittings, add a little starch solution, and titrate with iodine solution until first permanent blue colour.

1 ml. = 0·1187% tin, on 5 g.

In presence of tungsten, etc., a modified method using sodium chloride and a nickel reduction is used.
[See Robertshaw and Bromfield, *Analyst*, 1944. 340–3.]

TITANIUM

Determination of Titanium in High Chromium Steels. Separation from Chromium

Prepare a standard by weighing out 0·5 g of a steel containing no titanium, but about the same amount of chromium as sample and treat as follows :

Dissolve 0·5 g steel in 20 ml. H_2SO_4 (1 : 3). When completely dissolved, add 3 g potassium chlorate and allow to simmer until all the chromium is oxidized, and then take down until crystals begin to separate out. Dilute to 150 ml. with water and boil clear. Cool slightly (add 5 g ammonium chloride if high nickel present. This will prevent this element from precipitating) and make ammoniacal. Collect precipitate containing all the iron and titanium on a large filter paper and wash *well* with hot water. Dissolve percipitate in 1 : 5 hydrochloric acid. Add 15 ml. H_2SO_4 (conc.) and boil down to fumes. Remove from the plate diluting to 200 ml. Boil clear and cool. Add 20 ml. hydrogen peroxide and 2 or 3 ml. syrupy phosphoric acid to remove any colour due to the iron.

Make up the standard to 200 ml., and run in standard titanium solution, until the colours match in Nessler tubes when both solutions are diluted to the same volume.

1 ml. = 0·1% Ti on 0·5 g.

Standard Titanium Solution

Fuse 0·2081 g TiO_2, in platinum crucible with potassium bisulphate, extract in 100 ml. 1% H_2SO_4. Make up to 250 ml.

Hydrogen Peroxide

Dissolve 6–8 g sodium peroxide in 250 ml. 1:3 H_2SO_4 and make up to 1 litre.

Notes:

(1) Sometimes it is necessary, owing to incomplete removal of the chromium in the first precipitation, to carry through a second precipitation, before oxidation.

(2) Ammonium persulphate can be used in place of potassium chlorate to oxidize the chromium; in this case do not take down to crystals, as with the chlorate.

Generally speaking the colorimetric estimation of titanium is usually recommended, with or without removal of most of the nickel and chromium.

For steels and alloys containing very high molybdenum and tungsten a caustic soda precipitation of the iron and titanium could be accomplished, the tungsten and molybdenum, also vanadium remaining in solution.

Titanium in Steels free from Tungsten and Vanadium and containing not more than 2% Chromium

This method is also suitable for cast iron.

Weigh out 0·5 g sample into 250 ml. squat beaker and dissolve in 50 ml. sulphuric acid (1 : 7).

When completely dissolved oxidize with nitric acid (sp. gr. 1·42) and boil well until all brown fumes are removed.

Remove from the plate and filter through a small filter pad, washing with a little dilute (5%) sulphuric acid. Transfer pad to platinum crucible, dry and ignite, remove from the muffle and add 2 or 3 drops, sulphuric acid (conc.) followed by a few drops of hydrofluoric acid to remove silica.

Evaporate to dryness on the hot plate and fuse the residue with potassium bisulphate (2 g) until a clear solution is obtained, extract the cooled residue in the original filtrate, which should be taken down to fumes to remove nitric acid (avoid fuming too strongly to form insoluble chromic sulphate).

Remove from the plate, cool, add 100 ml. hot water and take salts into solution.

Prepare a blank solution of a titanium free steel exactly as described above, this should contain approximately the same amounts of nickel and chromium, if not, add equivalent quantities of these metals or solutions of their salts.

Transfer to 100 or 200 ml. graduated cylinders adding a little dilute phosphoric acid to decolorize the iron, also 5 ml. hydrogen peroxide (10 vols. or 3% strength.)

Compare and estimate the titanium as in the previous method.

Notes:

(1) If a brown colour is seen to develop, due to the presence of vanadium, this can be separated from titanium by a caustic soda precipitation of the titanium.

In such a case the hydrogen peroxide solution containing the titanium is poured into hot caustic soda solution in excess. Filter and wash the precipitate containing the iron and titanium and redissolve in hot sulphuric acid (1 : 7).

(2) The hydrogen peroxide should be at least 3% strength and the strength of the sulphuric acid must be at least 5% by volume in order to prevent hydrolysis of the titanium.

Cupferron Precipitation

Cupferron (Ammonium salt of nitrosophenylhydroxylamine)

1–2 g sample are dissolved in 50 ml. water to which has been added 7 ml. sulphuric acid (conc.).

When completely dissolved, the solution is cooled and diluted to a volume of 300 ml.

A 6% solution of cupferron is added in drops until the yellow precipitate begins to turn brown.

Allow to stand for 30 minutes.

Filter on a| pulp filter or Whatman 31 (12·5 cm.) containing a little pulp, washing with cold dilute sulphuric acid (2% strength,) containing a few drops of reagent.

Transfer the precipitate to a platinum crucible and ignite at 650° C., cool and add 2 or 3 drops sulphuric acid (conc.) followed by 5 ml. hydrofluoric acid and evaporate to dryness.

Fuse the ignited residue with 2 g potassium bisulphate and extract in sulphuric acid (1 : 7), in a squat 400 ml. beaker.

Estimate the titanium by the colorimetric method with a standard blank of fused potassium bisulphate containing no titanium.

Notes:

(1) If vanadium present, fuse ignited residue with 2 g sodium carbonate; extract with water and filter. The titanium is left insoluble on the filter. Wash well with water, ignite and fuse ash with potassium bisulphate and proceed for colorimetric estimation.

(2) The cupferron will separate titanium from aluminium but will precipitate copper.

Separation from Vanadium

Digest 4 g drillings in 50 ml. hydrochloric acid. When thoroughly dissolved, boil well for 5–10 minutes—remove from plate and filter.

Ignite residue and filter in platinum crucible and reserve.

To the filtrate add ammonia until a permanent precipitate is just noticed. Clear with hydrochloric acid, a little at a time, with frequent shaking. Place on the hot plate, add 10 g $Na_2S_2O_3$ and boil for 15 minutes. A precipitate will form due to the hydrolysis of titanium salts. Place filter and precipitate in the original crucible with the residue. Dry and ignite at a low temperature. Cover ignited precipitates with 2 g sodium carbonate and fuse for 10 minutes.

Extract in hot water and filter on ashless paper, washing with warm 2% ammonium nitrate solution. Dry and ignite at low

temperature. Add 2 g potassium bisulphate to the platinum containing the titanium and fuse again for 10 minutes. Cool, extract with sulphuric acid (1 : 4) until solution is complete.

Estimate the titanium by the colorimetric method.

Determination of Aluminium and Titanium in High Nickel Alloys. Mercury Cathode Separation

Titanium

Dissolve 0·5 g in 15 ml. conc. hydrochloric acid, and 15 ml. nitric acid. Add 7 ml. 1 : 1 sulphuric acid. Evaporate to fumes. Dissolve in 30 ml. water. Filter off siliceous residue, washing well with hot water. Adjust volume of filtrate to 150 ml. Add 15 ml. clean mercury and electrolyse at a current of 5 amp. until colourless. Whilst electrolysis is proceeding the silica may be ignited, volatilised with hydrofluoric acid, any residue found fused with potassium bisulphate and added to the electrolysis. (Note this is not generally necessary for routine work.) Remove the mercury and adjust the acidity of the electrolyte to 10% free acid (concentrated acid by volume) by addition of hydrochloric acid. Cool to room temperature and precipitate the titanium with cupferron. Filter through pulp, washing with 10% hydrochloric acid containing cupferron; preserve the filtrate for aluminium. Ignite the titanium precipitate to TiO_2 and weigh. For routine work no further steps are necessary if the electrolysis was complete. For special work it is desirable to fuse the residue and check for impurities.

Aluminium

Add 50 ml. conc. nitric acid to the titanium filtrate and evaporate to SO_3 fumes. (This large addition of acid normally gives a colourless solution. Any organic matter remaining needs more nitric acid.) Add 20 ml. water, pass through a filter into a 150 ml. beaker: boil solution with ammon. persulphate to remove residual Mn. Boil off excess persulphate.

Add a little tartaric acid, make alkaline with ammonia and pass sulphuretted hydrogen. Filter, washing with alkaline tartrate solution containing hydrogen sulphide. Acidify and boil off hydrogen sulphide and filter. (Note for routine work this procedure, i.e., the sulphide precipitation may generally be omitted.)

To the clear solution add ammonia and 10% acetic acid to faint acidity to neutral red indicator. Adjust volume to about 150 ml., heat 50–60° C. and add 15 ml. 2% 8-Hydroxyquinoline reagent, followed by 50 ml. ammonium acetate solution. Allow

to stand warm with occasional stirring until precipitate coagulates. Filter through tared Grade 4 sintered Gooch, wash well with hot water, dry at 105–110° C. and weigh as Al. $(C_9H_6ON)_3$.

$$Al(C_9H_6ON)_3 \times 0{\cdot}0587 = \text{gr. Al.}$$

Ammonium Acetate—30%

8-*Hydroxyquinoline* 2%. Dissolve the solid in N acetic acid. Add ammonia until a permanent precipitate is just produced. Warm gently until precipitate redissolves and filter into stock bottle.

2 *N Acetic Acid.* 38·4 ml. B.P. acid diluted to 100 ml.

TUNGSTEN

Determination of Tungsten in High Speed Steels

This is a general method available for the estimation of tungsten in all steels. With low tungsten steels, however, cinchonine is made use of to ensure complete precipitation of the tungsten.

Method.—2 g drillings are weighed into a 400 ml. squat beaker and covered with 75 ml. hydrochloric acid (sp. gr. 1·16). When completely decomposed which may take several hours, cautiously oxidize at boiling point with nitric acid (sp. gr. 1·42) a few drops at a time until oxidation is complete and no further effervescence takes place.

The solution is evaporated to paste, and baked at the edge of the plate if it is desired to determine the silicon.

Add 50 ml. hydrochloric acid (conc.) and boil down to about 15 ml., remove from the plate, diluting with 250 ml. hot water.

Allow to stand overnight (or for at least 3 hours) to enable the yellow tungstic oxide to settle out of solution.

Filter through an ashless paper pad (Whatman No. 31) removing all the tungsten by the aid of a policeman from the sides of the beaker. Wash with hot 2% nitric acid together with a few drops of hydrochloric acid and finally with hot water.

The filter is transferred to a platinum dish (previously weighed). The tungstic oxide film remaining on the beaker and funnel is removed by a small piece of filter paper moistened with ammonia which is added to the dish.

After igniting and weighing, add a few ml. hydrofluoric acid. Dish is dried, ignited and reweighed. The difference between the first weight, empty dish and the last weight will give the weight of tungstic oxide. The difference between the second and third weights is the weight of silica present.

In the event of the tungstic oxide being contaminated (usually iron and/or chromium oxide) to a pronounced extent, the residue should be treated as in following paragraph.

A faint green may be corrected by deducting 2–3 milligrams from the weighed tungstic oxide. These traces are usually from imperfect washing whilst the heavy traces are due to incomplete breaking down in the hydrochloric acid.

If badly contaminated cover the residue with 5 g sodium carbonate and fuse for 10 minutes at 900° C. Melt is then cooled, extracted in water and boiled to achieve complete solution of the sodium tungstate.

$$WO_3 + Na_2CO_3 = Na_2WO_4 + CO_2$$

The oxide of iron is filtered off, washed and ignited to Fe_2O_3.

The chromium, in solution as sodium chromate, is acidified with sulphuric acid, cooled and determined by titrating with standard N/10 ferrous ammonium sulphate and potassium permanganate solutions.

$$1 \text{ ml. N/10 } KMnO_4 = 0{\cdot}00254 \text{ g } Cr_2O_3$$

The weights of Fe_2O_3 and Cr_2O_3 are then deducted from the impure WO_3 giving the true weight of tungstic oxide. Then the weight of

$$\frac{WO_3 \times 0{\cdot}793 \times 100}{2} = \% \text{ Tungsten}$$

Much of the tungsten that separates with the silicon will be lost if ignitions are made at the customary high temperatures, for tungstic oxide begins to volatilize at about 800° C.

If the silica is high, a separate sample should be taken and a temperature of at least 1000° C. should be reached before weighing the crude silica followed by a temperature of 750–850° C. after treatment with sulphuric and hydrofluoric acids.

With low tungsten steels. Cinchonine precipitation

In the above method with steels containing less than 1% tungsten there is a tendency to get low results owing to incomplete precipitation. In this case use the following method:

5 g steel dissolved as in previous method. The solution is oxidized with nitric acid, evaporated to dryness and baked for half an hour. Remove from plate and cool. Take up in 50 ml. HCl, evaporate to 15 ml. Dilute to 250 ml. with hot water, adding 10 ml. 5% cinchonine hydrochloride. Stir well and allow to

stand overnight. Filter, wash with dilute 2% nitric acid to which has been added a few ml. HCl.

Finish as in preceding method.

Tungsten powder. Precipitation with mercurous nitrate

5 g sample are fused in platinum dish with potassium bisulphate. Melt is extracted with boiling water and a little H_2SO_4. Filter and wash with hot water; all the iron will now be in solution. The residue containing the tungsten is extracted with ammonia. Make just acid with nitric acid. Add 20 ml. saturated solution mercurous nitrate and add a few drops of ammonia; *the liquid must not be made alkaline.*

Stir to precipitate mercurous tungstate—first precipitated as a yellow precipitate, changing to black. Warm and filter, washing with dilute mercurous nitrate. Ignite at a moderate red heat until all Hg is expelled

Cool and weigh as WO_3.

Silicon and Tungsten in Staybrite Steels containing Titanium

Dissolve 5 g of sample in 50 ml. HCl. Oxidize with HNO_3 and evaporate to dryness. Take up in HCl and evaporate to low bulk. Dilute with water to 200 ml. and allow to stand overnight. Filter through pulp, washing with 1:5 HCl. Transfer to platinum dish, ignite and weigh. Treat with HF and H_2SO_4 and ignite again.

The loss in weight represents SiO_2. The residue of WO_3 is covered with about 5 g of sodium carbonate and placed in a closed muffle for 20 to 30 minutes. Place crucible in beaker containing 100 ml. hot water. Allow to stand on edge of plate until melt is dissolved. Remove crucible and wash with hot water. Boil the solution and filter through pulp.

The insoluble sodium titanate is dissolved through the pad with dilute H_2SO_4, oxidized with H_2O_2 and finished colorimetrically. The weight of the titanium should be calculated to TiO_2 and the weight deducted from the WO_3.

Analysis of tungsten carbide alloys

Weigh 1 g of sample into porcelain crucible. Add 5 g potassium nitrate. Fuse gently, taking care to avoid any spurting. When reaction ceases, fuse gently for 1 hour. Extract melt in hot water. Filter. Insoluble contains Fe, Co, Si, and trace W. Ignite insoluble in same crucible fusion was made in. Dissolve in conc. HCl. Evaporate to dryness and bake. Redissolve in HCl and filter off WO_3 and SiO_2. Remove SiO_2 as above, ignite and weigh WO_3 residue (1).

To this filtrate add 4 ml. H_2SO_4 and take down to fumes. Cool. Rinse down sides of beaker with H_2O and fume again. Make alkaline with NH_4OH, boil and filter. Dissolve insoluble in 8 ml. of 1:3 H_2SO_4 and precipitate with NH_4OH. Filter, combining the filtrates, add 35 ml. of conc. NH_4OH to the filtrate and electrolyse at 0·75 amps. for Co.

The insoluble is dissolved in HCl, re-precipitated with NH_4OH, filtered, ignited and weighed as Fe_2O_3.

To the filtrate from the fusion

Add HCl (about 6 ml.) to drive off nitrous fumes. When all brown fumes are driven off add 50 ml. conc. HCl and boil down to 25 ml. Dilute and filter. Wash with hot 5% HCl. Clean the beaker with filter paper moistened with NH_4OH and add this to the insoluble for ignition. Ignite. Temperature should be 780–830° C. (not over 850° C.). Weigh as WO_3 (2).

Add 10 ml. HNO_3 to filtrate and boil to dryness.

Moisten residue with a small amount HNO_3 and take to dryness to expel chlorides. Dissolve residue in 100 ml. hot H_2O. Stir vigorously and add 20 ml. of 20% mercurous nitrate and 1 drop NH_4OH. Filter, wash with 1% mercurous nitrate and ignite. Weigh as WO_3 and add to (1) and (2) for total W.

Separation of tungsten from small amounts of elements such as tin, columbium, tantalum

Digest the fully ignited tungstic acid with a moderate excess of ammonium hydroxide and filter.

Residue must be carefully examined for tungsten because some elements, notably iron, carry down appreciable amounts of it.

For the separation of tungsten from large amounts of columbium, see under that element.

VANADIUM

Determination of Vanadium and Chromium Together

The chromium is estimated in exactly the same way as that given under chromium after the addition of 5 ml. syrupy phosphoric acid.

Excess of 0·1N solution of ferrous ammonium sulphate is run in to the estimation and shaken vigorously. The excess is titrated with 0·1N solution of potassium permanganate until a pink endpoint which persists for 1 minute is reached.

Add 1 or 2 drops sodium nitrite (approx. 5%) to destroy the excess of permanganate, and turn the solution to a clear green.

Shake well whilst adding about 2 g urea, to destroy excess of nitrite.

Add 4 ml. of sodium diphenylamine sulphonate indicator prepared as under, also 1 g sodium fluoride to help bring up the colour and allow to stand from 5–10 minutes until the purple colour is established.

Titrate with 0·1N ferrous ammonium sulphate.

The end-point is reached when one drop turns the solution from purple to sea green.

1 ml. 0·1 N potassium permanganate = 0·0051 g vanadium.

In the above method the vanadyl sulphate is reoxidized, to meta vanadic acid by titration with standard potassium permanganate.

The full equation is as follows :

$$10(VO)SO_4 + 2KMnO_4 + 12H_2O = 10HVO_3 + 7H_2SO_4 + K_2SO_4 + 2MnSO_4$$

Oxidized Diphenylamine Sodium Sulphonate Indicator

100 ml. of 0·01 M diphenylamine sodium sulphonate or 0·2 g solid and 25 ml. concentrated sulphuric acid are diluted to 300 ml. in a litre volumetric flask.

To this a 0·1N solution of potassium dichromate is added with frequent shaking, until a definite change of colour from blue to purple occurs, then add 8 ml. excess.

Now add 0·1N ferrous ammonium sulphate with repeated shaking, until one drop causes a visible change in colour from bluish green to a clear deep green in the liquid when viewed in the neck of the flask.

Make up to 1000 ml. with cold water and the indicator will slowly settle out of solution. Decant supernatant liquid and reserve the solid which is shaken with water before use.

Determination of Vanadium. Colorimetric

Applicable to carbon and most alloy steels excepting high chromium and high-speed steels.

Weigh out 1 g sample, dissolve in 25 ml. sulphuric acid (1 : 7), when completely dissolved oxidize with 30 ml. nitric acid (sp. gr. 1·42) and boil off the brown fumes.

Dilute to 150 ml. with hot water and add 1 g sodium bismuthate until a permanent precipitate is formed. Boil 5–10 minutes.

Remove from the plate, cool and add 2 or 3 crystals of ferrous ammonium sulphate (or a few ml. sulphurous acid ; in the latter

case boil off SO_2), and boil for a few minutes. The solution is removed from the plate and made quite cold, oxidized with potassium permanganate to a permanent pink, 5 ml. phosphoric acid is added, followed by hydrogen peroxide (10 vols.).

(The filtrate from the arsenite method for manganese can be taken for the vanadium.)

Prepare a blank solution containing a vanadium-free steel (for preference one containing approximately the same amount of alloying elements as in the assay) exactly as in the method outlined above.

Transfer the solutions to graduated cylinders, dilute to 200 ml., pour back into original beaker and compare in Nessler tubes 100 ml. capacity. Add to the vanadium standard small amounts of ammonium meta vanadate solution, shaking well and allowing to stand for 3 or 4 minutes after each addition, until colours match.

Standard Vanadium Solution: 1·148 g ammonium meta vanadate/litre.

1 ml. ammonium meta vanadate solution = 0·05% vanadium on 1 g.

Notes:

(1) Avoid exposure to strong sunlight.

(2) Excess hydrogen peroxide exerts a slight bleaching action.

(3) *Fluorides and hydrofluoric acid have no action.* (*See* '*Titanium*'.)

(4) For ideal conditions absence of nickel, chromium and molybdates are necessary.

(5) Acids intensify colour.

(6) The vanadium is oxidized to brown pervanadic acid.

Hydrogen peroxide.—It is very necessary to use the fresh AR reagent. If kept in stock for any appreciable time there is danger of deterioration.

Gravimetric Methods for Determination of Vanadium

Precipitation as mercurous vanadate and subsequent weighing as vanadium pentoxide V_2O_5.

Note: The method is applicable only in the absence of substances which give precipitates with mercurous nitrate solution, e.g. chromates, arsenates, molybdates, tungstates and phosphates.

Method.—Fuse 0·5 g of the finely ground ore with 20 g sodium carbonate and 3 g potassium nitrate. Extract with water.

Nearly neutralize with nitric acid, evaporate nearly to dryness, take up in water and filter.

Residue contains Al and most of the silica.

The alkali vanadate solution should be made faintly acid with nitric acid.

Add 5 ml. of 20 volume hydrogen peroxide and then mercurous nitrate solution dropwise until after the precipitate has settled a further addition of 2–3 ml. of the reagent causes no precipitation.

Boil the covered beaker for 30 minutes to destroy the excess of hydrogen peroxide and then allow the grey precipitate to settle.

Filter through a weighed porous porcelain crucible. Wash well with water containing a few drops of mercurous nitrate. Ignite over a Mekker burner placing the porcelain crucible in a metal crucible. Ignite gently, to prevent mechanical loss, and then at red heat to constant weight.

$$\text{Residue} = V_2O_5$$

Ignition should be conducted in a fume cupboard because the mercury fumes are poisonous.

Estimation of Vanadium in High Chromium Nickel Steels

Dissolve 0·5 g sample in 50 ml. (1 : 7) sulphuric acid.

When completely dissolved oxidize with 8 g ammonium persulphate or 3 g potassium chlorate, take down to 20 ml. or until crystals begin to separate.

Dilute with 400 ml. hot water and boil to take all salts into solution. Cool, precipitate the Fe, Ti and V with ammonium hydroxide and 5 g ammonium chloride.

Allow to stand on the edge of the plate for 10 minutes.

Filter through a folded Whatman No. 31 (18·5 cm.) Filter paper needs washing well with HCl and water until comparatively free from yellow chromium salts.

Redissolve in hot 50% hydrochloric acid washing the paper well until free from iron.

Add 10 ml. sulphuric acid and take to fumes.

Remove from the plate, cool and add 100 ml. hot water and take salts into solution.

Carry through exactly as in the colorimetric method.

It is necessary to destroy the yellow colour due to the titanium with 2 or 3 drops hydrofluoric acid.

Note: Avoid using excess of ammonia in the precipitation.

ZIRCONIUM

Zirconium in Steels containing Chromium

Weigh out 2–5 g sample into 750 ml. beaker, add 75 ml. sulphuric acid (1 : 4) and digest until dissolved.

Dilute to 300 ml. with water and heat to boiling, adding 15 ml. 10% sodium phosphate and allow to stand at 70° C. for 30 minutes.

Filter through a Whatmans No. 40 paper, washing with 5% ammonium nitrate solution (to remove excess of phosphate). Ignite in a platinum dish.

Cover the residue with 2 g sodium carbonate and fuse, extract in hot water, adding a little ashless pulp, again filtering through a No. 40 filter paper, washing with ammonium nitrate 5% strength.

Ignite in original platinum dish, then cover residue with 3 g potassium pyrosulphate and fuse until melt is quite clear.

Extract in 100 ml. 10% sulphuric acid and make the volume to about 200 ml. 5% sulphuric acid. Add 10 ml. sodium peroxide solution 10% (100 vols.) to keep titanium in solution as pertitanate. Add 10 ml. sodium phosphate (10% solution) and allow to stand for 30 minutes at 70° C. Filter, washing as before.

Ignite in the original platinum dish, cover the residue with 2 g sodium carbonate, fuse and extract in hot water, add a little ashless paper pulp filtering and washing as before.

Ignite to zirconium oxide in original platinum dish.

$$\frac{\text{Wt. of zirconium oxide} \times 0{\cdot}7403}{\text{Wt. taken}} = \% \text{ Zr}$$

Note: Prolonged washing with the ammonium nitrate solution will cause hydrolysis of the zirconium phosphate thus introducing errors.

Tungsten if present.—Should be removed at the beginning from hydrochloric acid solution, by oxidation with nitric acid to WO_3 and filtering.

To recover Zr the WO_3 is dissolved from the pad with ammonia and the residue remaining (containing the Zr) is dissolved in hot hydrochloric acid and added to the filtrate from the tungsten.

The solution now contains all the titanium. Add 75 ml. 1 : 4 sulphuric acid and boil down to fuming to remove the hydrochloric acid. Cool. Add 300 ml. hot water to take all the salts into solution. Proceed as in above method.

Determination of Zirconium in Steel

η-propyl arsonate precipitation and ignition to the dioxide ZrO_2.

Interfering Elements

A second precipitation is necessary when large quantities of iron

are present. Tungsten should be removed after oxidation. Zirconium is precipitated quantitatively in dilute sulphuric acid with η-propyl arsonic acid.

Method.—Weigh out 2 g of sample, cover with 50 ml. hydrochloric acid (conc.) and digest until dissolved. Oxidize with nitric acid (conc.) and take down to dryness, baking at 100–110° C. for half an hour. (Higher baking will bring about the formation of basic iron salts.)

Take salts into solution with 15 ml. hydrochloric acid and add 200 ml. hot water. Filter, wash the residue and reserve the filtrate. Ignite the residue in platinum crucible, add a few drops of hydrofluoric acid and heat to remove silica. Fuse the residue with sodium carbonate, extract in hot water, filter and wash. Ignite residue and fuse with potassium pyrosulphate, extracting in 100 ml. hot water together with 2 or 3 drops of sulphuric acid (conc.).

Filter and wash with hot water, adding the filtrate to the reserved filtrate.

Dilute to 150 ml. with hot water, bring to the boil and precipitate the Zr by the addition of 50 ml. aqueous 5% solution of η-propyl arsonic acid. Stand on the edge of the plate for one hour.

Filter through a Whatman's No. 31 paper pad, washing well with hot water. Transfer filter pad and precipitate into the original beaker and digest with 10 ml. hydrochloric acid (conc.).

Dilute with hot water to 150 ml., bring to the boil and add 10 ml. η-propyl arsonic acid.

Allow to stand one hour on the edge of the hot plate, filtering and washing as before, and removing every trace of precipitate from the sides of the beaker. Transfer to platinum crucible. Ignite at a temperature 1000–1050° C., to ZrO_2 which contains 74·03% Zr.

Estimation of Zirconium in Steels containing Columbium and Tungsten

Treat as in previous method as if tungsten were present.

Filter off silicon, and some of zirconium, columbium and tungsten oxides. Transfer to platinum crucible, igniting at sufficient temperature to burn off the paper, cool and weigh. This residue will also contain iron and phosphorus. Remove the silicon with a few drops of hydrofluoric acid—take to dryness. Fuse with 5 g potassium carbonate, cool and extract in 150 ml. warm water in a 400 ml. beaker. Boil well and filter through a No. 30 filter pad, washing the beaker thoroughly with a little 2% potassium carbonate.

Reserve the filtrate which contains columbium, tungsten and

phosphorus. Transfer the filter paper which contains the zirconium as potassium zirconate to the original beaker, washing in every trace of zirconium, add 20 ml. hydrochloric acid (conc.) and heat for 20 minutes.

Dilute to 200 ml. with hot water, add a few drops of methyl orange and make just ammoniacal. Boil well, filter and wash with hot water. Ignite in the same crucible as before and cool and weigh as mixed oxides of Fe, Zr, and P.

Recovery of the Zirconium

Fuse the mixed oxide of Fe, Zr and P obtained as above with potassium bisulphate (3 g). Cool and dissolve the melt in 10 ml. hydrochloric acid (conc.).

Add this solution to the first filtrate, and precipitate the zirconium with propylarsonic acid or as phosphate.

Ref. *Analysis of Steel*, Chemists United Steels Corporation, p. 257-8.

STELLITE

In these high cobalt, tungsten, carbon and chromium alloys, some difficulty may be experienced in breaking up the complex carbides and particularly is this so in the case of the higher carbon members of the series.

Sulphuric acid has practically no action on these alloys, so that the only method open is to take into solution with hydrochloric acid (See note).

It is usually only necessary to estimate combined carbon, iron, chromium, manganese and tungsten, the cobalt being taken by difference.

Chromium.—0·5 g sample is weighed out into a 650 ml. conical beaker—also weigh out at the same time a standard stainless steel to be carried through under the same conditions.

Dissolve in 70 ml. hydrochloric acid (sp. gr. 1·16) and when the carbides have completely broken down, oxidize with nitric acid (sp. gr. 1·42) add 7 ml. sulphuric acid (conc.) and fume (*not* too strongly). Remove from the plate, take up when cold with hot water, and boil clear. Continue method as for stainless steel either Vignal or persulphate method, adding 20 ml. sulphuric acid (sp. gr. 1·86) together with 5 ml. syrupy phosphoric acid to clarify the end-point. Make quite cold and titrate with 0·1 N ferrous ammonium sulphate and permanganate, exactly as for a stainless steel.

Silicon and Tungsten

Take 2 g and treat as in the usual method for tungsten steel.

Iron

0·5 g sample is dissolved in hydrochloric acid. When completely broken up oxidize with nitric acid. Add 7 ml. sulphuric acid (conc.). Take down to fuming. (Fume *not* too strongly.) Take up when cool, in hot water and boil clear, oxidize the chromium with 10 g ammonium persulphate, boil for half an hour. Remove from the plate, cool and precipitate the iron with ammonium hydroxide (sp. gr. 0·88). At the point of neutralization or just before (1) add 5 g ammonium chloride, allow to stand on the edge of the plate for 20 minutes, and filter through a large folded paper washing well with hot water.

Redissolve in hydrochloric acid and reprecipitate if necessary, (2) oxidizing the chromium in sulphuric acid solution as before. Finally the ferric hydroxide is dissolved in hydrochloric acid and 7 ml. sulphuric acid (conc.) added.

Take to fumes, remove from the plate, cool, and redissolve the sulphate of iron in hot water. Pass a current of washed H_2S gas through the solution for 20 minutes, place on the hot plate and boil for half an hour keeping the volume constant.

Cool and titrate with weak $KMnO_4$ (1·8234 g per litre) 1 ml. = 0·003221 g Fe.

The precipitate may also be dissolved in hydrochloric acid about 20 ml. (sp. gr. 1·16), heated to boiling and oxidized with 1 g potassium chlorate added in two portions and boiling well after each addition. Wash down the sides of the flask. Dilute to 100 ml., add 50% ammonium hydroxide solution carefully until $Fe(OH)_3$ is just *not* precipitated. Follow with 25 ml. sulphurous acid.

The solution is then diluted with 250 ml. hot water, the excess of the reducing agent expelled, the solution cooled to room temperature and titrated with 0·1 N potassium dichromate using potassium ferricyanide as external indicator. (1 ml. 0·1 N $K_2Cr_2O_7$ = 0·005585 g Fe.)

Note: When nickel is present, the stellites are soluble in sulphuric acid, and hydrochloric acid solution with subsequent fuming is not needed.

(1) As long as ammonium chloride is present in solution we have minimum amount of absorption of cobalt by the iron, but this will tend to cause a small amount of chromium to come out of solution and be precipitated by the ammonium hydroxide, and so a second precipitation of the iron is usually necessary.

In the absence of ammonium salts it is noticed that the more alkaline the solution from which the ferric iron has been precipitated, the greater is the nickel and chromium absorbed.

(2) After the sulphate has been dissolved, and if a green solution is noticed, this will be due to chromium, so remove by another persulphate oxidation of the chromium and further precipitation of the iron.

Carbon

Usually 1 g taken, finely ground, and covered with red lead—estimate as carbon in steel.

Manganese

ZnO separation, followed by sodium bismuthate or chlorate method quite satisfactory.

Cobalt

Usually by difference.

Typical Analyses

	C.C.	*Si*	*W*	*Cr*	*Co*	*Fe*
Deloro Grade 1	2·13	0·71	15·14	31·28	49·06	1·18
Haynes Grade 6	0·70	0·90	15·60	32·2	49·2	1·4
Haynes Grade 1	0·50	1·60	4·3	28·3	63·9	1·4
	0·80	1·90	13·2	28·9	51·5	3·7

FERRO ALLOYS

Manganese Alloys

Low Carbon Ferro Manganese C 0·25%		Manganese 92%
High Carbon Ferro Manganese C 6·9%		Manganese 82%
Silicon Spiegel C 1·5%	Silicon 16%	Manganese 20%
Spiegeleisen C 4·0%	Silicon 0·7%	Manganese 20%

All samples should be finely ground in an agate mortar.

Determination of Carbon

Weigh out 0·5–2 g sample according to carbon content, place in combustion boat covered with red lead. Ignition temperature 1000° C. Proceed as for 'Carbon in Steel'.

Silicon.—As in Steel '*Aqua Regia*' or 'Sulphuric Acid' method.

Sulphur.—Combustion method—or gravimetric barium chloride precipitation as barium sulphate.

Phosphorus.—Dissolve 1 g alloy in *aqua regia.* A few ml. HF added to remove most of the silica. Boil down to paste, take up in 20 ml. hydrochloric acid, evaporate to dryness and bake. (Not too strongly, to avoid formation of basic iron salts.) Take up in 20 ml. nitric acid (conc.) and evaporate to 10 ml., dilute with 100 ml. hot water and filter—oxidize with permanganate, reduce with hydrochloric acid or SO_2 and carry through as in 'Stainless Steel'.

Manganese.—Most manganese alloys are soluble in nitric acid; difficulty may be experienced in some alloys, in which case dissolve in *aqua regia,* removing the hydrochloric acid and finishing by the chlorate method.

It is usual to use the bismuthate method. Dissolve 0·11 g sample in 50 ml. nitric acid (sp. gr. 1·2). Digest until all the sample has been dissolved, adding a few drops of hydrofluoric acid if necessary. Boil off nitric fumes, cool and oxidize with 2 g sodium bismuthate, boil well until a slight precipitate is produced, then clear with 2 or 3 crystals ferrous ammonium sulphate. Boil for a few minutes, remove from the plate and cool.

If the manganese is high—transfer the solution containing the manganese to a 500 ml. flask, make up to the mark and shake well.

Pipette 50 ml. of solution into a 350 ml. flask, adding 35 ml. nitric acid (sp. gr. 1·2). Carry this on at exactly as in the bismuthate method, adding 2 g sodium bismuthate, allowing to stand for 10 minutes, with repeated shaking, afterwards filtering through an asbestos plug. Titrating with standard 0·1 N ferrous ammonium sulphate and permanganate. 1 ml. = 1% Mn on 0·11 g.

Silicon Alloys

High silicon low carbon alloys with or without graphite. Silicon 20–90%.

Graphite.—Determined as in ' Cast Iron'.

Carbon.—For total carbon use 2·727 g as in 'Steel'.

Silicon.—Alloys soluble in acid, attack with *Aqua regia.*

Alloys insoluble in acid have to be opened out by fusion. Fuse 0·5 g sample in nickel crucible with 4 g sodium peroxide

extract in 400 ml. beaker in presence of hydrochloric acid. Carry through in exactly the same manner as for silicon in steel. It is, however, necessary to evaporate and bake for the second time to obtain further traces of silica. Proceed as in steel.

If 'graphitic' silicon is observed, brush the residue into a nickel beaker, adding a solution of 25% caustic soda. Stand in a warm place until solution is complete, then wash carefully into a 400 ml. squat beaker containing 150 ml. hot water acidified with hydrochloric acid (50%).

Carry through the method as in 'Steel', evaporating the solution and carefully baking twice to obtain every trace of silica.

Ferro Tungsten and Tungsten Powder

Tungsten.—Weigh out 1 g sample into platinum crucible which has been previously weighed.

Add 10–15 ml. nitric acid (sp. gr. 1·2). When completely decomposed add cautiously 5 ml. sulphuric acid and take down to fumes on the hot plate.

Cool and extract the tungsten in a 400 ml. beaker, adding 20 ml. hydrochloric acid (conc.) and 100 ml. hot water.

Wash the crucible free from every trace of tungstic oxide, removing any remaining trace with a filter paper moistened with ammonia, and boil the solution down to 10–15 ml. Dilute with 250 ml. hot water and allow to stand overnight.

Filter exactly as described under 'Tungsten', washing with hot water containing a few drops of nitric acid.

Place on the suction pump and transfer to crucible. Ignite at 800–850° C.

Weigh as mixed oxide $WO_3 + Fe_2O_3$ (1)

Fuse ignited tungstic oxide with sodium carbonate to remove any trace of iron—this is filtered, well washed, dried and ignited to Fe_2O_3, and weighed (2).

Finally this is again fused with sodium carbonate to remove any remaining trace of tungstic oxide, well washed, dried, ignited as before.

Then % tungsten = (Wt. (1) — Wt. (2)) × 79·3.

Ferro Tungsten	Tungsten Powder
80/85%	98/99%

A rough check on tungsten powder is to roast to a constant weight and note the increase in weight.

Chromium Alloys

High carbon ferrochromium 70–75% chromium 6% C
Low carbon ferrochromium 75–80% chromium.

High carbon ferrochromium

Carbon.—Combustion carbon carried through on finely ground 0·5 g sample covered with preheated red lead.

Chromium.—Thoroughly mix and fuse 0·5 g sample in a nickel crucible with 8 g sodium peroxide, until the melt is quite clear, extracting the residue in 100 ml. hot water. Boil well and acidify with sulphuric acid (conc.).

If a brown coloration or pink colour is not observed add a few drops of permanganate 2% strength until a permanent pink persists. Boil well and add 2 or 3 crystals manganous sulphate and boil for a further 10 minutes. Cool and filter through asbestos pad.

Titrate with 0·1N standard ferrous ammonium sulphate and potassium permanganate.

1 ml. ferrous ammonium sulphate = 0·3467% Cr on 0·5 g sample.

Ferro Vanadium

Vanadium.—Digest 0·5095 g finely ground sample in 50 ml. (1 : 7) sulphuric acid, when completely dissolved oxidize with a few ml. nitric acid (conc.). (If an insoluble residue is noticed this must be filtered off, ignited, cooled well, mixed and fused with 2 g sodium carbonate together with 0·1 g potassium permanganate.) This is then cautiously acidified with sulphuric acid and added to the main solution.

Dilute the solution to 300 ml. with hot water bringing to the boil and oxidizing with potassium permanganate (10 g/litre) until after boiling a pink tint persists, showing the complete oxidation of the vanadium, and a slight brown precipitate is formed.

This is then cleared with a few drops of sulphurous acid and boiled well to entirely remove any trace of sulphur dioxide.

The solution is now cooled, 5 ml. phosphoric acid added and oxidation carried through exactly as in the method for chromium and vanadium.

When a permanent pink is established after allowing the solution to stand 5 minutes, destroy the excess of permanganate with 3 or 4 drops sodium nitrite (5% strength), shake well and add 8 ml. sodium diphenylamine sulphonate (prepared as in 'Vanadium'), shaking well before use and adding 1 g sodium fluoride. Allow to stand 5 minutes for the blue colour to develop, and titrate with

standard ferrous ammonium sulphate which has previously been standardized against standard 0·1 N permanganate.

$$V\ \% = \frac{\text{ml. ferrous ammonium sulphate}}{\text{weight taken}} \times 0{\cdot}5095$$

Typical Analysis

Ferro Vanadium — 35/50% V

Ferro Molybdenum—70/75% Mo

Molybdenum.—Weigh out 0·5 g sample into 400 ml. beaker, and decompose with 25 ml. nitric acid (conc.), together with 30 ml. hydrochloric acid (sp. gr. 1·16). Take down to 20 ml. and dilute with 100 ml. hot water.

Transfer to separating funnel, washing in every trace of the molybdenum solution.

Weigh out 20 g caustic soda into 650 ml. beaker, adding 250 ml. hot water. Bring to the boil and pour the acid solution containing the molybdenum in drops into the hot caustic soda solution, with vigorous shaking, finally washing into the caustic soda every remaining trace of molybdenum solution.

Transfer to 500 ml. flask, make up to the mark with boiling water and observe the temperature for correction. Transfer the solution back to 650 ml. conical beaker, shake well, and filter off 200 ml. of the clear molybdenum solution at the above temperature.

Transfer this clear solution to a 650 ml. conical flask, make just acid with hydrochloric acid (5 ml. excess), boil well and add 20 ml. 4% lead acetate solution followed by 50 ml. ammonium acetate exactly as made under the estimation of molybdenum.

Bring to the boil and allow to stand for one hour at 70° C. on the edge of the hot plate. Filter through a Whatman's No. 30 paper pad, washing well with hot water containing 2% ammonium acetate.

Carefully place on the suction pump, transferring the precipitate into a porcelain or silica crucible. Ignite at 650° to lead molybdate (higher temperature of ignition should be avoided); this should be quite white. Transfer the ignited lead molybdate to the original 650 ml. beaker and decompose with 25 ml. hydrochloric acid (sp. gr. 1·16), followed by a few ml. nitric acid (conc.).

Reprecipitate the molybdenum as lead molybdate without further additions of lead acetate, by diluting the clear solution to 300 ml. with hot water, adding ammonium hydroxide until neutralized, then add a further 5 ml. hydrochloric acid (sp. gr. 1·16), followed by a further 50 ml. ammonium acetate. Bring to the boil, allow to stand 1 hour as before and filter.

Ignite at 650° C. to lead molybdate.

$$\frac{PbMoO_4\ g}{\text{weight of fraction (0·2 g)}} \times 26{\cdot}14 = \%\ Mo$$

Ferro Titanium

Titanium.—0·5 g sample is dissolved in 50 ml. sulphuric acid, (1 in 7).

When completely dissolved the solution is removed from the plate and cooled.

Dilute with hot water to 200 ml. and neutralize with ammonia until a precipitate is formed; again cool. 10–15 ml. saturated sulphurous acid is added and the precipitate just taken into solution with a few drops hydrochloric acid (conc.).

10 ml. glacial acetic acid is added, followed by 25 g ammonium acetate—the solution is heated to boiling and the precipitate allowed to settle on the edge of the hot plate.

The precipitate is filtered on a Whatman's No. 31 filter paper and washed with very dilute (2%) acetic acid, dried and ignited.

Fuse cautiously the ignited residue with 4 g sodium carbonate in a platinum crucible. When the melt is clear, cool and extract in 200 ml. hot water. Filter and wash with a little 2% ammonium nitrate; dry and ignite. Cool.

Again fuse with 4 g sodium carbonate extracting with 15–20 ml. hydrochloric acid (conc.). Reprecipitate using 10 g sodium thiosulphate. The precipitated titanium is washed, dried, ignited and weighed.

Fuse the ignited residue with 4 g potassium pyrosulphate extracting in 100 ml. water, together with 10 ml. sulphuric acid (conc.). Cool, make up to 250 ml. with cold water.

Estimation of the iron

Take 10 ml. of this solution, add 1 ml. tartaric acid (50%) and 1 ml. thioglycollic acid, transfer to Nessler cylinders, make ammoniacal and compare the violet colour against a similar solution containing 10 ml. standard solution of ferric alum.

1 ml. = 0·0001 g Fe.

Calculate this to Fe_2O_3 and deduct from weight of precipitate after thiosulphate precipitation and ignition.

$$\text{Weight of } TiO_2 \times 0{\cdot}5995 = \text{titanium.}$$

Carbon free Ferro titanium 20–25% titanium.

Determination of Iron in Titanium Alloys

Fuse 0·5 g of sample with potassium bisulphate. Extract the melt with 10% sulphuric acid, keeping the volume of liquid as low as possible.

To the solution add 1 g tartaric acid. Pass hydrogen sulphide through the solution until the iron is completely reduced. Then make slightly alkaline with ammonia solution, and treat again with hydrogen sulphide to precipitate the iron as FeS.

Filter, washing the precipitate with dilute colourless ammonium sulphide. Dissolve the FeS in hot 1 : 1 hydrochloric acid. Boil down to *circa* 20 ml. Add a few drops of stannous chloride solution to just decolorise the iron. Cool to room temperature, dilute slightly, and add 15 ml. of saturated mercuric chloride solution. Add 50 ml. of phosphoric acid solution (*) and 2–3 drops of sodium diphenylamine sulphonate solution.

Titrate with potassium bichromate solution (2·832 g per litre).

$$1 \text{ ml.} = 0{\cdot}003221 \text{ g Fe.}$$

*Phosphoric Acid solution is made by diluting 150 ml. H_2SO_4 plus 150 ml. H_3PO_4 to 1 litre.

STANDARD SOLUTIONS FOR FERROUS ANALYSIS

Decinormal Sodium Carbonate

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$$
$$Na_2CO_3 = 105{\cdot}994$$

Weigh accurately a clean silica (or platinum) dish and a light glass sitrring rod, and into the dish weigh 8·5 g of pure sodium bicarbonate. Heat gently on a gauze, stirring continuously with glass rod to prevent spurting caused through the escape of CO_2 and H_2O. When all action has ceased, cool and reweigh, re-heat until constant weight is obtained, which should be 5·36 g Na_2CO_3.

Now weigh accurately, still using dish, 5·2997 g Na_2CO_3. Dissolve in water and make up to 1 litre at 60° F.

Decinormal Sulphuric Acid

$H_2SO_4 = 98{\cdot}08$ (sp. gr. 1·84)

Normal solution contains 49·04 grams/litre, i.e. $\frac{49{\cdot}04}{1{\cdot}84}$ ml./litre = 26·6 ml./litre.

Dissolve 26·6 ml. sulphuric acid (conc.) in water, cool, and make up to 1 litre. To prepare 0·1N or any other strength solution use this normal solution as required.

Standardize against 0·1N sodium carbonate solution using methyl orange as indicator.

Decinormal Caustic Soda

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

$NaOH = 40{\cdot}005$

Normal solution contains 40 g per litre.

Dissolve 40 g caustic soda in water, cool, and make up to 1 litre. For 0·1N solution dilute 100 ml. of N to 1 litre and standardize against 0·1N sulphuric acid using phenolphthalein as indicator.

1 ml. = 0·003374% P on 4 g sample = 0·0282 g oleic acid.

$$46NaOH + 2((NH_4)_3PO_4 12\ MoO_3) = 2Na_2HPO_4 + 21Na_2MoO_4 + 3(NH_4)_2\ MoO_4 + 22H_2O$$

Decinormal Potassium Dichromate

$$K_2Cr_2O_7 + FeSO_4 + 7H_2O = Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3\ 7H_2O$$

$$K_2Cr_2O_7 = \frac{294{\cdot}212}{6} = 49\ 035$$

For 0·1N soluton dissolve 4·9035 g pure salt in water and make up to 1 litre.

1 ml. = 0·005584 g Fe
= 0·0010986 g Mn (as $KMnO_4$)
= 0·0027465 g Mn (as MnO_2)

Weak Potassium Dichromate

This solution is used in conjunction with ferrous ammonium sulphate of a similar strength for estimation of chromium in nickel chrome steels where chromium does not exceed 2%.

Dissolve 2·832 g in water and make up to 1 litre.

This solution is sometimes known as $\frac{N}{17{\cdot}3}$. This however is only approximate.

1 ml. = 0·001572 g Mn (persulphate method)
= 0·0010 g Cr.

Decinormal Potassium Permanganate

$$10\ FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

$$5\ SbCl_3 + 2KMnO_4 + 16HCl = 5SbCl_5 + 2KCl + 2MnCl_2 + 8H_2O$$

$$KMnO_4 = \frac{158{\cdot}026}{5} = 31{\cdot}6052$$

Dissolve 3·1605 g pure salt in water and make up to 1 litre.

1 ml. = 0·005584 g Fe
= 0·00601 g Sb
= 0·0017265 g Cr
= 0·0010986 g Mn (as $KMnO_4$)
= 0·0027465 g Mn (as MnO_2)
= 0·0067 g $(COONa)_2$ (used as a standard)

Weak Potassium Permanganate

This solution is used in conjunction with weak $K_2Cr_2O_7$ and ferrous ammonium sulphate, for persulphate manganese and chromium estimations.

Dissolve 1·8234 g pure salt in water and make up to 1 litre.

1 ml. = 0·001 g Cr
= 0·003221 g Fe
= 0·003467 g Sb
= 0·00064866 g Mn (as $KMnO_4$)
= 0·0015845 g Mn (as MnO_2)
= 0·003865 g $(COONa)_2$

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + H_2O$$

Cf. *reactions with $KMnO_4$*

Decinormal Ferrous Ammonium Sulphate

$$FeSO_4\ (NH_4)_2SO_4\ .\ 6H_2O = \frac{392{\cdot}144}{10} = 39{\cdot}2144$$

Dissolve 39·2144 g salt in a fresh mixture of 500 ml. water, plus 100 ml. sulphuric acid (conc.), cool thoroughly and make up to 1 litre.

Standardize against 0·1N potassium permanganate or potassium dichromate. This salt whilst being considerably purer than ferrous sulphate is, to a considerable extent, hygroscopic and it is always

necessary to weigh out a little in excess of the above figure (i.e. up to 39·5 g).

For equivalents see 0·1N $KMnO_4$.

Weak Ferrous Ammonium Sulphate

Dissolve 22·622 g pure salt in a fresh mixture of 500 ml. water and 100 ml. sulphuric acid (conc.), cool thoroughly and make up to 1 litre.

Standardize against weak potassium permanganate, or potassium dichromate.

For equivalents see Weak $KMnO_4$.

(In practice it is necessary to weigh 22·8 g per litre, see note above.)

Decinormal Sodium Thiosulphate

$$Na_2S_2O_3 \cdot 5H_2O = \frac{248{\cdot}202}{10} = 24{\cdot}8202$$

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

Dissolve 24·8202 g pure salt in water and make up to 1 litre.

Standardize against copper sulphate or, preferably, electrolytically pure copper.

$$2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2$$
$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

1 ml. = 0·006357 g Cu.

Decinormal Iodine

$$I = \frac{126{\cdot}92}{10} = 12{\cdot}692$$

Dissolve 12·692 g re-sublimed iodine together with 30 g potassium iodide in water and make up to 1 litre.

Standardize against 0·1N sodium thiosulphate.

1 ml. = 0·005935 g Sn
= 0·00601 g Sb

When a titration is not interfered with by the presence of acid the following solution can be made.

Dissolve 4·9035 g $K_2Cr_2O_7$ in water, add 50 ml. of 30% sulphuric acid, cool and add a solution of 40 g KI in water. This solution contains 12·692 g iodine as above.

Weak Iodine for Sulphur

$$H_2S + I_2 = 2HI + S$$

This solution is calculated to liberate iodine in solution so that 1 ml. = 0·0005 g sulphur.

Dissolve exactly 1·5296 g pure potassium dichromate in water. Add 15 ml. sulphuric acid (1 : 2), cool, and add to this a solution containing 15 g potassium iodide and make up to 1 litre.

Standardize against a thiosulphate solution of similar strength or preferably against a steel of known sulphur content.

1 ml. = 0·010% S on 5 g sample
= 0·001983 g Cu

Weak Sodium Thiosulphate

This solution corresponds with the weak solution of iodine for sulphur estimation, and may be used if required in the estimation of sulphur or for standardizing the iodine after having previously standardized it against pure copper sulphate or electrolytic copper.

Dissolve 7·7422 g in water, make up to 1 litre.

For equivalents see Weak Iodine.

Decinormal Silver Nitrate

$$AgNO_3 + HCl = AgCl + HNO_3$$

$$AgNO_3 = \frac{169{\cdot}888}{10} = 16{\cdot}9888$$

Dissolve 16·9888 g pure salt in water and make up to 1 litre.

1 ml. = 0·003546 g Cl_2

Standard Silver Nitrate for Nickel

$$Ni = 4KCN = 2AgNO_3$$

$$58{\cdot}68 = 260{\cdot}416 = 339{\cdot}776$$

$$\frac{339{\cdot}776}{58{\cdot}68} = 5{\cdot}7907 \text{ g}$$

Dissolve 5·7907 g pure salt in water and make up to 1 litre. The salt should be sufficiently pure to be regarded as standard.

1 ml. = 0·001 g Ni

Standard Potassium Cyanide for Nickel

$$Ni = 4KCN = 2AgNO_3$$

$$58{\cdot}68 = 260{\cdot}416 = 339{\cdot}776$$

$$\frac{260{\cdot}416}{58{\cdot}68} = 4{\cdot}4372$$

Potassium cyanide cannot be obtained sufficiently pure to use the theoretical weight, so an excess must be taken and standardized against $AgNO_3$.

Dissolve 10 g KCN and 10 g (approx.) KOH in water and dilute to 2 litres. Titrate against $AgNO_3$ and from titration calculate the amount of water to add to 2 litres. On titration of this corrected solution they should balance.

Ammonium Vanadate

Dissolve 1·15 g pure salt and make up to 1 litre.

1 ml. = ·0005 g V

Ammonium Nitro Molybdate

For precipitation of phosphorus in steel and phosphor bronze.

Grind finely 100 g pure ammonium molybdate and dissolve in 200 ml. boiling water. Cool, and add 200 ml. ammonia (sp. gr. 0·880). In another vessel (winchester) mix 750 ml. of water and 500 ml. nitric acid (conc.) and cool. When both solutions are cold, add the ammonia solution to the nitric acid solution a few ml. at a time, dissolving, as soon as formed, any molybdic acid by shaking and cooling.

Ammonium Citrate

$3NH_4OH + H_3C_6H_5O_7 . H_2O = (NH_4)_3C_6H_5O_7 . H_2O + 3H_2O$

Weigh into large beaker 600 g finely divided citric acid. Add 100 ml. of water and dissolve with 380 ml. ammonia (sp. gr. 0·880.) Make up to 1 litre.

20 ml. = 12 g citric acid.

Ammonium .Acetate

Mix 488 ml acetic acid (glacial) with 500 ml. water and add 400 ml. ammonia (sp. gr. 0·880). Dilute as required.

Ammoniacal Cadmium Chloride

Mix 6·25 g pure cadmium chloride with 1 litre water and add 500 ml. ammonia (sp. gr. 0·880).

Phenolphthalein

Dissolve 0·2 g solid in 100 ml. methylated spirits.

Note: All reagents must be to A.R. standard, and freshly boiled, freshly distilled water should be used.

PART FOUR

Complete Analysis of Ores, including those of Aluminium, Copper, Iron, Lead, Manganese, Tin, Zinc.

Complete Analysis of Slags, including those of Copper, Iron, Lead, Tin.

CHAPTER VIII

THE ANALYSIS OF ORES

COMPLETE ANALYSIS OF ALUMINIUM ORE (BAUXITE)

The ore should be ground to pass a 90-mesh sieve.

Loss on Ignition

Heat 1 g in a platinum crucible at 900° C. for one hour.

Loss of weight = Loss on ignition.

Silica

Fuse the dried and ignited residue with 10 g of ' fusion mixture ' (see Chapter II) in a platinum crucible at a full red heat for 30 minutes, extract melt with water and HCl, evaporate to dryness, take up with HCl, dilute, filter, wash, ignite, weigh the impure SiO_2.

Fuse again with $KHSO_4$, extract melt with 5% H_2SO_4, filter, wash, dry, ignite, weigh SiO_2.

Mix the two filtrates and make up to 250 ml., using various amounts of the same, as under :

Ferric Oxide

Take 25 ml., reduce and titrate with $K_2Cr_2O_7$ as usual.

Alumina

Take 50 ml., dilute to 200 ml., heat, add NH_4OH, filter off $Fe_2O_3 + Al_2O_3 + TiO_2$, wash well, dry, ignite and weigh mixed oxides, deduct weight of Fe_2O_3 and TiO_2, and calculate Al_2O_3.

Titanium Oxide

Take 5 ml., make up to 15 ml. with 5% H_2SO_4, containing 20 ml. of H_2O_2 (20 vol.) per 500 ml. and estimate colorimetrically, as described under 'Titanium'.

Lime, Magnesia, Oxide of Manganese and Alkalis are estimated as in iron ores.

COMPLETE ANALYSIS OF COPPER ORE

(Bamford and Harris, *The Metallurgists' Manual.*)

Silica

Dissolve 1 g of finely-ground ore in 20 ml. of HNO_3 (1 : 1), evaporate to dryness, take up in HCl, dilute, boil, filter, wash, ignite and weigh SiO_2 and insoluble matter.

Sulphur

Boil filtrate and add 10 ml. $BaCl_2$ (10%), agitate and allow to settle, filter, wash well, ignite and weigh $BaSO_4$. Factor, $BaSO_4$ to S = 0·1374.

Add H_2SO_4 to filtrate, evaporate nearly to dryness, take up with H_2O, filter and discard the precipitate of $BaSO_4$.

Copper

Remove copper from the filtrate by electrolysis and weigh as such.

Iron, Aluminium and Phosphorus (as oxides)

Add 2 ml. HNO_3 to solution, after removal of copper, and precipitate the iron by the 'basic acetate' method (see Chapter II); filter, wash, ignite and weigh as $Fe_2O_3 + Al_2O_3 + P_2O_5$. Then Fe and Al can be estimated exactly as described under iron slags, but phosphorus is best determined on a separate sample, as described under Blast Furnace Slag.

Make the filtrate from the precipitation of Fe and Al alkaline with NH_4OH, warm and pass H_2S, filter off any precipitate of Zn, Mn, Ni and Co, wash, reserve filtrate for estimation of Ca.

Manganese

Dissolve the precipitate in hot conc. HCl with a little HNO_3, add 20 ml. sodium acetate and again pass H_2S, filter and estimate manganese in the filtrate, as described under 'Iron Slags'.

Cobalt

Dissolve the precipitate (containing Zn, Ni, Co) in *aqua regia*, make alkaline with KOH, add acetic acid until solution is acid, and then add conc. solution of KNO_2 equal to half the volume of solution, allow to stand for 24 hours, filter, wash with 10% solution of potassium acetate, dry and ignite the potassium cobalt nitrite, moisten with a little H_2SO_4 and re-ignite. The precipitate has the composition $2CoSO_4 + 3K_2SO_4$. (Factor = 0·1417.)

Alternatively, the cobalt may be estimated as Co_3O_4, as described under 'Cobalt'.

Nickel

To the filtrate from the cobalt precipitation add NH_4Cl and NH_4OH, just acidify with HCl, boil and add 20 ml. of a 1% alcoholic solution of dimethylglyoxime, make just ammoniacal and precipitate nickel, filter and treat as described under 'Nickel'.

Zinc

Pass H_2S through the filtrate from the nickel, after decomposing excess of glyoxime with HNO_3, and again making alkaline with NH_4OH; filter, wash, ignite carefully and weigh as ZnO, or redissolve and estimate by 'phosphate' method.

Calcium

Boil off H_2S from the filtrate obtained from precipitation of the Zn, Mn, Ni, Co; add NH_4OH and 10 ml. NH_4Cl, boil and add 20 ml. ammonium oxalate (both solutions 2N), allow to stand, filter, wash, dry, ignite and weigh as CaO. (Factor, CaO to Ca = 0·7143.)

Magnesium

To filtrate add 50 ml. strong NH_4OH and 5 ml. of a 20% ammonium phosphate solution, carefully and with constant stirring; allow to settle, filter, wash with dilute NH_4OH several times, dry, ignite and weigh as $Mg_2P_2O_7$. (Factor, $Mg_2P_2O_7$ to MgO = 0·2187.)

Silver

This is determined by the combined 'wet and dry' method described under 'Silver'.

COMPLETE ANALYSIS OF IRON ORES

The usual routine analyses conducted for blast furnace control are: moisture, total iron, ferrous iron, SiO_2, Al_2O_3, CaO, MgO, S and total loss on calcination.

Additional analyses are TiO_2 P_2O_5, MnO, combined H_2O, alkali and in the case of flue dust and sinter — C as coke.

The ironstone as received from the mines and quarries is thoroughly mixed and quartered until a sample of about 50 g is

obtained. This is dried at 105° C. and ground to pass a 100 mesh B.S.S. sieve. A suitable sample is taken for the determination of moisture. (This sample is retained in an airtight container.)

Moisture

10 g of sample are weighed on to a 3 in. cover glass and dried for 2 hours at 105° C. Cool and weigh.

Loss in weight × 10 = % moisture.

Total Iron

Solutions required: *Mercuric Chloride*, cold saturated solution.

Stannous Chloride

150 g $Sn Cl_2$ are dissolved in 500 ml. of 50% HCl by volume. Warm if necessary. When dissolved dilute to 2500 ml. with 50% HCl.

Barium Diphenylamine Sulphonate Indicator

1·2 g of barium diphenylamine sulphonate are dissolved in 60 ml. of H_2SO_4 (sp. gr. 1·84). When dissolved pour into 900 ml. of cold saturated sodium phosphate solution.

Standard Potassium Dichromate

8·77 g $K_2Cr_2O_7$ per litre.

1 ml. = 1% Fe on 1 g sample.

Standardize in either of the following ways:

(1) Dissolve 2·1 g of ferrous ammonium sulphate in 100 ml. of distilled water and 10 ml. of H_2SO_4 (sp. gr. 1·84), contained in a 400 ml. conical beaker. Cool and add 5 ml. of barium diphenylamine sulphonate indicator and titrate to purple colour. (30 ml. of $K_2Cr_2O_7$ solution should be used).

(2) 0·501 g of Swedish bar iron is weighed into a 500 ml. conical flask, to which has previously been added one or two grams. of $NaHCO_3$. 100 ml. of 20% H_2SO_4 are added and a bunsen valve is inserted. When complete solution has been effected, cool and dilute with about 200 ml. of cold distilled water. Add 5 ml. of indicator and titrate to purple colour.

(0·501 g of Swedish bar iron requires 50 ml. of $K_2Cr_2O_7$).

Method.—Weigh 0·5 g of sample, transfer to a 1 inch porcelain crucible and ignite at about 500° C. for 2 minutes in order to oxidize sulphides. Cool and carefully transfer to a 500 ml. conical flask. Moisten with about 10 ml. of distilled water and bring to the boil, whilst boiling add 50 ml. of HCl (sp. gr. 1·16)

and bring back to boiling. Add not more than 4 drops of HF and simmer to effect complete solution. (For calcined ironstone, solution is assisted by the addition of $SnCl_2$ solution until the brown colour is just discharged). Add stannous chloride from a burette until the yellow colour is just discharged and add 5 drops in excess. Dilute with cold distilled water to a bulk of about 300 ml. Add 15 ml. of mercuric chloride solution, mix thoroughly and allow to stand at least 5 minutes. Then add 5 ml. of barium diphenylamine sulphonate indicator and titrate with standard potassium dichromate.

$$\text{ml.} \times 2 = \% \text{ Fe on 0·5 g of sample.}$$

Ferrous Iron

Weigh 0·5 g of sample and transfer to a 500 ml. conical flask. Moisten with 10 ml. of water, add 1 g of $NaHCO_3$, 50 ml. HCl (sp. gr. 1·16) and 4 drops of HF. A bunsen valve is inserted and the contents of the flask digested for 5 to 10 minutes. Carefully wash and remove the bunsen valve and dilute with about 250 ml. of cold distilled water. Add 10 ml. of H_3PO_4 (sp. gr. 1·75) and 5 ml. of barium diphenylamine sulphonate indicator. Titrate with standard $K_2Cr_2O_7$ to a purple colour.

$$\text{ml.} \times 2 = \% \text{ Fe on 0·5 g of sample}$$

SiO_2, Al_2O_3, CaO and MgO

Weigh 0·5 g of sample and intimately mix with 3 or 4 g of fusion mixture in a platinum crucible of suitable size. Cover with a lid. Heat at about 500° C. for 5 minutes and finally at 950° C. for 15 minutes. Cool and place crucible and lid in a 6-inch porcelain basin. Extract the melt with a minimum of hot 50% HCl by volume. Wash the lid and crucible with cold distilled water and if necessary add 10–15 ml. of HCl (sp. gr. 1·16) to the crucible and bring to the boil on the hot plate. Transfer to the original extract and wash the crucible clean. Add a further 20 ml. of HCl (sp. gr. 1·16) to the dish and take carefully to dryness on the hot plate, taking care to avoid loss through spattering. Cool and moisten the dry cake with a few ml. of HCl (sp. gr. 1·16) from a burette. Take to dryness as before and bake strongly until the cake is almost black in colour. Cool and take up in 30 ml. of HCl (sp. gr. 1·16). When complete solution of the iron salts is effected, dilute with an equal volume of hot distilled water and boil until all salts are in solution. Filter through a pulp pad, which has been previously washed with 10 ml. of HCl (sp. gr. 1·16), into a clean 500-ml. conical flask. Clean the dish thoroughly, transferring precipitate and washings

on to the pad. Wash twice with hot 50% HCl (by volume), and finally six times with hot distilled water. Dry the pad by suction and transfer pad and precipitate to a suitable silica capsule. Ignite carefully, cool and weigh.

$$\text{Milligrams} \times 200 = \%\ SiO_2.$$

For more precise work SiO_2 should be determined by volatilization with HF.

The filtrate after removal of SiO_2 is used for Al_2O_3, CaO, and MgO.

The filtrate is oxidized with one or two ml. of HNO_3 (sp. gr. 1·42) and boiled until the bulk is reduced to about 100 ml. Cool and add 2 ml. of bromine. Make just ammoniacal and boil for 2 or 3 minutes to expel excess NH_3. Filter through a Whatman No. 31 12·5 cm. paper, retaining the filtrate in a clean 750 ml. conical flask. Wash three times with hot water. Transfer the mixed hydrates to the original 500 ml. conical flask and dissolve in 6 ml. of HCl (sp. gr. 1·16). Repeat the bromine and ammonia separation, and filter through the original paper. Wash four times with hot water, combining the two filtrates in the 750 ml. conical flask. This filtrate is used for the determination of CaO and MgO. The mixed hydrates are transferred to the original 500 ml. conical flask and dissolved in 6 ml. of HCl (sp. gr. 1·16). This solution is used for the estimation of Al_2O_3.

Alumina

To the solution of the mixed hydrates add 15 ml. of a cold saturated solution of sodium phosphate, carefully add NH_4OH (sp. gr. 0·880) until a faint permanent precipitate is formed. Just dissolve this precipitate with HCl (sp. gr. 1·16) added dropwise from a burette, and 1·5 ml. in excess. Then add 12 ml. of glacial acetic acid and 10 g sodium thiosulphate crystals. Dilute with boiling distilled water to about 350 ml. and boil for 10–15 minutes. Add 5 ml. of ammonium acetate and boil for a further 5–10 minutes. Filter through a Whatman No. 31 12·5 cm. paper, washing 12 times with hot distilled water. Transfer to a silica capsule and dry on the hot plate until paper is charred and the precipitated sulphur is eliminated. Ignite gently at first and finally at about 900° C. for 5 minutes. Cool and weigh as $Al\ PO_4$. A blank of 2 milligrams is deducted.

$$\text{Milligrams} \times 83{\cdot}6 = \%\ Al_2O_3 \text{ on } 0{\cdot}5 \text{ g sample.}$$

If appreciable amount of TiO_2 is present, or suspected, a variable proportion of this oxide will be precipitated with the

$AlPO_4$ and the method adopted for its separation from the combined phosphates after ignition is as follows :

Titania

The ignited $Al\,PO_4$ is fused with 2 or 3 g of fusion mixture in a platinum crucible. Extract the melt with hot distilled water. The alumina remains in solution, whilst TiO_2 is precipitated. Filter through a pulp pad, retaining the filtrate in a 600 ml. conical flask. Wash the pad and precipitate five times with hot water. Remove filtrate for determination of Al_2O_3 as previously set out. The pad and precipitate is dried by suction and ignited in a silica capsule. Cool and add a small piece, (about 1 g) of potassium bisulphate. Carefully fuse for 2 or 3 minutes. The melt is cooled and extracted in a clean 250 ml. squat beaker with 30 ml. 5% H_2SO_4. Cool, filter if necessary, and transfer to 100 ml. Nessler tube. Add 2 ml. of H_2O_2 (10 vols.) and the yellow colour is compared with a standard solution of TiO_2.

Standard Solution of TiO_2

Weigh 0·75 g K_2TiF_6 into a platinum dish. Two or three ml. of H_2SO_4 (sp. gr. 1·82) are added and evaporated to strong fumes. The procedure is carried out three times in order to expel all the fluorine. The mass is dissolved in 5% H_2SO_4 and diluted to 250 ml. Standardization is not necessary as $K_2\,Ti\,F_6$ is exceptionally pure.

$$K_2\,Ti\,F_6 \rightarrow TiO_2$$
$$240{\cdot}3 \qquad 80{\cdot}09 \quad \text{i.e. } 1\ TiO_2 \equiv 3\ K_2TiF_6$$
$$\therefore\ 0{\cdot}75\ g\ K_2\,Ti\,F_6 \equiv 0{\cdot}25\ g\ TiO_2$$
$$\therefore\ \text{diluted to } 250\ ml. \quad 1\ ml. \equiv 0{\cdot}001\ g\ TiO_2$$

Lime

The filtrate from the Br_2 and NH_4OH separation is brought to the boil. Carefully add 20 to 25 ml. of a cold saturated solution of ammonium oxalate. Continue boiling for 5 minutes and allow to stand in a warm place for 30 minutes. Filter through a pulp pad and wash six times with warm water (40 to 50° C.). The filtrate and washings are retained in a clean 900 ml. beaker. After washing the original 750 ml. flask free of ammonium oxalate, add to it 50 ml. of 10% H_2SO_4. Transfer pad and precipitate to the flask and shake vigorously to break up the pulp pad. Add 200 ml. of boiling water and titrate at a temperature of 70° C. with N/5·6 $K_2Mn_2O_8$.

1 ml. of N/5·6 $K_2Mn_2O_8 \equiv 1\%$ CaO on 0·5 g sample.

Standard $K_2Mn_2O_8$

Dissolve 5·75 g $K_2Mn_2O_8$ in about 250 ml. of warm water. Filter through an ignited asbestos pad. Dilute to 1 litre with cold distilled water.

Standardize against pure sodium oxalate.

Weigh 0·5 g of A.R. sodium oxalate into 400 ml. conical beaker. Dissolve in 100 ml. of 10% H_2SO_4. Heat to about 80° C. and titrate at a temperature 70–75° C.

0·5 g A.R. $Na_2C_2O_4$ requires 41·8 ml. of N/5·6 $K_2Mn_2O_8$.

Rapid Determination of CaO

Weigh 0·2 g of sample into a 1-inch porcelain crucible and ignite for 2 minutes at about 500° C. Cool and carefully transfer to a clean 400 ml. beaker, marked at 50 ml. and at 100 ml. From a burette, add 10 ml. of HCl (sp. gr. 1·16) and digest for 2 or 3 minutes and then add 0·2 g of NaF. Digest until residue is white and dilute with about 20 ml. hot water. Carefully add 25% NH_4OH until a precipitate just forms. Clear with 8 drops HCl (sp. gr. 1·16) and dilute to 50 ml. mark with hot distilled water. Now add 2 g of ammonium oxalate crystals and shake well until all the iron is reduced and calcium oxalate is precipitated. Dilute to 100 ml. mark with boiling water and boil for 2 minutes. Allow to stand 10 minutes. Filter and wash as previously set out. Titrate with N/14 $K_2Mn_2O_8$.

1 ml. N/14 $K_2Mn_2O_8 \equiv$ 1% CaO on 0·2 g sample
N/14 $K_2Mn_2O_8$ contains 2·22 g per litre.

Magnesia

The filtrate from the CaO separation, contained in a 900 ml. beaker is acidified with 70 ml. of HNO_3 (sp. gr. 1·42) and evaporated to dryness. A glass rod or a few small pieces of porcelain minimize bumping during this evaporation. Moisten the dry residue with 10 ml. of HCl (sp. gr. 1·16) and about 20 ml. of hot distilled water. Boil to effect complete solution. Make just ammoniacal, using methyl orange as an indicator. Filter through a pulp pad retaining the filtrate in a 500 ml. conical flask. Wash five times with hot water. The bulk at this stage should be about 150 ml. The fitrate is just acidified with HCl (sp. gr. 1·16) from a burette and then add 10 ml. of cold saturated sodium phosphate solution. Now add 50 ml. of NH_4OH (sp. gr. 0·880) and insert a well fitting rubber bung. Shake vigorously for 2 or 3 minutes and allow to stand several hours in a trough of cold water. Filter through a pulp pad. Remove all precipitate adhering to the sides

and bottom of the flask with a 'bobby'. Wash at least six times with cold 5% NH_4OH. Transfer pad and precipitate to a silica capsule and ignite gently at the front of the muffle until all paper is burnt. Ignite finally at 900° C. to $Mg_2P_2O_7$, cool and weigh.

Milligrams × 72·4 = % MgO on 0·5 g sample.

Rapid MgO for Furnace Control

Solutions required:

Acid solvent. 80 ml. HCl, 40 ml. HNO_3, 10 ml. H_2SO_4

Ammonium carbonate. 30 g in 100 ml. H_2O (freshly prepared).

Weigh 0·5 g of sample into a 1 inch porcelain crucible. Gently ignite for 2 minutes at mouth of the muffle. Cool and transfer to a 250 ml. squat beaker. Add 15 ml. of acid solvent and 2 drops HF. Simmer until dissolved and then take to fumes. Cool and dilute with 80 ml. H_2O and 4 ml. HNO_3 (sp. gr. 1·20). Boil, and carefully add 2·5 g solid ammonium persulphate. *Boil for 7 minutes* to precipitate any Mn which may be in the sample. Filter through a pulp pad, retaining filtrate in a 400 ml. tall beaker. Wash three times with hot water. Add ammonia in slight excess and 1·5 g solid ammonium oxalate. Boil until dissolved and *carefully* add 10 ml. ammonium carbonate solution. Boil a further minute. Allow to stand for 1 or 2 minutes and filter through a Whatman No. 41 paper into a 750 ml. conical flask. Wash once with hot water. Transfer mixed precipitate to the original 400 ml. beaker and re-dissolve in a minimum of HCl. Again just make ammoniacal and add 5 ml. saturated ammonium oxalate and 10 ml. ammonium carbonate. Filter and wash once. Repeat this last separation, washing the mixed precipitate three times with hot water. To the combined filtrate add two or three drops of litmus or other suitable indicator and HCl until just acid. Add 5 ml. saturated sodium phosphate solution and 50 ml. ammonia. Stopper and shake for 5 minutes. Cool and allow to stand for 30 minutes. Filter through a pulp pad and wash well with 5% ammonia (8 washings). Dry the pad and transfer to a silica capsule, ignite at mouth of muffle until fully charred and finally at full heat of muffle. Cool and weigh.

$Mg_2P_2O_7$ × 72·4 = % MgO (on 0·5 g of sample).

For those operators who object to the use of HF in dissolving the sample the following procedure may be adopted.

Weigh 0·5 g of sample into a 1 inch porcelain crucible. Ignite gently for two or three minutes. Cool and carefully transfer to

platinum crucible. Intimately mix with 1 g of fusion mixture and place in the muffle at a temperature of about 950° C. for 10 minutes. Cool and place the crucible in a 250 ml. squat beaker and extract the fritted mass with 10 ml. of 25% H_2SO_4. Simmer until dissolved, adding small quantities of hot water, as needed, to prevent precipitation of SiO_2. Dilute with 80 ml. of hot water and add 2·5 g of ammonium persulphate. *Boil for 7 minutes* to precipitate any manganese which may be in the sample. Filter through a pulp pad, retaining the filtrate in a 400 ml. tall form beaker. Wash three times with hot water. Add NH_4OH (sp. gr. 0·880) in slight excess, using litmus as an indicator. Then add 1·5 g solid ammonium oxalate and boil until dissolved. Carefully add 10 ml. of freshly prepared ammonium carbonate solution, (30%), and boil for 1 minute. Allow to stand for 2 minutes and filter through a Whatman No. 31 12·5 cm. retaining the filtrate in a 750 ml. conical flask. Wash once with hot water. Transfer the mixed precipitate to the original 400 ml. beaker and dissolve in a minimum of HCl. Again just make ammoniacal and add 5 ml. of saturated ammonium oxalate solution and 10 ml. of ammonium carbonate solution. Filter and wash once with hot water. Repeat this last separation, washing the mixed precipitate three times with hot water. The combined filtrates and washings should not exceed 300 ml. Just acidify with HCl (sp. gr. 1·16), 15 ml. should be sufficient, and then add 10 ml. of cold saturated sodium phosphate solution. Now add 50 ml. of NH_4OH (sp. gr. 0·880) and insert a well fitting rubber bung, shake well for 5 to 7 minutes and allow to stand 20 to 30 minutes in a trough of cold water. Filter through a pulp pad and wash eight times with cold 5% NH_4OH after removing all the precipitates adhering to the sides and bottom of the flask. Dry by suction and transfer pad to a silica capsule. Ignite gently at the front of the muffle until all the paper is burnt. Ignite finally at 900° C. to $Mg_2P_2O_7$. Cool and weigh.

$$Mg_2P_2O_7 \times 72{\cdot}4 = \% \text{ MgO on } 0{\cdot}5 \text{ g sample.}$$

Total Calcination

Weigh 1 g of sample into a 1 inch porcelain crucible. Ignite gently, at about 500° C. for 5 minutes and for a further 30 minutes at 950° C. Cool and weigh.

$$\text{Loss in weight} \times 100 = \% \text{ total calcination.}$$

Total Sulphur

Weigh 1 g of sample into a 250 ml. squat beaker. Moisten with 5 ml. of distilled water and add a few small crystals of $KClO_3$.

Then add 15 ml. of *aqua regia* (5 ml. HNO_3 (sp. gr. 1·42) and 10 ml. HCl (sp. gr. 1·16)). Evaporate carefully to dryness and bake for 20 minutes. Cool and add 10 ml. HCl (sp. gr. 1·16) from a burette and evaporate to a paste. Cool and add 5 ml. HCl from a burette and dilute with 15 to 20 ml. of hot distilled water. Boil and filter through a pulp pad, wash four times with hot water and retain the filtrate in a 250 ml. tall beaker. Precipitate the sulphur by the addition of 15 ml. of filtered 10% $BaCl_2$ at about 70° C. Bring to the boil and maintain boiling for 5 minutes. Allow to stand in a warm place for 3 hours. Filter through a pulp pad, previously washed with 5% HCl. Wash twice with cold 5% HCl and finally with warm distilled water. Dry pad by suction and transfer to a silica capsule. Ignite gently at the front of the muffle and finally at dull red heat until white. Cool and weigh as $BaSO_4$. Use electric plate throughout. If gas plates are used a blank estimation should be conducted.

Milligrams $BaSO_4 \times 13{\cdot}74 =$ % sulphur on 1 g.

Rapid Determination of Sulphur

Weigh 1 g of sample and intimately mix with 0·2 g of CaO and 0·2 g MnO_2, both to be free from sulphur. The mixture is carefully transferred to a 1 inch porcelain crucible and ignited in an electric muffle for 10 minutes at 500 to 550° C. Cool and carefully transfer the ignited ironstone to a 250 ml. squat beaker.

Add from a burette 7 ml. of HCl (sp. gr. 1·16.) Cover with a watch glass and just bring to the boil. Digest for 5 to 10 minutes on the electric hot plate but do not maintain boiling. Dilute with about 10 ml. hot distilled water and boil for 1 minute. Filter at once through a pulp pad into a 250 ml. tall beaker. Wash four times with hot distilled water and precipitate the sulphur with 15 ml. of filtered 10% $BaCl_2$. Proceed as set out previously.

The addition of CaO and MnO_2 may be omitted if the ironstone contains appreciable CaO (above 5%) or the total sulphur is low. 2·7% CaO absorbs 1·5% S.

P_2O_5

Weigh 1 g. of sample into a 250 ml. squat beaker, dissolve in 15 ml. of *aqua regia* and evaporate to dryness. Bake for 10 minutes. Cool and re-dissolve the cake in 10 ml. of HCl (sp. gr. 1·16). Evaporate carefully to a paste. Take up in 25 ml. HNO_3 (sp. gr. 1·20) and filter through a pulp pad into a 400 ml. tall conical beaker. Bring to the boil and oxidize with 0·2 g of $K_2Mn_2O_8$. Clear the precipitated MnO_2 with a few crystals $FeSO_4$ and dilute with 25 ml. of cold distilled water. Now add 5 ml. NH_4OH (sp.

gr. 0·880) and swirl the beaker to dissolve precipitated iron hydroxide from the sides of the beaker, boil, and precipitate P with 20 ml. of ammonium nitro-molybdate. Shake for 2 minutes and allow to stand for 10 minutes. Filter through a pulp pad, washing twice with 2% HNO_3 solution and finally free from acid with 2% KNO_3 solution. Titrate with N/1·35 NaOH and N/1·35 H_2SO_4 using phenolphthalein as indicator.

N/1·35 NaOH = 34 g per 1000 ml.
N/1·35 H_2SO_4 = 20 ml. per 1000 ml.
0·5% phenolphthalein in industrial spirit

Ammonium Molybdate Solution

375 g ammonium molybdate crystals dissolved in 2000 ml. distilled water.

Ammonium Nitro Molybdate

1000 ml. of ammonium molybdate solution poured into 1000 ml. of HNO_3 (sp. gr. 1·20).

MnO

Weigh 0·1 g of sample and intimately mix with 1 g of fusion mixture in a platinum crucible. Fuse for 10 minutes at 950° C. Cool and extract the melt with 20 ml. of Mn solvent in a 250 ml. squat beaker and boil to effect complete solution. Transfer to a 250 ml. conical flask and dilute to a bulk of about 80 ml. with hot distilled water. Add 1 ml. of 1% $AgNO_3$ solution and 1 g of ammonium persulphate crystals. Boil for 2 minutes, make quite cold and titrate with standard sodium arsenite solution.

1 ml. Na_3AsO_3 = 0·1% Mn, 0·129% MnO } on 0·1 g sample.

Standard Sodium Arsenite

1·28 g As_2O_3 + 10 g Na_2CO_3 are dissolved in hot water. Filter, cool and dilute to 4000 ml.

Manganese Solvent

2100 ml. H_2O
450 ml. HNO_3
150 ml. H_2SO_4

Determination of Alkalis in Ironstones

Weigh 3 g of the ore into a porcelain dish and dissolve in HCl and a few drops of HNO_3, evaporate to dryness. (No need to bake.) Redissolve in 10 ml. HCl and 20 ml. water, dilute and filter

into porcelain dish. Ignite the insoluble residue in a platinum crucible and treat it with from 10 to 30 drops of H_2SO_4 and sufficient HF to decompose all silicates. Evaporate down till all the H_2SO_4 is driven off, dissolve in water, with a little HCl if necessary and add to the filtered ferric solution. Neutralize the bulk of the acid, add a small excess of $BaCl_2$ and filter off the precipitated $BaSO_4$. Heat the filtrate to boiling, add an excess of ammonium carbonate, make up to 305 ml. and preserve 200 ml. of the clear filtrate. In order to detect any remaining Fe, Al, Mn, Ba, Ca, Mg or P, evaporate the filtered 200 ml. to dryness, bake on the plate, extract with hot water and filter off any insoluble portion.

The clear filtrate is acidified with HCl, re-evaporated to dryness in a tared dish, ignited to very dull redness to drive off ammonium salts and weighed as a mixture of sodium and potassium chlorides.

To the residue in the dish, add a little water, in which the residue should dissolve perfectly, and a solution of platinic chloride. Evaporate on the water bath until the mass in the dish solidifies on cooling, add a little water to dissolve the excess of platinic chloride, and then an equal volume of alcohol. Filter on a Gooch crucible, wash with alcohol until washings run through perfectly colourless, dry at 120° C. and weigh as potassium platinic chloride. This weight multiplied by 0·19411 gives the weight of K_2O. Then multiply the weight of potassium platinic chloride by 0·30712 which gives the weight of KCl. Subtract this from the weight of the mixed alkali chlorides previously obtained and the difference is the weight of NaCl, which, multiplied by 0·53077, gives the weight of Na_2O.

Carbon as Coke in Blast Furnace Flue Dust and Sinter

Weigh 1 g of sample into a 250 ml. tall beaker. Moisten with 10 ml. of hot water and add 0·7 g NaF. Boil until the sodium fluoride is dissolved and then add 50 ml. of boiling HCl (sp. gr. 1·16). Impart a swirling motion to the beaker to avoid clotting. Simmer gently for 20–30 minutes and dilute with 50 ml. hot distilled water. Simmer for a further 10 minutes and filter through a wet Whatman No. 54 12·5 cm. filter paper. Wash twice with cold 5% HCl and finally five times with hot water. Wash the carbon, as coke from the paper into a 3 inch silica dish with a fine jet of warm water, and evaporate to dryness on the water bath. When completely dry, cool and weigh. Ignite at about 900° C., cool and re-weigh. The loss in weight × 100 = % C as coke on 1 g sample.

Combined Water. The following apparatus is required :

A Pyrex glass tube $\frac{1}{2}$ inch diameter by 12 inches long is fitted

with well fitting stoppers. At the inlet end is connected some suitable dessicant, such as H_2SO_4, $CaCl_2$ or Anhydrol. The exit end carries a weighed calcium chloride tube, connected to a gentle suction.

Method.—Weigh 1 g of sample and transfer to a previously ignited porcelain boat.

Place the boat and its contents just within the exit end of the Pyrex tube and insert stopper.

Commence suction and apply local heat (bunsen burner) to maintain the boat at a temperature of about 300° C. for 10–15 minutes.

Re-weigh the $CaCl_2$ tube.

Increase in weight × 100% = combined H_2O.

COMPLETE ANALYSIS OF LEAD ORE (GALENA)

[J. J. Morgan, *The Analysis of Ores, Metals and Fuels.*]

Moisture

Estimate on 100 g by heating to constant weight in a steam oven. Loss = moisture %.

Siliceous Matter

Dissolve 1 g in 20 ml. HNO_3 (sp. gr. 1·4), add 1 ml. bromine and digest, at gentle heat, transfer to porcelain dish, add 2 ml. H_2SO_4, evaporate to fumes, cool, add 100 ml. H_2O, filter, wash, dry, transfer to weighed crucible, ignite paper separately, moisten ash with a drop of HNO_3, then a spot of H_2SO_4, evaporate off acid, ignite and weigh. Weight = SiO_2 + $PbSO_4$.

Boil precipitate with ammonium acetate, to which NH_4OH has been added, allow to settle and filter, repeat the treatment, wash well, dry, ignite and weigh SiO_2.

Lead

Difference between first and second weighing gives *approximate* lead content. For accurate determination, titration with ammonium molybdate on a separate sample is recommended.

Silver

Unless the ore contains a fair amount of silver, it is not advisable to estimate in the 'wet' way on such a small sample. The authors advise the running of a 'dry' assay of lead ore, and subsequent cupellation for silver, as described under 'Silver'.

Copper

Pass H_2S through the filtrate from the estimation of SiO_2 (and Pb), filter, attack the precipitate with Na_2S to dissolve out Sb_2S_3, dissolve the CuS with HNO_3 and estimate the copper by titration with $Na_2S_2O_3$, or electrolytically.

Antimony

Acidify the filtrate from the Na_2S treatment of H_2S precipitate, and pass H_2S, allow to stand, filter, wash, dry, ignite carefully (separately from paper), moisten with a little fuming HNO_3, evaporate carefully, ignite strongly and weigh as Sb_2O_4. (Factor = 0·7895.)

Iron

Boil off H_2S from the original filtrate from H_2S precipitation of copper, oxidize with HNO_3, add $(NH_4)_2CO_3$ and redissolve the *faint* precipitate obtained with a little HCl, add ammonium acetate, and boil, filter, wash, dissolve precipitate in a little HCl, reprecipitate and redissolve. To the combined filtrate add water and estimate iron by precipitation with NH_4OH, wash, ignite and weigh as Fe_2O_3. (Factor = 0·6994.)

Zinc

Acidify filtrate with acetic acid, pass H_2S, filter, wash, dissolve precipitate in a little HCl, adjust acidity and estimate zinc by the 'phosphate' method.

Sulphur

Estimate exactly as described in 'Copper Ore'.

COMPLETE ANALYSIS OF MANGANESE ORE (PYROLUSITE)

[Brearley and Ibbotson.]

Silica and Barium Oxide

Digest 1 g with 20 ml. HCl, evaporate down, add 3 ml. HCl and 150 ml. H_2O, add 1 ml. H_2SO_4, and allow to stand. Filter, ignite precipitate, fuse with Na_2CO_3, extract with HCl and a drop of H_2SO_4, allow to stand, filter, ignite and weigh $SiO_2 + BaSO_4$.

Volatilize off SiO_2 with HF and H_2SO_4. Loss = SiO_2. Weigh residue as $BaSO_4$. Calculate to BaO. (Factor = 0·6570.)

To the filtrate from this fusion and extraction add NH_4OH, and

filter off Fe and Al hydroxides and add to the precipitate obtained below. The filtrate contains lime and should be added to the main solution below.

Iron, Aluminium

To the main filtrate add 5 g NH_4Cl and an excess of NH_4OH, filter off Fe and Al. Dissolve this precipitate, together with any small amount obtained above, in HCl, and estimate Al by the 'phosphate' method. Boil filtrate with HNO_3, and precipitate Fe with NH_4OH, redissolve in HCl and estimate by $K_2Cr_2O_7$ in the usual way.

Manganese

To the main filtrate add water, and precipitate manganese by means of Br and a small excess of ammonia, boil and filter *quickly*, wash with 3% HNO_3, ignite at high temperature to Mn_3O_4. (Factor = 0·7205.)

As a more accurate check, estimate the manganese on a separate sample, as described under 'Manganese'.

Lime

To the filtrate add NH_4OH and ammonium oxalate, filter and estimate CaO as usual.

Sulphur (total)

Digest 2 g with HCl in presence of $KClO_3$, filter, fuse the residue with Na_2CO_3, extract melt with H_2O, filter, mix the two filtrates, adjust the acidity with NH_4OH so as to make faintly acid, precipitate with $BaCl_2$, and weigh as $BaSO_4$ as usual.

Phosphorus

Attack 2 g with HCl, filter, voltalize residue with HF and H_2SO_4, add the H_2SO_4 solution to the main filtrate, precipitate iron and phosphorus as a basic ferric compound, redissolve in HNO_3, and estimate phosphorus by the lead molybdate method as described under 'Phosphorus'.

COMPLETE ANALYSIS OF TIN ORE (CASSITERITE)

[Morgan.]

Moisture

Determine on 100 g, by heating in a steam oven at 100° C. until constant weight is obtained. Loss = percentage of moisture.

Tungstic Acid

Digest 2 g of the dried and finely-powdered ore with 50 ml. HCl and 2 ml. HNO_3, dilute, filter, wash, digest the residue with a few millilitres of strong ammonia, filter into a weighed porcelain dish. Repeat the treatment with ammonia, evaporate the combined filtrates to dryness, ignite strongly, weigh as WO_3.

$$\text{Weight} \times 50 = \text{percentage tungstic acid.}$$

Note: Should a very exact determination be necessary, the methods given under 'Tungsten' may be used.

Tin Oxide

Dry, ignite, and weigh the residue (insoluble in ammonia), as insoluble plus tin oxide. Treat this residue exactly as described for assay of tin ore under 'Tin'.

Alternatively, apply the same method on the original ore, using the modification necessitated by the presence of tungsten (if present), as described under 'Tin'. In either case calculate SnO_2 to Sn.

$$(SnO_2 \times 0{\cdot}7877 = \text{Sn.})$$

Copper Oxide

Pass H_2S through the filtrate from WO_3 estimation, filter, dry, ignite and weigh as CuO. Alternatively, redissolve and use the colorimetric method.

$$\text{Weight} \times 50 = \%\ \text{CuO.}$$

Iron Oxide

Boil off H_2S from filtrate, oxidize with HNO_3, dilute, add NH_4OH, boil, filter, wash, dissolve precipitate with a drop of HCl, reduce, titrate with $\frac{N}{10}$ $K_2Cr_2O_7$ as usual. Alternatively redissolve and use the colorimetric method.

$$\text{Iron found} \times 50 \times 1{\cdot}43 = \%\ Fe_2O_3.$$

Sulphur

Fuse 3 g with Na_2O_2, extract with water, add HCl, filter, add $BaCl_2$ to filtrate and proceed as described under 'Sulphur'.

$$BaSO_4 \times \frac{100 \times 0{\cdot}1374}{3} = \%\ \text{S.}$$

Arsenic

Dissolve 5 g in HNO_3, dilute, add excess of ammonia, pass

H_2S, allow to stand, filter, wash, dissolve precipitate and estimate as $Mg_2As_2O_7$ by the usual method.

If the estimation of the constituents of the gangue, i.e. lime, phosphorus, etc., is necessary, proceed exactly as in iron ores.

COMPLETE ANALYSIS OF ZINC ORES (BLENDE)

Dissolve 2 g in 15 ml. HCl, evaporate to dryness. Take up with 15 ml. *aqua regia*, cool, add 10 ml. H_2SO_4, evaporate to fumes, cool, add 150 ml. H_2O, boil, allow to stand, filter, wash with cold dilute H_2SO_4 (10%), and then with cold water.

Lead

The residue is SiO_2, insoluble matter, and $PbSO_4$. Dissolve in hot ammonium acetate, filter, wash. Boil filtrate and estimate lead by titration with ammonium molybdate, as described under 'Lead'.

Ferric Oxide and Alumina

Neutralize original filtrate with Na_2CO_3 solution until a precipitate just forms, dissolve in 3 ml. acetic acid, add 6 ml. sodium acetate, boil for half a minute, filter, wash.

Estimate the Fe and Al in the precipitate exactly as in iron ore.

Manganese Oxide

To the filtrate add 5 ml. bromine, and then add excess of NH_4OH, stir, and allow to settle, boil off excess of NH_4OH, filter, wash, dry, ignite and weigh as Mn_3O_4. ($Mn_3O_4 \times 0{\cdot}9301 = MnO$.)

Lime

To filtrate add 10 ml. NH_4Cl solution and make alkaline with NH_4OH, boil and add 20 ml. hot ammonium oxalate solution, boil for several minutes, filter, wash well with hot water, dry, ignite at high temperature for 30 minutes, weigh as CaO.

Alternatively, the calcium may be estimated by dissolving the oxalate precipitate in H_2SO_4 and titrating with $KMnO_4$ as under " Calcium ".

Magnesia

Warm filtrate, add 50 ml. strong ammonia, add slowly and with stirring 5 ml. of 20% ammonium phosphate. Allow to settle,

filter, wash well with dilute NH_4OH, dry, ignite carefully, finally at a high temperature for 60 minutes, weigh as $Mg_2P_2O_7$. (Factor, $Mg_2P_2O_7$ to MgO = 0·3621.)

Zinc

Weigh 1 g into a 300 ml. beaker, attack with 6 ml. HNO_3 and take to dryness, take up in 20 ml. HCl, and allow to simmer for 10 minutes, dilute to 150 ml., add several millilitres of bromine water and sufficient NH_4OH to redissolve $Zn(OH)_2$. Boil for about half a minute. Filter rapidly through corrugated filter paper, wash three times with hot 10% NH_4OH.

Neutralize filtrate with HCl, add 10 ml. yellow $(NH_4)_2S$, followed by 10 ml. HCl, dilute to 350 ml., heat to just below boiling, and titrate in the usual way with $K_4Fe(CN)_6$, as described under 'Zinc'.

CHAPTER IX

THE ANALYSIS OF SLAGS

ANALYSIS OF A COPPER SLAG

Reduce the slag to a fine powder in an agate mortar, weigh out 2 g into a platinum dish, add 10 ml. HF, allow to stand for one hour, stir well with platinum wire occasionally, add 2 ml. conc. H_2SO_4, evaporate to a syrup on water bath, and finally volatilize the SiO_2.

Copper

Take up with HCl, add water, warm, and pass H_2S, filter off copper and arsenic as sulphides, wash, redissolve in HNO_3, add a drop of $FeCl_3$ and then excess of NH_4OH, filter, wash, evaporate filtrate to small bulk, and determine copper colorimetrically or electrolytically.

Arsenic

Redissolve the precipitate (formed by $FeCl_3$ and NH_4OH from above) in HCl, and precipitate As as sulphide, filter, wash, dissolve in HNO_3, dilute, add 'magnesia mixture', allow to stand for several hours, filter, wash and weigh as $Mg_2As_2O_7$. (Factor, $Mg_2As_2O_7$ to As = 0·4827.)

Ferric Oxide and Alumina

To the filtrate from the first precipitation of copper and arsenic add a drop of HNO_3, boil off H_2S, add NH_4Cl and NH_4OH and filter off $Fe(OH)_3$ + $Al(OH)_3$, filter, wash, ignite and weigh as combined oxides. Redissolve in HCl and estimate Fe by titration with $K_2Cr_2O_7$, calculate Al_2O_3 by difference.

Lime

To the filtrate add ammonium oxalate, stir well, allow to stand for some time, filter, wash, ignite, weigh as CaO.

Magnesia

Evaporate filtrate to half bulk, add NH_4OH and ammonium phosphate, stir well, allow to stand for several hours, filter, wash,

ignite and weigh as $Mg_2P_2O_7$. (Factor, $Mg_2P_2O_7$ to MgO = 0·3621.)

Alkalis

Evaporate filtrate to dryness, heat strongly, cool and weigh as KCl + NaCl.

Silica

Fuse 1 g with 6 g of 'fusion mixture' (see Chapter II) in a platinum dish, extract melt with HCl and water, filter, take filtrate to dryness, take up with HCl, filter, dry, ignite and weigh as SiO_2.

Volatilize with HF and H_2SO_4 as usual. Loss = SiO_2.

Specific Gravity

It is often useful to know the specific gravity of a copper or a lead slag. This can be done by any ordinary approximate method.

ANALYSIS OF IRON SLAGS

Blast Furnace Slag

A 'complete' analysis may be taken to mean the determination of the following constituents, reported in the order as stated: SiO_2, Al_2O_3, CaO, MgO, MnO, S, and FeO.

Silica

Take 0·5 g in a 250 ml. squat beaker. Add 15 ml. of hot water, cover with watch glass and bring to boiling. Now add 10 ml. of hot conc. HCl and impart a gentle swirling motion to the beaker until liquid is well on the boil. Allow to boil briskly until a jelly is formed, then add 5 drops HNO_3, from dropping bottle, place beaker on asbestos pad until apparently dry and finally bake strongly on plate for 20 minutes. Remove from plate, allow to cool a little then add 20 ml. conc. HCl. Allow to boil gently for exactly 2 minutes and then dilute with an equal bulk of boiling water. Filter through pulp pad, taking care that all the silica is removed with a 'bobby' from the sides and bottom of the beaker. Wash pad twice with conc. HCl and boiling water and finally four more washes with boiling water only. Ignite cautiously at first at mouth of muffle, then strongly in the hottest part for 10 minutes. Cool off and weigh.

$$\text{Weight} \times 200 = \%\ SiO_2.$$

SiO_2 and Al_2O_3

Proceed as for silica, only receive filtrate in a 750 ml. conical flask. Wash the silica precipitate thoroughly as described. The bulk after washing may be about 200 ml.

Add 15 ml. of saturated Na_2HPO_4 solution, followed by concentrated NH_4OH, added preferably from a burette, until a permanent white precipitate is formed.

Add concentrated HCl from a burette slowly to dissolve this precipitate, then add a carefully measured 1·5 ml. in excess. Dilute to about 300–350 ml. with water, add 15 ml. glacial acetic acid, a few pieces of ashless filter paper and 10 g $Na_2S_2O_35H_2O$.

Shake well, place on hot plate and heat to boiling. Continue boiling for 5 minutes, then add 5 ml. ammonium acetate solution and boil for further 5 minutes.

Remove from plate, allow to stand for two or three minutes and filter through Whatman No. 31 12·5 cm. paper, make sure that all the precipitate has been transferred from the flask to the paper, and wash thoroughly with hot water (almost boiling). It is essential that the precipitate of $AlPO_4$ should be washed free from alkali salts, or a fused precipitate will result on ignition, with consequent error in the figure obtained.

Transfer the precipitate to silica or porcelain crucible and place in front of the muffle to dry, avoid loss by spurting due to too rapid heating.

When dry and the paper begins to char, advance the crucible until it is just inside the muffle. Allow most of the paper to burn away then place in hot part of muffle and ignite until completely white. Cool and weigh as $AlPO_4$.

Using 0·5 g sample, % Al_2O_3 = wt. of precipitate × 83·6.

CaO and MgO—Long Method

0·5 g is weighed and transferred to a 400 ml. conical beaker. Add about 50 ml. of water, heat to boiling, add 15 ml. conc. HCl, and agitate vigorously until the slag has completely dissolved. Continue boiling for 2 minutes, then add a few drops of conc. HNO_3.

Cool under the tap until the solution is lukewarm. Add NH_4OH to produce a permanent precipitate then add about 2 ml. of liquid bromine and shake well. Add a further small quantity of NH_4OH to ensure the presence of a slight excess. Heat to boiling and boil for 1 minute only. Make sure that there is a distinct odour of ammonia at this stage, but avoid a large excess.

[*Note:* The aim here is to produce the complete precipitation of hydroxides of Fe, Al, etc., together with hydrated MnO_2 with the least possible excess of NH_4OH. The addition of the bromine in ammoniacal solution causes the precipitation of the manganese in an oxidised form, viz. as MnO_2H_2O.]

Filter through a No. 1 15·0 cm. paper into a 750 ml. conical flask and give three washes with hot water. Swill the precipitate back into the flask and redissolve in 20 ml. conc. HCl, warming, if necessary, on the hot plate. Cool, and repeat the precipitation with NH_4OH and Br_2 in exactly the same way as described above.

Filter through the paper used for the first filtration, transfer the precipitate and wash thoroughly with hot water. The volume of the filtrate should be about 200 ml.

Heat the filtrate to boiling and add cautiously 30 ml. of saturated $(NH_4)_2C_2O_4$ solution. Boil for 2 minutes, remove from hot plate and allow to settle.

Filter through a pulp pad, taking care to transfer the whole of the precipitate, and wash thoroughly with lukewarm water.

To a clean 400 ml. conical beaker add 50 ml. of cold water and 7 ml. conc. H_2SO_4, dilute to 200 ml. with hot water and heat almost to boiling. Carefully transfer the calcium oxalate precipitate to this hot solution, shake well, and titrate with $KMnO_4$ solution to a permanent pink colour.

1 ml. N/2·8 $KMnO_4$ solution = 0·01 g CaO
= 2·0% on 0·5 g.

Magnesia

To the filtrate from the oxalate precipitation add 70 ml. conc. HNO_3. Warm gently at first until the reaction due to the liberation of bromine has subsided, then heat more strongly and evaporate to dryness.

Remove from the hot plate, and allow to cool. Rinse round the beaker with water, add 10 ml. conc. HCl and 50 ml. water. Cover the beaker and heat to boiling. Boil for 2 minutes, allow to cool somewhat, then add a few drops of methyl orange indicator. Add NH_4OH until just alkaline, boil for 1 minute and filter through a No. 31 12·5 cm. paper into a 500 ml. conical flask. Wash well with hot water.

The volume of the filtrate should be about 150 ml.

Add HCl from a burette to make the solution just acid, add 10 ml. saturated Na_2HPO_4 solution, followed by 40 ml. conc. NH_4OH. Place a tight fitting bung in the flask and shake vigorously for several minutes. Remove and rinse the bung, cover the

flask with watch glass and allow to stand several hours before filtration.

If the magnesia figure is required urgently continue shaking fairly frequently for at least half an hour after which filtration may be safely carried out. It is advisable to cool the flask in the sink when not being shaken.

Filter off the precipitate of magnesium ammonium phosphate through a pulp pad and do not omit to 'bobby' the flask, even though this operation should seem unnecessary. Wash thoroughly with cold 5% NH_4OH solution.

Ignite gently at first in the front of the muffle. When the paper has burnt off, but the precipitate is still black, advance the crucible to the hot part of the muffle and continue heating until the precipitate is completely or almost white. Cool and weigh as magnesium pyrophosphate.

On 0·5 g sample, MgO% = weight of $Mg_2P_2O_7 \times 72{\cdot}4$.

Manganese Oxide—MnO

0·1 g of slag is weighed and transferred to a 200 ml. conical flask. Add about 30 ml. hot water and heat to boiling. Continue boiling and add 10 ml. manganese solvent, agitating vigorously until solution is complete.

Dilute to 100 ml. with hot water, add 2 ml. of $AgNO_3$ solution (1%) and about 2–3 g of $(NH_4)_2S_2O_8$. Heat to boiling and boil for 1 minute.

Make quite cold and titrate with sodium arsenite solution. The end point is not particularly sharp and care is necessary to ascertain it correctly.

1 ml. Na_3AsO_3 solution = 0·001 g Mn
= 0·129% MnO on 0·1 g.

Manganese Solvent

Water	2100 ml.
Nitric acid	450 ml.
Phosphoric acid (sp. gr. 1·75) ..	150 ml.

Standard Arsenite Solution

Dissolve 1·28 g As_2O_3 and 10 g Na_2CO_3 in a little water, filter and make up to 4000 ml.—Standardize against a known manganese pig iron.

Iron—as FeO

Weigh 1 g of slag and transfer to a 500 ml. conical flask. Add 50 ml. of hot water, heat to boiling, add 10 ml. conc. HCl and agitate until the slag has dissolved. Continue boiling for about 2 minutes to expel H_2S.

Remove from hot plate, add 4 drops of $SnCl_2$ solution, dilute to about 300 ml. with water, add 2 ml. saturated $HgCl_2$ solution. Shake well, and allow to stand for 5 minutes. Add indicator solution (as used for ironstone) and titrate with $K_2Cr_2O_7$ solution.

1 ml. $K_2Cr_2O_7$ solution = 0·01 g Fe
= 1·0% Fe on 1 g sample
= 1·29% FeO on 1 g sample.

Sulphur (as Sulphide)

0·5 g is weighed and transferred together with a few pieces of granulated Zn to a 750 ml. conical flask, part of a standard S evolution apparatus.

Before assembling the apparatus, moisten the slag with about 30 ml. of hot water. Connect up and introduce, through the funnel, about 30 ml. of hot 75% HCl. Heat gently at first and agitate the flask frequently to avoid 'sticking'. When the slag has dissolved, heat to boiling and boil for about 1 minute. Disconnect the delivery tube, place solution directly under the iodine burette, add 30 ml. conc. HCl and titrate with constant stirring and as quickly as possible, to a permanent *blue* end-point, using starch solution as an indicator.

Starch Solution

0·5% freshly prepared. Use 2 ml. for each determination.

Standard Iodine N/32

Dissolve 4 g iodine and 12 g potassium iodide in 50 to 100 ml. water. Filter through a pad of ignited asbestos and dilute to 1 litre. Standardize as follows : Dissolve 0·2 g sodium thiosulphate in about 25 ml. water, add 2 ml. of starch solution and titrate. This should require 25·8 ml. N/32 iodine.

1 ml. = 0·1% S on 0·5 g.

[The foregoing methods apply to rapidly cooled soluble slags.]

Determination of Alkalis in Blast Furnace Slags containing High Magnesia

Intimately mix in an agate mortar 1 g of the floured sample with 1 g ammonium chloride (A.R.) and 8 g of calcium carbonate.

Transfer to a platinum crucible and with lid only slightly moved to one side heat over a small flame or at entrance to muffle for 20 minutes, then for 45 minutes at dull red heat (not exceeding 650° C.). Allow to cool, then wash into a porcelain dish, break down any lumps with a pestle and make up volume to about 120 ml. Digest, on a warm plate, for 30 minutes with occasional stirring. Filter through a pulp pad and wash several times with hot water to a volume of about 250 ml. Add a few ml. of ammonia and an excess of ammonium carbonate, boil for 1 minute, then filter through a pulp pad, washing well with water containing 3% ammonia. The filtrate is then evaporated in porcelain to a bulk of about 40 ml. and made strongly alkaline with 10 ml. of ammonia (sp. gr. 0·880). Then add not more than 3 drops of a 10% solution of ammonium phosphate and a few drops of ammonium oxalate which must be quite free from sodium and potassium salts. The liquid is allowed to stand for some hours, being occasionally shaken. Any ammonium magnesium phosphate, together with any calcium oxalate which precipitates, is filtered off and washed with ammonia water, the filtrate and washings being received in a clean 20 oz. beaker.

The alkaline liquid is boiled down until almost free from ammonia, made faintly acid with HCl, and 5 ml. of standard solution of $FeCl_3$ are added. The liquid is brought to boiling and dropwise dilute ammonia is poured down the lip of the covered beaker until in slight excess. The contents of the vessel are then quietly digested until the phosphate of iron has settled out and the liquid is clear. The precipitate is filtered off and washed with hot water, the filtrate and washings being received in a porcelain basin. The filtrate is then evaporated to dryness and ammonium salts very carefully volatilized by ignition. Cool, take up with a little water, add 5 drops of 10% barium chloride solution to precipitate any sulphate and allow to settle in a warm place for 20 minutes. Without filtering, precipitate excess barium and any traces of calcium by the addition of ammonia and a small quantity of ammonium oxalate. After allowing reasonable time for complete precipitation, filter through a small paper into a small porcelain dish, wash with 3% ammonia water, keeping bulk as low as possible. Evaporate to dryness, ignite gently, cool, moisten with a few drops of HCl, dry, re-ignite, cool and weigh. Wash out soluble residue into another dish, ignite the empty dish and weigh. Difference in weights equals the total chlorides of potassium and sodium. Treat the solution with 1 ml. of perchloric acid (sp. gr. 1·20) and evaporate to the point of white fumes. Add a few ml. of water and repeat evaporation to nearly dryness. Cool, treat with

95% alcohol, washing three times (15 ml. each) by decantation. Dry at about 120° C., cool and re-weigh. Difference in weight equals amount of $KClO_4$ and this × 0·5381 = KCl.

Obtain NaCl by difference. Calculate to oxides.

A blank estimation should be done along with the sample as a check on the purity of chemicals and distilled water.

It is also preferred to use porcelain vessels instead of glass throughout the method if possible.

Standard Solution of $FeCl_3$

Dissolve 2·505 g of Swedish bar iron in 35 ml. of strong HCl solution and then add 3 ml. of strong HNO_3 to oxidize the iron. The solution is boiled down and finally very gently evaporated, until crystals of $FeCl_3$ begin to separate. These are re-dissolved in cold water and the solution made up to 250 ml. (1 ml. = 0·01 g Fe.)

'ACID' OPEN-HEARTH SLAG

Silica

Fuse 2 g with 5 g Na_2CO_3, extract the melt with water, add HCl, evaporate to dryness, take up with HCl and filter. Ignite SiO_2 as usual.

Iron and Aluminium

Treat the filtrate with ammonium acetate and filter off *iron* and *aluminium hydroxides*, estimate these constituents as in Blast Furnace Slag.

Lime and Magnesia

Separate manganese with bromine and NH_4OH, and estimate *lime* and *magnesia* in the filtrate, as described under 'Blast Furnace Slag'.

Manganese

Estimate directly on 0·5 g. Dissolve in HCl and HF, estimating this constituent exactly as in fireclay.

Sulphur

Fuse 2 g with Na_2CO_3, remove SiO_2 as above, add $BaCl_2$ to the filtrate, and weigh $BaSO_4$.

Phosphorus

Attack 2 g with HNO_3 and HF, evaporate to low bulk, estimate as in Steel.

'BASIC' OPEN-HEARTH SLAG

Silica

Dissolve 1 g in HCl, evaporate down with HCl, bake, take up in HCl, filter ignite and volatilize as usual. Fuse any residue with Na_2CO_3, dissolve melt in HCl and add to main filtrate.

Iron and Alumina

Neutralize solution, add 2 to 3 ml. acetic acid, boil, add ammonium acetate, filter off precipitate, dissolve in HCl and take one portion (say one-third) for estimating *iron*. This may be done by reprecipitation as hydroxide, dissolving in HCl, and titration with $K_2Cr_2O_7$ as usual.

The remaining portion (two-thirds) is treated for the estimation of aluminium by the 'phosphate' method, as described under 'Aluminium'.

Note: This aluminium phosphate precipitate will be impure, and may contain chromium, vanadium and titanium. A separation by fusion may be effected, but such procedure is seldom necessary.

Lime
Magnesia
Manganous Oxide } As in 'Blast Furnace Slag'.
Sulphur

Phosphorus—as in 'Acid' Open Hearth Slag.

Chromium Oxide

Dissolve 5 g in HCl, add 15 ml. H_2SO_3, boil, add 3 ml. HNO_3 and boil, dilute, add slight excess of NH_4OH, boil, filter, wash. Dissolve the precipitated oxides of iron, aluminium, chromium and phosphorus with dilute H_2SO_4 (1 : 4), dilute to 250 ml. with warm water, add $KMnO_4$ solution until a permanent pink colour is obtained on boiling for some minutes. To the boiling solution add conc. HCl to clear. Add 150 ml. hot water, boil off chlorine and cool.

Add excess of ferrous ammonium sulphate and titrate back with $K_2Cr_2O_7$.

LEAD SLAG

Lead

Dissolve 2 to 5 g in HCl with a few millilitres of HNO_3, evaporate to dryness, take up with HCl and water, add 5 ml. H_2SO_4,

and evaporate to fumes, dilute to 100 ml. with water, boil, settle, wash with cold 10% H_2SO_4, reserve filtrate for estimation of Cu (q.v.). Wash the residue from paper with a minimum of hot water, add 5 g ammonium acetate, boil, refilter on the same paper, wash with hot dilute ammonium acetate and estimate lead by titration with ammonium molybdate.

Silica

Dry the residue, which consists of $BaSO_4 + SiO_2$, and weigh. This residue is evaporated with HF and H_2SO_4, and the loss in weight = SiO_2.

The residue can now be treated as follows :

Barium

Fuse with 5 to 6 g $Na_2CO_3 + K_2CO_3$ in a nickel crucible, extract with hot water containing a little NH_4OH, filter, wash with very dilute NH_4OH until free from sulphates. Dissolve precipitate off filter with HCl and water, refilter through the same paper and wash. Make filtrate alkaline with NH_4OH, then just acid with acetic acid and add excess of K_2CrO_4, boil, settle, filter, wash with dilute ammonium acetate until free from soluble chromate, dry, ignite at moderate temperature, weigh as $BaCrO_4$. (Factor, $BaCrO_4$ to Ba = 0·5422.)

Copper

To the original filtrate add HCl and pass H_2S, filter off any precipitate of copper sulphide, wash, redissolve in a little HNO_3 and estimate copper by thiosulphate titration.

Oxides of Iron, Aluminium and Chromium

Boil filtrate free from H_2S, oxidize with HNO_3, and add NH_4Cl and NH_4OH, filter, wash well, redissolve and reprecipitate, wash, ignite, weigh as combined oxides, redissolve in HCl. Estimate iron by titration with $K_2Cr_2O_7$, and calculate Al_2O_3 by difference. Estimate Cr, if present, separately as in basic open hearth slag.

Zinc Oxide

To the filtrate add $(NH_4)_2S$, filter, wash and redissolve in HCl. Estimate Zn either by 'phosphate' method or by ferrocyanide titration.

Lime

Boil down to small bulk, add ammonium oxalate, filter, wash, ignite, and weigh as CaO.

Magnesia

To the filtrate add *aqua regia* and boil down. Repeat twice, add water, make just alkaline with NH_4OH, and add Na_2HPO_4, agitate, allow to settle for several hours, filter, wash, ignite and weigh as $Mg_2P_2O_7$. (Factor, $Mg_2P_2O_7$ to MgO = 0·3621.)

Sulphur

Dissolve 2 g in *aqua regia*, evaporate down, add HCl and re-evaporate, dilute, filter, add $BaCl_2$, and estimate S in solution as $BaSO_4$.

The amount of sulphur in the insoluble portion must also be determined by a fusion with 'fusion mixture' + KNO_3 (see Chapter II), extract the melt with water, acidify with HCl and estimate sulphur as above.

Gold and Silver

Use the pot fusion method, as described under 'Gold' for siliceous ore.

TIN SLAG

SLAG FROM BLAST FURNACE OR REVERBERATORY FURNACE SMELTING TIN DROSSES

The slag is crushed fine in an agate mortar and put through a 60 to 80-mesh sieve.

Tin

Weigh 1 g and digest with 20 to 30 ml. conc. HCl in a 100 ml. beaker, cover with clock glass, warm for 15 minutes, break up SiO_2 and undecomposed slag with a glass rod and continue heating. Add a crystal of $KClO_3$, dilute to 150 ml. with water, reduce with iron nails and titrate with iodine as usual.

Copper

Weigh 1 g and digest with HCl exactly as in the estimation of tin, evaporate to dryness, take up with HCl and again evaporate and bake for 5 minutes, take up with HCl and filter off SiO_2 through a filter pad. Make filtrate alkaline with NH_4OH, boil and add $(NH_4)_2CO_3$, cool, filter, estimate copper in the filtrate either by the colorimetric method or by thiosulphate titration.

Lead

Weigh 1 g and treat exactly as in the estimation of copper, up to the point of the second evaporation to dryness, filter off SiO_2 and add H_2SO_4 to the filtrate, cool and filter off $PbSO_4$, wash, dissolve in ammonium acetate and estimate lead by the 'chromate' method.

Note: Occasionally in some slags there is difficulty in completely obtaining a solution. It is therefore recommended that a fusion or preferably a double fusion with mixed Na_2CO_3 and K_2CO_3 be made, the melt extracted with water and HCl and the solution thus obtained treated in the same way as the acid solution.

Arsenic

Weigh 1 g into an ordinary distillation flask, distil over and titrate with iodine in the usual manner—see under 'Arsenic'.

Iron

If iron content is required it may be estimated, together with the lead, as follows :

Dissolve 1 g in HCl and $KClO_3$, cool, add KOH till alkaline, boil and precipitate with Na_2S, filter, wash, redissolve precipitate in HNO_3, make alkaline with NH_4OH and precipitate Pb and Fe by addition of $(NH_4)_2CO_3$. Dissolve precipitate in 5 drops of HNO_3, make just alkaline with NH_4OH, add acetic acid, boil and estimate lead by titration with potassium chromate. After completion of titration filter, wash, add HCl and estimate Fe by the colorimetric method.

PART FIVE

The Analysis of Refractory Materials.
Analysis of Coal and Coke.

CHAPTER X

THE ANALYSIS OF REFRACTORY MATERIALS

Sampling

The sample sent to the laboratory should have been ground to 30 mesh.

Empty the whole of the sample on to a piece of clean paper, cone and flatten out to a circle three times. With a spatula take a nine-point sample in the usual way.

In the event of a heterogeneous sample quartering-down should be carried out.

Dry the sample at 100–110° C.

Loss on Ignition

Weigh 5·0 g of sample into an ignition crucible. Heat gently near the front of the muffle for 15 minutes then gradually move to the hottest zone and heat for 1 hour. Cool in desiccator, weigh and report % loss.

Note: Ferrous oxide and manganous oxide are converted to Fe_2O_3 and Mn_3O_4 respectively and for this apparent increase in weight due allowance should be made.

FIRECLAY

Silica

Grind the ignited sample in an agate mortar to pass 180 mesh. This operation requires care since the hard particles are likely to fly during grinding and be lost from the sample. Dry the sample again before weighing out for analysis. Weigh 5 g of anhydrous Na_2CO_3 and 1 g of the sample into a platinum crucible, and mix with a spatula. Put the lid on the crucible and fuse in muffle for 30 minutes.

Extract the melt when cold with dilute HCl transferring the contents into a 7 inch porcelain basin. Evaporate to dryness on a water bath and bake for 6 hours. Bake for a further hour in an air

oven at 110° C. Take up residue with 50 ml. 1 : 1 HCl and warm to dissolve salts. Filter through a Whatman No. 41, 11 cm. paper and wash with hot water until free from chlorides. Return the filtrate and washings to the porcelain basin, evaporate to dryness and repeat the baking. Take up with 50 ml. 1 : 1 HCl, warm to dissolve, filter, and wash as before. Collect filtrate in a 500 ml. graduated flask. Ignite the silica in a platinum crucible, cool and weigh. Precipitated silica picks up moisture fairly rapidly and should be weighed without delay. Add 5 ml. pure HF and 1 ml. of H_2SO_4 and evaporate on a sand bath until fuming ceases. Finally ignite in the muffle to constant weight. Report loss in weight as % SiO_2. Fuse the residue in the crucible with 0·5 g of Na_2CO_3, extract with HCl and add to the main solution.

Al_2O_3, Fe_2O_3 and TiO_2

Make up the solution from the SiO_2 estimation to 500 ml. in the graduated flask. Using a dry 250 ml. graduated flask, divide into two equal portions and transfer each to a 600 ml. beaker. Boil, add a few drops of methyl red and add NH_4OH until colour of solution changes to yellow. Boil for 1 minute and filter through a Whatman No. 41 paper, 15 cm. diameter. Wash well with a hot 2·5% ammonium nitrate solution reserving filtrate. One of these precipitates is to be used for the total Al_2O_3, Fe_2O_3 and TiO_2 and the other for the Fe_2O_3 and TiO_2. It is not necessary to 'policeman' out either precipitation beaker at this stage. With a washbottle wash both precipitates from the filter paper back to their respective beakers and with care this can be done quantitatively by finally opening out the paper on a clock glass. Redissolve each precipitate in 50 ml. (1 : 1) HCl and set aside the one to be used for Fe_2O_3 and TiO_2.

Dilute the other to about 300 ml. and re-precipitate the Al_2O_3 etc., as before. Filter, 'policeman' out beaker thoroughly and well wash the precipitate. Particular attention must be given to the washing owing to the nature and bulk of precipitate.

Dry, ignite strongly and weigh the total oxides in a tared platinum crucible.

Fe_2O_3 and TiO_2

Transfer the solution set aside for Fe_2O_3 and TiO_2 to a 250 ml. graduated flask and make up to the mark.

Fe_2O_3

Pipette 2·5 ml. of the solution into a colour tube and 5 ml. of

the standard iron solution into another colour tube; add 3 drops of conc. nitric acid to each. Make up each volume to 7·5 ml. with water and add 2·5 ml. of strong ammonium thiocyanate solution to each. Dilute the stronger coloured solution with weak thiocyanate solution until matched. When 'standard' tube = 10·0 ml. the ml. of sample × 0·16 gives % Fe_2O_3.

TiO_2

Pipette 25 ml. into a silica basin and evaporate to dryness on the water bath. Add 25 ml. of 20% sulphuric acid and warm to dissolve the residue. Transfer solution to a 100 ml. Nessler glass, add 1 ml. of 20% H_3PO_4, 2·5 ml. of H_2O_2 (20 vols.) and make up to the 50 ml. mark with water. Prepare a comparison Nessler glass by adding the same amounts of H_2SO_4, H_3PO_4 and H_2O_2. Run in from a burette standard titanium sulphate solution until the colour matches the sample. If the TiO_2 content of the sample is over 4% only half the bulk of the sample should be used for matching.

Calculate % TiO_2.

The Al_2O_3 is obtained by subtracting $Fe_2O_3 + TiO_2$ from the weight of total oxides.

MnO

Boil down the filtrate from the Al_2O_3 precipitation to about 200 ml., add 10 ml. HCl and filter if necessary. Add 25 ml. of bromine water, stir and allow to stand 10 minutes. Make slightly alkaline with ammonia, boil and filter if any manganese is present. Wash with hot water and ignite to Mn_3O_4 (× 0·9301 = MnO).

CaO

To the solution from the MnO estimation add 25 ml. hot ammonium oxalate solution, boil and allow to stand overnight. Sometimes the calcium oxalate precipitate is contaminated by traces of alumina. This can be judged by the appearance of the precipitate. In such a case, filter, wash, ignite the precipitate and re-dissolve in HCl. Add slight excess of NH_4OH, filter if necessary and re-precipitate the calcium oxalate.

Filter through a double Whatman No. 40, 11 cm. filter paper, wash well and ignite strongly to constant weight.

Report % CaO.

MgO

Evaporate filtrate from the CaO estimation to about 200 ml.

Add 2 to 3 g of diammonium phosphate, stir until dissolved, then add NH_4OH until slightly alkaline followed by 20 ml. excess. Allow to stand overnight. Filter through a Whatman No. 40, 11 cm. paper and wash with 5% NH_4OH. Ignite in a crucible (not platinum) slowly at first to burn off paper and then strongly to constant weight.

$$\text{Weight of } Mg_2P_2O_7 \times 0{\cdot}3621 = MgO.$$

Total Alkalis (Lawrence Smith)

Weigh 1 g very finely ground material and intimately mix with 5 g $CaCO_3$ and 0·5 g NH_4Cl. Put in Lawrence Smith crucible and with a small Bunsen burner start heating the top of the charge in the crucible and gradually lower the burner to heat up the bottom of the charge. This should take 4–5 minutes and during this time the ammonium chloride is decomposed. Now use a larger burner and heat the whole mass to a good red heat and maintain at that temperature for 40–60 minutes. The heat should not be sufficient to vitrify the mass too much. Extract sintered mass with water into a silver basin, evaporate to low bulk, filter into a silica basin and wash about ten times. Dry residue and ignite paper in a platinum dish. Brush into an agate mortar, crush, mix with 0·3 g NH_4Cl and repeat sintering, etc., collecting the filtrate in the silica dish already containing the main filtrate. Concentrate filtrate, cool, precipitate CaO with $(NH_4)_2CO_3$ and a little NH_4OH, filter into a platinum basin and wash about ten times. Carefully evaporate to dryness and heat to remove ammonium salts. Take up with a little water, add a few drops of ammonium oxalate, heat and allow to stand. Filter through a double 11 cm. No. 40 paper. Evaporate to dryness (examine to see if any further precipitate separates out), take up with a few ml. of H_2SO_4 (20%). Drive off excess acid, heat to a dull red and weigh the double sulphates.

Wash double sulphate into a 250 ml. beaker, dilute to 150 ml., acidify with HCl, add 2 g NH_4Cl, boil, add 10 ml. 1% picric acid, add 15 ml. $BaCl_2$ (10%), boil, allow to stand overnight for precipitate to settle, decant and filter on to (double) 11 cm. papers. Wash free from soluble salts, dry, ignite, etc. Calculate SO_3 (Factor = 0·343).

$$\text{Then } K_2SO_4 + Na_2SO_4 - 2SO_3 = K_2O, Na_2O.$$

Estimation of K_2O in Alkalis. Perchlorate Method

Follow the Lawrence Smith method up to the stage immediately before separation of CaO, etc., with $(NH_4)_2CO_3$. Remove

any sulphates present with $BaCl_2$, filter, etc., and then separate CaO, etc., as explained in alkalis method. Add a few ml. HCl and evaporate to dryness to remove excess. Take up residue in 20 ml. hot water and add one and a half times the theoretical quantity of $HClO_4$ (20%) necessary to decompose all salts present. Evaporate, with frequent stirring, to a syrupy consistency, until all odour of HCl has gone and white fumes of perchloric acid appear. Avoid evaporating off much perchlorate and should this be done add a little water. Stir the cold syrupy contents of the dish with 20 ml. of 'wash' alcohol (alcohol 96% containing 0·2% $HClO_4$), allow to stand and decant off the clear liquid into a weighed Gooch crucible. Repeat the alcohol washing and decantation. To the residue in the dish add 0·3 g $HClO_4$ and a little water and gently warm to remove alcohol. Cool, wash the residue into the Gooch with 'wash alcohol'. Any adsorbed $HClO_4$ is washed out of precipitate with a few ml. pure C_2H_5OH. Dry Gooch and contents at 120–130° C., cool and weigh. From $KClO_4$ calculate K_2O. (Factor = 0·340.)

In all about 50–70 ml. C_2H_5OH are required for the washing of the $KClO_4$.

Caution: Owing to the powerful oxidizing properties of $HClO_4$ handle cautiously.

Reactions: $KCl + HClO_4 = KClO_4 + HCl$.

Note: For evaporating down the water bath possesses no advantage over the hot plate except that the evaporation is slower and less liable to spit. If time is limited it is quite safe to evaporate to a low bulk on the hot plate or over a moderate burner.

Solutions

(1) *Standard titanium sulphate solution*

Heat an intimate mixture of 0·1 g TiO_2 and 3 g ammonium persulphate in a platinum fish until the vigorous reaction ceases. Drive off excess ammonium persulphate by heat. Heat the residue with 5 ml. of conc. H_2SO_4 until the acid fumes copiously. Pour the cold solution into 800 ml. water. Add 50 ml. conc. H_2SO_4 and make solution up to 1 litre.

The solution is standardized by precipitation of $Ti(OH)_4$ by ammonia, igniting and weighing as TiO_2.

Note: The use of a B.D.H. Lovibond Nesslerizer for the estimate of TiO_2 eliminates the necessity of using a standard $TiSO_4$ solution.

(2) *$FeCl_3$ $\frac{N}{50}$ strong solution.*

Iron wire (piano)	0·56 g
HCl (pure)	10 ml.
Few crystals $KClO_3$	

Dissolve the iron wire by warming with the acid and $KClO_3$. Cool, and make up to 500 ml. with water.

(3) *Standard Fe solution*

Strong $FeCl_3$ = 5 ml.
HCl = 5 ml.
Dilute up to 500 ml.
1 ml. = 0·000016 g Fe_2O_3.

(4) *Strong thiocyanate solution*

Dissolve 150 g ammonium thiocyanate in water and dilute to 300 ml.

(5) *Weak thiocyanate solution*

25 ml. of strong solution diluted to 100 ml.

(6) *Bromine Water*

Saturate water with bromine.

(7) *Ammonium Oxalate*

Dissolve 4 g in 100 ml. boiling water.

Notes:

(1) SiO_2 Estimation. The double evaporation and baking is only necessary for very accurate work. SiO_2 recovered on second bake is usually less than 0·5%.

(2) A small amount of Pt is usually dissolved by the fusion and for accurate work this must be deducted from the Al_2O_3.

Rapid Estimation of Al_2O_3, TiO_2 and Fe_2O_3 in Clays, Firebricks, etc. [Cashmore & Cowling, *Trans. Brit. Cer. Soc.*, Vol. XLV, 1946.]

10 g of NaOH pellets are melted in a silver crucible until clear. Allow to cool and add 0·5 g of finely ground ignited sample.

To make the sample sink in the molten soda, moisten it with a few drops of alcoholic caustic soda solution. Cover with a lid and heat carefully over a small Bunsen flame for 5 minutes.

Transfer to the front of a muffle and gradually raise the temperature to 700–750° C. Heat for about 20 minutes. Remove, cool slightly and then rotate carefully so as to spread the melt over the crucible. This facilitates extraction.

When cool, cautiously add small quantities of hot water and gradually cover the melt with water. Transfer the extract by means of a funnel to a 250 ml. graduated flask, cool, make up to the mark and thoroughly shake. Finally wash the crucible and lid with diluted HCl keeping the washings separate for the Fe_2O_3 estimation.

About 5 minutes after the bulk of the precipitate has settled, filter exactly 50 ml. into a 50 ml. graduated flask using a dry Whatman No. 52 or 54 paper. Complete the filtering of the bulk into a 250 ml. graduated flask through the same filter paper. The bulk filtrate and the residue will be required later for the Fe_2O_3 and TiO_2 estimation.

Transfer the 50 ml. of filtered solution to a 250 ml. graduated flask and rinse out the flask with small quantities of water to give a final bulk of about 70 ml. Carefully neutralize with HCl (sp. gr. 1·19) adding slowly about 3 ml. from a burette and then dropwise using congo-red paper as indicator or until the end-point, the approach of which is indicated by a development of cloudiness. The disappearance of the cloudiness, sensitive to one drop, exactly coincides with the point at which the congo-red paper just turns blue. Add 2–3 drops in excess. Sometimes after neutralization the solution shows a slight turbidity due to traces of silver or silica but this is quite different from the cloudiness due to $Al(OH)_3$.

Note: The critical part of the method is the precipitation of the aluminium oxine complex.

Cool to below 20° C. This is important in order to prevent the formation of basic acetate of aluminium as well as oxyquinolate when the oxine is added.

To the cooled solution add from a burette standardized 8-hydroxyquinoline (oxine) solution (approximately 1·5%). The amount of oxine required is obtained from the following formula:

$$\frac{0{\cdot}1 \times P \times 8{\cdot}5}{}$$

where $0{\cdot}1$ = weight of sample
P = assumed Al_2O_3 content in %
$8{\cdot}5$ = ratio of $C_9H_7NO : Al_2O_3$.

This is normally 35 ml. of oxine solution as the required 50%

excess has been allowed for in the 1·5% strength of the standard solution.

After allowing time for draining read burette very accurately. Add 12 ml. of a 25% solution of sodium acetate to precipitate the oxyquinolate. Place the closed flask in a warm place for about 20 minutes. Heat on the edge of a hot plate at 90° C. for 10–15 minutes so that the liquid just simmers but does not boil. To avoid loss of oxine, which is rather volatile at that temperature, fit the flask with a cork carrying a 60 cm. glass tube, which serves as a reflux condenser. Wash the tube with hot distilled water when finished to give a volume of 200 ml. This will prevent any recrystallization of the oxine during subsequent cooling. Allow to cool at room temperature for a while and then immerse in cold water. When at room temperature make up to 250 ml. with water and shake carefully but well.

(a) Volumetric Finish

After settling, filter through dry Whatman No. 40 papers into two 100 ml. dry graduated flasks for two parallel titrations. The filtrate which contains an excess of oxine is transferred to a 250 ml. conical flask.

Acidify with 10 ml. of conc. HCl, cool slightly and add an excess of a standard solution of potassium bromide-bromate in the following way: add 6 to 8 ml. of bromide-bromate, close the flask with a rubber bung (to prevent loss of bromine) and shake thoroughly. A few drops of a 1% aqueous solution of indigo-carmin are then introduced. If the colour of the solution quickly changes from green to yellow an excess of bromine is present, but if the green colour persists more bromide-bromate must be added until the solution becomes yellow. The bromide-bromate must be added slowly with careful shaking to prevent the formation of insoluble dibromo-hydroxyquinoline during titration. On the other hand loss of bromine must be avoided.

After 2 minutes add 5 ml. of 5% KI solution and titrate the free iodine with standard thiosulphate using starch solution near the end-point. A brown precipitate of a compound of iodine with the dibromo compound may separate during the titration. This is decomposed during the titration and does not affect the end-point.

Run a duplicate blank using 10 ml. oxine solution, acidified with 10 ml. conc. HCl diluted to 150–180 ml., titrated with bromide-bromate in excess as described and back titrated with KI and thiosulphate.

Calculation

1 ml. N/5 $KBrO_3 \equiv$ 0·0045 g Al or 0·0085 g Al_2O_3

$\%Al_2O_3 = (3{\cdot}5\ x - 2{\cdot}5\ y)\ 0{\cdot}8501,$

where x = ml. of N/5 bromide-bromate $\equiv$ 10 ml. of oxine

y = ,, ,, N/5 ,, ,, $\equiv$ 100 ,, ,, sample.

Note: Subtract from the % Al_2O_3 the small amount of Fe_2O_3 which passes into solution and which is determined later.

(b) Gravimetric Finish

Filter the aluminium-oxine complex through a clean, tared crucible having a porous bottom and wash thoroughly with hot water. Dry in an oven at 130° C. to constant weight. As the precipitate sticks tenaciously to glass the precipitation should be carried out in a flask with a wide neck.

Fe_2O_3

Fe_2O_3 must be determined in the original residue and in the filtrate as before mentioned. Use the ammonium thiocyanate colorimetric method.

Filtrate

Acidify the filtrate in the flask with conc. HCl, cool and make up to 250 ml. Take 25 ml. of this solution in a Nessler glass, add a few drops of HNO_3 and match colour by running standard iron solution into another Nessler glass from a burette.

Standard Fe_2O_3 solution, 1 ml. $\equiv$ 0·000016 g Fe_2O_3.

% Fe_2O_3 = ml. of standard Fe_2O_3 solution $\times$ 0·04. (*a*)

This amount must be subtracted from the Al_2O_3 content.

Residue

Dissolve the residue on the paper in hot diluted HCl into the original 250 ml. graduated flask (use crucible washings).

Well wash, cool and make up to 250 ml.

Take 2·5 ml. of this solution and match against standard Fe_2O_3 solution as for 'Filtrate'.

% Fe_2O_3 = ml. Standard Fe_2O_3 solution $\times$ 0·16 $\times$ 2. (*b*)

$$\text{Total } Fe_2O_3 = a + b.$$

TiO_2

Take 25 ml. of 'Residue' solution and evaporate to dryness in a silica dish on the water bath. Add 25 ml. of 20% H_2SO_4 and warm

to dissolve. Dilute, cool and filter off the SiO_2. Collect the filtrate and washings in a Nessler glass and determine colorimetrically using the H_2O_2 method.

Standard Solutions

Sodium thiosulphate N/5 = 50 g/litre standardized against
Potassium dichromate = 9·81 g/litre
Bromate-bromide N/5 = 5·6 g $KBrO_3$ + 20 g KBr/litre
8-Hydroxyquinoline = 15 g/litre.

Make up hydroxyquinoline solution as follows :

Mix to a paste with a few ml. of conc. acetic acid and then add more acid until a clear solution is obtained. A total of 120 ml. of acid should be used. Make up nearly to the total volume with water, then from a burette add ammonia solution dropwise until a slight precipitate is just produced. Redissolve this precipitate either by the addition of dilute acetic acid or by warming. Let stand for some hours and filter off insoluble matter. This solution will keep.

Equations involved

$$AlCl_3 + 3C_9H_7ON = Al(C_9H_6ON)_3 + 3HCl$$
$$C_9H_7OH + 2Br_2 = C_9H_5ONBr_2 + 2HBr$$
$$KBrO_3 + 5KBr + 6HCl = 6KCl + 3Br_2 + 3H_2O$$
$$Br_2 + 2KI = 2KBr + I_2$$
$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

BASIC REFRACTORIES

Analysis of Corundum, Fused Alumina and Other Materials of High Alumina Content

Breaking Down Corundum Lumps

This can be done to some extent by heating to 600–700° C. and quenching in water.

If only a steel percussion mortar and an agate mortar are available this analysis should be carried out in two parts. The use of a crystallized alumina mortar and pestle would not materially affect the percentage of other constituents so that the analysis could be carried out in full on one sample.

Grind sample 20 mesh in an iron mortar and remove iron with a magnet.

Then grind two samples (A and B) 180 mesh as follows :

Sample 'A' in steel percussion mortar
Sample 'B' in agate mortar

SiO_2. Use sample 'A'

Fuse 1 g with about 15 g of $KHSO_4$. Keep just fused in the front of a muffle for 1 hour, afterwards raising to dull red until fusion is complete. Extract with 50% HCl and estimate SiO_2 as for 'Clay Analysis'.

SiO_2, Al_2O_3, Fe_2O_3 and TiO_2. Use sample 'B'

Fuse with $KHSO_4$ and remove SiO_2 as before. Reserve filtrate.

Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO

Make filtrate up to 500 ml. in a graduated flask and complete as for 'Clay Analysis'.

Report SiO_2 figure from Sample 'A' and the remainder of constituents from Sample 'B'. Al_2O_3 is taken by difference from 100%.

Note: Several per cent. of SiO_2 can be removed from an agate mortar in grinding hard aluminous materials.

Analysis of Zirconia

Fuse 1 g of the finely ground dried sample with $KHSO_4$. This is best carried out by adding the sample a little at a time to the melt, with occasional swirling. The fusion should be complete in about half an hour at a red heat.

Cool and dissolve in 50% HCl into a 7 inch porcelain basin, evaporate to dryness. Add 10 ml. of conc. H_2SO_4, fume on a sand bath or hotplate. Take up with 50 ml. of 50% HCl and filter off the silica.

Complete the silica estimation in the usual way with HF. Fuse the residue from the SiO_2 estimation with a little $KHSO_4$, dissolve in diluted H_2SO_4 and add to the main filtrate. Boil and after cooling make up to 500 ml.

Preliminary Test for TiO_2

Take 25 ml. and examine colorimetrically using H_2O_2 method (do not add H_3PO_4).

Fe_2O_3

Take 25 ml. and estimate colorimetrically by thiocyanate method.

Rare Earths

Take 50 ml. and examine for the presence of rare earths by precipitation as oxalates.

Total Oxides (Covering ZrO_2, TiO_2, Fe_2O_3, Rare Earths, Al_2O_3)

Take 100 ml. of cold solution, add 5 g NH_4Cl and then NH_4OH in slight excess. Boil for 1 to 2 minutes, filter and wash with 2% NH_4NO_3. The filtrate will contain any Cu, Mn, Ca and Mg that may be present. Re-dissolve the precipitate in diluted H_2SO_4 and HCl, re-precipitate, filter and well wash with hot 2% NH_4NO_3. Ignite total oxides to constant weight.

ZrO_2 and TiO_2

Take 100 ml. of cold solution, precipitate and filter off total oxides as above. Redissolve in 100 ml. hot 5% H_2SO_4, the precipitate may require prolonged boiling to completely dissolve.

Carefully neutralize the solution to give an acidity of approximately 1% H_2SO_4 by volume, pass H_2S through the solution to remove metals of the H_2S group and to reduce the iron. Filter if necessary. Keep the volume of solution down to about 200 ml. and add 2 g of powdered tartaric acid. Make the solution ammoniacal and saturate with H_2S to precipitate the iron. Allow to settle on the water bath, filter and wash with NH_4Cl containing a

little $(NH_4)_2S$. The precipitate will consist of sulphides of Fe, Mn, Zn and Co if present.

Acidify the filtrate to approximately 10% H_2SO_4 by volume, boil to expel H_2S and filter again if necessary.

Reduce the temperature of solution to 5 to 14° C. and add excess of a cold 6% solution of cupferron. Allow to react 5 minutes, filter and thoroughly wash with cold 10% HCl. Clear filtrate and washings indicates complete precipitation of Zr and Ti.

The colour of the precipitate indicates the amount of Ti present since the Zr precipitate is pure white and the Ti is yellow. A brown coloration indicates Fe, or less likely, V.

Carefully dry precipitate, ignite and weigh as ZrO_2. If TiO_2 and rare earths are present fuse the residue with $KHSO_4$. Dissolve in 10% H_2SO_4, make up to 100 ml. and estimate TiO_2 and rare earths on separate 50 ml. portions.

Estimation of Zirconia using Mandelic Acid

Follow the procedure given for 'Analysis of Zirconia' up to the precipitation of the hydroxides with ammonia and washing with 2% ammonium nitrate solution (see 'Total Oxides' section).

After washing with ammonium nitrate solution, wash once with distilled water and dissolve precipitate back into original beaker with hydrochloric acid. Dilute the solution to about 200 ml. (hydrochloric acid concentration 20%). Warm to 85° C. and add 50 ml. of 16% mandelic acid solution. Allow to stand at 85° C. for half an hour and filter through a No. 40 filter paper. Wash with a hot solution containing 2% hydrochloric acid and 5% mandelic acid. Transfer to an ignited and weighed platinum crucible and burn off to the oxide. Weigh as ZrO_2.

Analysis of Zirconium Silicate (Zircon)

Fuse the dry (not ignited) sample with a mixture of 1 g Na_2O_2 plus 3 g NaOH at a low temperature in a nickel crucible, with constant swirling, for about half an hour.

Cool, extract with hot water into a porcelain basin and filter through a 540 (hardened) Whatman paper into another porcelain basin. Wash crucible and basin with hot water.

Acidify the filtrate with HCl and evaporate on the water bath. Ignite the residue on the filter paper in a platinum crucible and fuse for half an hour with $KHSO_4$. A clear melt should be obtained.

Cool, dissolve in diluted HCl and add to the main filtrate. Proceed with the analysis as for 'Zirconia'.

CHROME-MAGNESITE.

[Pigott, *Chemical Analysis of Ferrous Alloys.*]

Attack 0·5 g of finely floured sample by fusion in a Pt crucible with 10 g potassium bisulphate at 400–500° C. for about 2 hours, cool and leach the result with 200 ml. 50% HCl in a porcelain dish.

SiO_2

Evaporate to dryness and bake at 120° C. for 1 hour. Take up with 100 ml. 50% HCl and 100 ml. water, heat to dissolve soluble salts. Filter through paper pulp wash with hot 5% HCl. Ignite the precipitate in a Pt crucible, cool and weigh. Treat the residue with HF and H_2SO_4, evaporate, heat strongly and reweigh. Report loss in weight as SiO_2.

Any residue is fused with 1 g potassium bisulphate, the melt is leached with dilute HCl as before and added to the main solution (filtrate from SiO_2 precipitation).

Al_2O_3, FeO_3, TiO_2

Dilute the above solution to 400 ml. and make just ammoniacal. Boil to coagulate the precipitate of mixed hydroxides, filter and wash with hot 2% ammonium nitrate solution. Dissolve precipitate in hot 50% HCl and re-precipitate with ammonia. Combine and reserve both filtrates (to be used later for Mn, Ca and Mg estimation).

Dissolve the precipitate in hot 50% HNO_3 and add about 1–2 g $KClO_3$, evaporate and add more $KClO_3$ if necessary until all chromic salts (green) have been converted to chromate (orange). Dilute to 300 ml., make just ammoniacal, boil to coagulate the hydroxide precipitates of Al, Fe and Ti (Cr as chromate does not interfere now), filter, wash with hot 2% ammonium nitrate and ignite in a Pt crucible. Cool and weigh as mixed oxides.

Fuse the oxide residue with 3 g potassium bisulphate, dissolve the melt in 100 ml. 10% H_2SO_4 and divide into two equal portions,

Fe_2O_3.—One portion is used for determining Fe either colorimetrically (as under 'Fireclay', or volumetrically—see under 'Iron') —often reported as FeO.

TiO_2.—The other portion is used to determine Ti colorimetrically (as under 'Fireclay').

Al_2O_3 is obtained by difference. Deduct from the weight of mixed oxides *twice* the Fe and Ti estimations which have been converted to their respective oxides.

Cr_2O_3 may be determined volumetrically by standard methods (see under 'Chromium') or gravimetrically as follows:

Treat the filtrate from the previous precipitation with H_2SO_3 until the green colour of chromic salts has been obtained. Boil off excess SO_2, cool and make just ammonical. Reboil to coagulate the hydroxide precipitate, filter wash with hot 2% ammonium nitrate and ignite in a Pt crucible. Weigh as Cr_2O_3.

MnO.—By precipitation with ammonia and bromine (as under 'Fireclay').

CaO.—By precipitation and ignition of the oxalate (as under 'Fireclay').

MgO.—By precipitation as phosphate and ignition to pyrophosphate (as under 'Fireclay').

DOLOMITE AND LIMESTONE (Also Lime).

[Pigott, *loc. cit.* and others]

Loss on Ignition (due to moisture, carbon dioxide and organic matter removed).—Heat 1 g of finely powdered sample in a Pt crucible for 15–30 minutes at 800–900° C., cool and weigh.

SiO_2.—Dissolve 1–3 g of finely powdered sample in 10–25 ml. water and 15–30 ml. 50% HCl. Evaporate to dryness, bake, redissolve in 30 ml. 50% HCl, dilute, boil and filter off SiO_2. Ignite and volatilize exactly as under 'Fireclay'.

Fe_2O_3 + Al_2O_3.—To the filtrate from above (plus any residue after volatilization which is first dissolved in conc.HCl),precipitate the mixed hydroxides with ammonia. Ignite and weigh as mixed oxides, from which Fe may be estimated as under 'Fireclay' and Al_2O_3 obtained by difference.

CaO.—The above filtrate is diluted and a suitable fraction taken for CaO estimation by precipitation as calcium oxalate which is dissolved in 10% H_2SO_4 and titrated at 80° C. with standard $KMnO_4$ solution (see under 'Calcium').

MgO.—To the filtrate from CaO estimation, add 100 ml. HNO_3 and evaporate to dryness. Redissolve in 30 ml. 10% HCl, make slightly ammoniacal and filter off any residue (discard). Cool, add 10 ml. 10% ammonium phosphate followed by one third of the volume present of ammonia. Stir vigorously and stand overnight. Filter on paper pulp, wash with 5% NH_4OH and ignite in porcelain carefully at first (to burn off the paper) then at 700–800° C. Weigh as magnesium pyrophosphate.

CO_2.—Best determined with the standard Schroetter apparatus.

S.—Treat a 2 g sample with 20 ml. bromine water followed by 20 ml. 50% HCl. Evaporate to dryness and gently bake. Redissolve in 20 ml. water and filter off SiO_2, washing well with hot water.

Dilute the filtrate to about 250 ml., heat to boiling and add 10 ml. 10% $BaCl_2$ solution dropwise. Stir and allow to stand for a few hours. Filter through paper pulp and wash with hot water. Ignite and weigh as $BaSO_4$.

MAGNESITE

[Brearley and Ibbotson, *The Analysis of Steel Works Materials.*]

Silica

Dissolve 1 g in 20 ml. HCl, evaporate to dryness, take up with HCl and water, filter, wash well, ignite, volatilize with HF. Loss = SiO_2.

Alumina and Ferric Oxide

To the filtrate from the above estimation add a few grams of NH_4Cl, and NH_4OH, boil and filter quickly; the combined oxides may be estimated together or separately exactly as described under 'Analysis of Fireclay'.

Lime

Dilute the filtrate very considerably, add several grams of NH_4Cl, and then add ammonium oxalate, heat the solution, stir well, cool and filter, redissolve the precipitate in HCl, and reprecipitate in a solution which is just ammoniacal, estimate the lime as CaO as usual.

Magnesia

Acidify the filtrates from the estimation of lime, evaporate to some definite bulk, and take 150 ml., add 50 ml. strong NH_4OH and an excess of a saturated solution of sodium ammonium phosphate, stir well, allow to settle for several hours, filter on pulp filter, wash with water containing NH_4OH, dry, ignite and weigh as $Mg_2P_2O_7$. Report as MgO.

Manganese Oxide

As in 'Fireclay'.

Phosphate

Attack 5 g with HCl, filter, volatilize the SiO_2, dissolve any

insoluble residue, and add it to filtrate. Add NH_4OH and filter off basic ferric phosphate. Dissolve in HNO_3 and estimate phosphorus by the 'lead molybdate' method, as described under 'Phosphorus'.

NEUTRAL MATERIALS

CHROME BRICK

[Brearley and Ibbotson]

Iron

Ignite 2 g in a platinum crucible until a constant weight is obtained. Fuse 0·5 g of this with Na_2O_2 in a nickel crucible, dissolve melt in water, allow to settle and filter through pulp by decantation. Wash well with water. Dissolve precipitate in dilute HCl, adding the solution to the vessel containing the bulk of the oxides. Dissolve these oxides in HCl, make alkaline with NH_4OH, filter and ignite the precipitated Fe, Mn, and Al. Treat the precipitate with HCl until the Fe is dissolved, dilute with water and estimate Fe by the volumetric dichromate method (see under 'Iron').

Boil down the filtrate, make neutral and then just alkaline and saturate with H_2S to separate any nickel; filter off and wash with water.

Lime

Boil down the filtrate and add NH_4OH and ammonium oxalate, filter through pulp, washing with hot water containing a few drops of NH_4OH, ignite and weigh as CaO.

Magnesia

Boil down filtrate and add about one-third its volume of NH_4OH and an excess of a saturated solution of sodium phosphate, allow to settle for some time, filter through pulp, wash with NH_4OH, ignite and weigh as $Mg_2P_2O_7$. Calculate to MgO.

Silica

Fuse 0·5 g with Na_2O_2 in a nickel crucible, dissolve melt in water and filter, ignite residue and fuse again with Na_2O_2, extract melt with water and add an excess of HCl, evaporate down to dryness on a water bath, take up again in HCl, dilute and filter off SiO_2, ignite, weigh, volatilize with HF and H_2SO_4, weigh again. Loss = SiO_2.

Alumina.

To the filtrate from the SiO_2 estimation add a faint excess of HCl, then sodium phosphate and enough ammonium acetate to destroy the free HCl, filter, wash, ignite and weigh as $AlPO_4$, and calculate to Al_2O_3.

Chromium

Chromium may be best estimated on a separate sample by giving a peroxide fusion and titrating with standard ferrous ammonium sulphate and $KMnO_4$ solutions (see under 'Chromium').

Analysis of Ceramic Materials containing Silicon Carbide

Sampling

Crush as fine as possible in a percussion mortar without attempting to grind the silicon carbide unduly. Take a sample for analysis, of about 1 g, by quartering down to avoid segregation.

SiO_2

Transfer sample to a weighed platinum dish, treat with a few drops of H_2SO_4 and 5 ml. HF. Evaporate carefully to fumes. Repeat with 5 ml. HF until sample appears completely broken down and the silicon carbide looks fairly clean. Evaporate to dryness, ignite and weigh.

Loss = SiO_2.

Note: A correction has to be made for alkalis converted to sulphates—see below.

SiO_2 and SiC

To the residue in the crucible add 5 g $KHSO_4$ and fuse just inside a muffle for 30 minutes. Raise the temperature of the fusion until fumes of SO_3 cease to be evolved, at the same time avoiding excessive frothing.

Cool, extract melt with 50% HCl, transfer to a 7 inch porcelain basin, evaporate to dryness and bake. Take up with 50 ml. of 50% HCl, warm to dissolve salts and filter through a Whatman No. 41, 11 cm. paper. Transfer residue to a Pt crucible, ignite and weigh. Total residue = SiO_2 + SiC.

Treat with a few drops of H_2SO_4 and 5 ml. HF, evaporate to dryness, ignite and reweigh. Residue = SiC.

If SiC is not clean it will be necessary to re-fuse with $KHSO_4$. Add the SiO_2 figure to the main HF estimation.

Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO

Collect filtrate (s) from SiO_2 and SiC in 500 ml. flask and proceed as for 'Clay Analysis'.

Alkalis

As for 'Clay Analysis'.

Correction for SiO_2 (due to alkali sulphate formation)

$$\begin{array}{ccccc} Na_2O & \rightarrow & Na_2SO_4 & \therefore 1\%\ Na_2O \text{ would result in a gain} \\ 62 & & 142 & \text{of } 1{\cdot}29\%\ SO_3 \\ K_2O & \rightarrow & K_2SO_4 & \therefore 1\%\ K_2O \text{ would give a gain of} \\ 94{\cdot}2 & & 174{\cdot}2 & 0{\cdot}85\%\ SO_3 \end{array}$$

Evaluation of the Purity of Silicon Carbide

The usual impurities are Si, SiO_2, Fe and C.

Si

Treat 10 to 20 g of sample with 10% solution of NaOH in a platinum basin. Heat gently until evolution of hydrogen ceases. Dilute to a fairly large bulk, filter through a porous crucible, wash well with hot water, dry and weigh.

$$\text{Loss in weight} = \text{Si} (+ \text{ some } SiO_2).$$

SiO_2 + C (Free)

Treat 10 to 20 g of the Si free sample with a little HF and a few drops of H_2SO_4. Evaporate to dryness and heat at a dull red heat to constant weight.

$$\text{Loss in weight} = SiO_2 + \text{C}.$$

Note: A correction must be made for conversion of Fe to Fe_2O_3.

Fe

Digest the residue with hot conc. HCl to extract the Fe_2O_3. Dilute, filter and wash. Collect filtrate, make up to a known volume and estimate Fe colorimetrically with ammonium thiocyanate using a standard Fe solution.

$$100\% - \%\ \text{total impurities} = \%\ \text{silicon carbide}.$$

Porosity of Firebricks, Cupels and Other Burnt Ceramic Ware

Brush away all loose particles from the sample which should be at least about 1 cubic inch.

Dry in an air oven, cool in desiccator and weigh (A). Place sample in a beaker beneath a bell jar and exhaust bell jar for 10 minutes using a 'Hyvac' or other good pump.

Close the tap on the pump and suck in distilled water to cover the sample. This is accomplished by having a delivery tube through the rubber cork in the bell jar reaching into the beaker containing the sample.

Break vacuum and allow to stand overnight in the case of very small pores. For coarse structures 1 hour is sufficient.

Suspend the sample from a balance (using a strand of very thin wire) into a suitable beaker containing sufficient water to cover the sample. The beaker is supported on a stool which covers but stands clear of the balance pan. Use an equal length of wire as a counterpoise.

Weigh and note weight (B).

Very carefully and quickly wipe the water from the outside of the sample and weigh in air (C).

$$\text{Porosity } \% = \frac{C - A}{C - B} \times 100.$$

Estimation of Iron Soluble in HCl when present in very small quantities in Ceramic Materials

Method A using Thioglycollic Acid

Weigh 2 g sample into a 200 ml. beaker having a 50 ml. mark. Add 50 ml. of 50% HCl (from a stock solution known to be iron free).

Boil gently for half an hour, cool, make up to 50 ml. with distilled water. Stir and allow to stand until clear.

Transfer 25 ml. of the clear solution to a Nessler cylinder.

Make just alkaline with NH_4OH and then just acid with HCl. Cool to room temperature. Add 5 drops of thioglycollic acid and 2 ml. of 20% solution of citric acid.

Add NH_4OH from a burette until solution turns red and then add a further 0·5 ml. Make up to 50 ml.

Make suitable standards by adding to about 40 ml. of water in a Nessler tube a known volume of Fe solution, 5 drops of thioglycollic acid and 0·5 ml. excess of NH_4OH (sp. gr. 0·880).

These standards must be made immediately after the test colours have been developed. The colours should not be matched until 15 minutes after their development.

The standard Fe solutions must contain no HNO_3 as oxidizing agents interfere.

The standard Fe solution should contain 0·00001 g per ml.

Method B

Weigh 2 g of sample into a 200 ml. beaker with a 50 ml. mark. Add 50 ml. of 50% HCl containing 1% of HNO_3.

Boil for half an hour, cool, make up to 50 ml. with distilled water, stir and allow to stand until clear. Transfer 25 ml. of the clear solution to a Nessler cylinder. Make up to 50 ml. mark with distilled water and add 5 ml. of ammonium thiocyanate solution (150 g made up to 300 ml.).

From a burette run in standard iron solution, 0·5 ml. at a time, to the blank solution until the colours match.

Analysis of Sodium and Potassium Silicates

K_2O or Na_2O

Place approximately 3 to 4 g in a dry stoppered weighing bottle and weigh.

Wash out into a 250 ml. beaker, dilute to 100 ml. and add 1 ml. of 0·01% methyl orange.

Titrate with $\frac{N}{2}$ H_2SO_4 until a faint pink colour appears.

$$K_2O\ \% = 4{\cdot}7 \times \frac{\text{ml. of acid}}{\text{weight taken}} \times \text{Normality}$$

$$Na_2O\ \% = 3{\cdot}1 \times \frac{\text{ml. of acid}}{\text{weight taken}} \times \text{Normality}$$

SiO_2

Weigh out 3 to 4 g into a 7 inch porcelain basin as above, and dilute to 50 ml. Add 25 ml. of conc. HCl, evaporate to dryness on the water bath and then bake on the hot plate for 1 hour.

Take up in 50% HCl and warm to dissolve salts.

Filter through Whatman No. 41 11 cm. paper, well wash with 50% HCl and finally hot water.

Ignite in a platinum crucible, weigh.

Treat with a few drops of H_2SO_4 and 5 ml. HF, evaporate to dryness, ignite and reweigh.

$$\text{Loss in weight} = SiO_2.$$

Analysis of French Chalk, Talc, etc.

Loss on Ignition

As for 'Clay Analysis'.

Analysis of the Dried Sample

SiO_2

Weigh out 1 g and estimate SiO_2 as for 'Clay Analysis'.

Al_2O_3, Fe_2O_3, TiO_2

These impurities should be small in which case they are estimated together.

To the filtrate from the SiO_2 estimation, add 10 g NH_4Cl and precipitate with NH_4OH in the usual way. Should the precipitate be large it should be redissolved and reprecipitated. Wash, ignite and weigh the combined oxides.

CaO and MgO

Estimate as in 'Clay Analysis'.

CHAPTER XI

THE ANALYSIS OF COAL AND COKE

This chapter will be devoted to a general discussion and review of standard and more recent methods for the analysis of coal and coke, together with their application. No attempt will be made to give the voluminous experimental details of the various methods, but references are given where such details may be obtained.

Official publications dealing with standard methods for the analysis of coal and coke, have been available for many years.[1, 2, 3, 4] In this country two such compilations are well known ; one published by the Fuel Research Board and the other by the British Standards Institution. More recently the British Coke Research Association has formed a Panel[5] to prepare a list of recommended methods for use within the coking industry. Although the work of this Panel is well-advanced its recommendations have not yet been made generally available.

It is, of course, essential to view standard methods from the right perspective. They are often a compromise of differing viewpoints of members of the standardizing committee, and recent advances may be not included for some years. The methods may be tedious for routine control and may even contain blemishes, nevertheless, standard methods have advantages which are of such importance as to outweigh all their defects. They are based on procedures which have withstood the test of time, and they are only advanced after much deliberation and weighty consideration have been devoted to them. Thus, whilst a laboratory may use its own particular method which, it is felt, is as accurate as a standard method and much more rapid, in any case of dispute with outside laboratories only B.S. methods can be acceptable for settling that dispute.

Sampling

The importance of correct sampling cannot be over-emphasized when dealing with a heterogeneous material such as coal. It will be obvious that the analytical figures obtained subsequently will be worthless unless the sample is as truly representative as possible. Coal and coke are heterogeneous materials and the correct method for sampling them must be based on statistical principles.

Similarly the results obtained should be treated on a statistical basis as they will not be absolutely correct except by mere chance, but the probable error from the correct result will be predictable depending on the rigour with which the sampling is carried out. Details for the sampling of coal and coke and the probable error involved are fully outlined in B.S. 1017[6] and the instructions therein should be followed rigidly. Two injunctions which may be stressed here are that the sample should always be taken by a trained sampler and should never be less than the stated number of increments, which must be about the same weight and must be evenly distributed over the whole consignment.

Proximate Analysis

The term 'proximate analysis' includes the determination of moisture, ash, volatile matter and fixed carbon. These determinations are used as a rough assessment of the quality of a sample of coal and coke, and are often the only determinations made. The term 'ultimate analysis' is used in the same sense as for organic compounds, namely, the determination of the chemical elements present.

The Determination of Moisture

Moisture may exist in various forms in coal, but for normal purposes, the total moisture is considered as being comprised of *free* or *extraneous* moisture and *inherent* or *adsorbed* moisture. Free moisture may have been acquired during washing, from the weather or from other sources. When coal is exposed to the air it relinquishes the free moisture, but must be heated to 105° C. before the inherent moisture is expelled.

Methods for the determination of total moisture

(1) A 2 lb. sample of half inch size is heated to constant weight in an air-oven at 100–110° C. The time required usually occupies 5 to 6 hours. This method is only suitable for coals containing less than 4% moisture.

(2) A 2 lb. sample is heated with a petroleum distillate in a modified Dean-Stark apparatus. This method is suitable for all coals and requires a time of 6 to 8 hours.

(3) The sample is ground to pass a 6 B.S. sieve, reduced to 8 oz. and the loss in weight of a 10 g portion determined after heating in an oven at 105–110° C. for $1\frac{1}{4}$ to 3 hours. Alternatively 10 g of the B.S. mesh sample is treated as in (2). If the coal sample is visibly wet or of low rank it should be air-dried before grinding, by spreading it out in a thin layer on trays. It may then be exposed to free air circulation either at room temperature for 6 to 10

hours or at a temperature not exceeding 50° C. for 1¼ to 3 hours. The loss on air-drying is obtained by the differences in weight before and after exposure.

The total moisture 'as sampled' is then calculated by

$$M = M_1 + M_2 \left(1 - \frac{M_1}{100}\right)$$

Where M = total moisture as sampled.
M_1 = percentage loss on air-drying.
M_2 = percentage loss at 105° C. determined in the sample after air-drying.

For all the other determinations described the coal sample is used after crushing through 72 B.S. mesh. When the coal has been crushed through 72 B.S. mesh it will eventually come into equilibrium with the atmosphere and the moisture content will depend on the humidity of the ambient air. The coal is then in the 'air-dry' condition, and its moisture content (which is the inherent moisture of the coal) is termed 'the moisture content of the air-dry sample'. Obviously, it will bear no relation to the original moisture content of the sample, but as the rest of the proximate analysis is determined on the air-dried sample, a knowledge of this figure, together with the total moisture, is necessary for computing the proximate analysis of the coal 'as sampled'. It is thus possible to report the proximate analysis on two different bases, i.e. on the 'air-dried' basis and on the 'as-sampled' basis, and the basis used will depend on the purpose of the analysis. Brown and Bean[7] summarize the particular use of each basis as follows:

(1) To *compare* coals—use the 'air-dried' analysis.
(2) To *evaluate* coals—use the 'as-sampled' analysis.

It may also be mentioned at this stage that the moisture and ash figures of the 'air-dried' sample are also used to correct the ultimate analysis to the ash-free dry basis (or to other more refined bases) to assess the latter on the pure coal substance.

The determination of total moisture is time-consuming, and for purposes of industrial control more rapid methods would be of value, but this problem has yet to be overcome satisfactorily. Greenfield and Dummett[8] have described a method in which small coal (coking slack) is extracted with standard acid and the resulting change in concentration measured. This process does not remove all the inherent moisture,[9] and where this is high the error will be appreciable. In cases where coals of low inherent moisture content are used, the method might be standardized as a satisfactory means of assessing the approximate total moisture content. Similar difficulties were encountered by Belcher and

Spooner[9] in attempting to apply the methanol extraction method, and the rapid drying method which had proved successful for the rapid determination of moisture in coal ground through 72 B.S. mesh,[10] owing to the firm retention of the inherent moisture in the capillaries of the coal. More recently Schmidt and Seymour[11] have described a methanol extraction process which is being developed for the determination of surface moisture, but a certain amount of inherent moisture would also be removed and the method would only be applicable under the conditions cited above.

Mott and Spooner[12] have put forward a rapid method for the removal of surface moisture where a 2 lb. sample of through $\frac{1}{2}$ in. mesh coal is spread in a thin layer (0·7 gm/cm^2) in an oven at a temperature of 200° C. Under such conditions surface moisture is lost at a rate of 1% per minute, so that in 10 minutes a sample of coal containing 10% of moisture can be dried sufficiently to be crushed through 72 B.S. mesh. This is a great saving in time in preparing the sample, as under normal conditions several hours must be spent in air-drying a coal before it is crushed through 72 B.S. mesh. The method is not put forward for the determination of total moisture, as not all the adsorbed moisture is removed, but it can be adapted to such a purpose if the same coal is to be tested daily and the conditions are rigidly standardized and an empirical factor applied.

Methods for determination of moisture in the 'air-dry' sample

Moisture is determined on the air-dried sample from the loss in weight after heating a 2g portion at 105–110° C. until constant in weight. The sample is weighed into a shallow dish provided with a well-fitting cover. It is imperative that this cover be in position both when the dish is cooling in a desiccator and when the final weighing is made. Finely ground coal has powerful desiccating properties and is a more efficient desiccant than calcium chloride. The use of more powerful desiccants such as activated alumina or Anhydrone (magnesium perchlorate) have little advantage because when the desiccator is opened, laboratory air enters and equilibrium may not be re-estabished for about 2 hours.[13] Since the analysis sample would be removed after 15 or 30 minutes it can absorb an appreciable amount of moisture unless covered. Similarly if the dried coal is weighed uncovered, atmospheric moisture will be absorbed during the weighing. It may seem that unnecessary stress is being laid on what are obvious and simple precautions, but in our experience these are often omitted in industrial laboratories.*

* See also Belcher and Mott, *J. Appl. Chem.* 1952, **1**, 204.

Rapid methods for determining moisture have been advanced, and although most of these achieve their purpose, often only single samples can be treated at a time. Thus, for batch work the oven method would eventually prove more rapid. However, in cases where a rapid assessment of the moisture content of a single sample is required such a method may be applied with advantage. Examples of such rapid methods are Dolch's method[14] (extraction of water with ethanol under reflux followed by determination of the consolute temperature), Mannheimer's method[15] (extraction of water with methanol followed by a density determination) and Piatschek's[16] method (liberation of acetylene from calcium carbide).

Belcher and Spooner[10] examined Piatschek's method and found it subject to a number of variables. These investigators developed two rapid methods each of which furnishes the moisture figure in 10 to 15 minutes. In one method the coal is shaken with methanol, rapidly filtered and an aliquot of the filtrate mixed with carbon tetrachloride. Water is then added from a weight or microburette until a permanent turbidity appears. The difference between the weight of water thus added and that required by the original methanol gives the amount of water in the aliquot. In the other method, 0·5 g of coal contained in a shallow boat $\frac{1}{2}$ inch $\times$ $4\frac{1}{2}$ inch $\times$ $\frac{3}{8}$ inch is heated in a tube maintained at 110° C. Nitrogen is passed through at the rate of 100 ml. per minute for 10 minutes. The boat is then withdrawn, placed in a stoppered tube, cooled on a metal block and weighed. The loss in weight represents the moisture content of the coal. This latter method could be adapted to batch determinations by using several tubes surrounded by a jacket maintained at the requisite temperature. A greater accuracy than in any of the indirect methods could be achieved by attaching weighed absorption tubes containing a suitable desiccant, and finding their increase in weight. This would avoid the slight error involved by the inevitable reabsorption of moisture by the dried sample. Only the same number of weighings as in the indirect method would be involved. Thus two important advantages, both speed and accuracy (not always concomitant) would be realized. If it is desired to carry out the determination on larger quantities, 1·0 g samples require 15 minutes heating and 2·0 g samples require 25 minutes heating.†

Methods for the Determination of Ash

Ash differs from the original mineral matter of the coal both in

† A rapid direct method has been described by Belcher and Spooner, *Fuel*, 1947, **26**, 55.

composition and amount. Various changes occur during incineration, such as loss of combined water from shaley material, oxidation of pyrites to iron oxide and fixation of sulphur gases by bases. The last factor may cause errors during multiple determinations if the samples have a high lime content owing to absorption of sulphur oxides, evolved from the samples in the front of the muffle, by the ash of those at the back. In B.S. 1016 this source of error is eliminated by stepwise decomposition, first at 400° C. and later at 775° C. ± 25° C. With single samples the incineration need only be affected at the highest temperature.*

Few methods have been advanced for rapid determination of ash. Lategan[17] has recommended a volumenometer method depending on the difference in specific gravity between the coal substance and the inorganic constituents of the ash. This method would be of limited application because the specific gravity of the ash-producing constituents varies for different coals. Gross and Abramsky[18] claimed that comparison of the tints using a Pulfrich step photometer gave an error of 7% and with care only 2 to 3%. Moran[19] has described a method used for plant-control purposes which, it is claimed, can be completed in 20 minutes after taking the sample from the plant. It depends on rapid incineration of the sample contained in a boat in a stream of oxygen in a tube furnace. Belcher and Spooner[10] describe a similar method which takes 10 minutes for the combustion. The method is carried out simultaneously with the rapid moisture determination (p. 557) allowing both ash and moisture figures to be reported 15 minutes after the sample reaches the laboratory. The results obtained compared favourably with those obtained by the standard method.

Methods for the Determination of Volatile Matter

Volatile matter is determined by heating the coal, contained in a closed crucible, under standard conditions, the loss in weight being the volatile matter plus moisture. Since the moisture content of the sample will vary according to the humidity of the air, it is important that the moisture and volatile matter determinations should be determined about the same time, and at least on the same day.

Since the test is empirical, reproducible results can only be obtained by rigid control of the temperature and duration of heating (925° C. ± 15° C.) which should be regained within 3 minutes from the time of insertion of the crucible. To ensure this

* As an example of the importance of controlling the ignition conditions Crossley has recorded that a particular coal yielded from 7 to 9% ash according to the conditions employed for the ignition.

condition determinations are made singly. Although it might be possible to increase this number by using a stand of low heat capacity, the procedure could only be acceptable after exhaustive tests have been made.

In this connection Radmacher[20] has designed a special furnace which allows four tests to be made simultaneously. It is reported that the method gives similar results to those obtained by the standard German method using one crucible. A heating element is fitted into the lid of the furnace and the rheostat is adjusted during the test, so that the standard temperature is regained within 3 minutes from the time the crucibles were inserted.

Modifications to the standard method are necessary for certain coals, such as anthracites, which decrepitate. These are mixed with a small amount of a coking coal of about 25% volatile matter, or alternatively the initial rate of heating may be reduced by placing the crucible on an insulating asbestos disc. The latter procedure is always used for cokes, and in addition 2 to 4 drops of benzene are added to minimize oxidation.

An alternative to the muffle method is listed in B.S. 1016 in which the sample contained in a boat is heated in a tube furnace in a stream of nitrogen. By using a 4-tube furnace four samples may be treated simultaneously. The boats are heated initially at 600° C., raised to 925° C. in 40 minutes, and maintained at this temperature for seven minutes. Coals which decrepitate are heated initially at 400° C., otherwise the procedure is the same. The boats are allowed to cool in nitrogen before weighing. With certain reactive cokes the tube method must always be used since appreciable oxidation cannot be prevented in the muffle method.

The volatile matter is assessed as the loss in weight in the volatile matter test, less the moisture. The fixed carbon content, which is the other constituent of the proximate analysis, is given as the difference between 100 and the sum of the moisture, ash and volatile matter. The fixed carbon content finds little application and is seldom calculated in practice.

Methods for the Determination of Total Sulphur

Two methods[2] are widely used in this country for the determination of sulphur, namely, the Eschka method and the bomb method.[2] A third method, the sodium peroxide method,[1] is also recommended by the A.S.T.M. but finds little application in this country. The Eschka method is generally preferred where a large number of samples has to be dealt with, since the bomb method can only be applied to single samples and the time of

standing to allow sulphur trioxide mist to settle may interfere seriously with calorimetric determinations.

Many attempts have been made to expedite the Eschka method, but the lengthy time-honoured procedure still keeps its place in the standard specifications. Such attempts have involved both accelerating the time of ignition by adding oxidizing agents to the Eschka mixture, and by substituting titrimetric methods for the classical gravimetric finish. Although many methods for the titrimetric determination of sulphate exist, none compares with the gravimetric method in accuracy. Amongst the more popular of the older methods, the well-known chromate and the benzidine hydrochloride methods have been tried and found unsatisfactory. More recently some claims for sodium rhodizonate or tetrahydroxy-quinone indicators[21, 22] have been made when applied to the Eschka method, but in our hands these indicators have proved unsatisfactory, not only when applied to the Eschka determination but to any determination of the sulphate ion.*

In recent years Mantel and Schreiber[23] have carried out an extensive investigation of the Eschka method with a view to accelerating the ignition. A wide range of possible catalysts were examined, ammonium molybdate being found the most suitable. In addition, air is drawn through the muffle at a velocity of 10 litres per minute and 10–11 g of Eschka molybdate mixture used instead of the conventional 4 g. In an investigation of this method, B.C.R.A. Panel 1 found that complete ignition could be achieved in 90 minutes for coals and 120 minutes for cokes, by suitable regulation of the temperature of the muffle without addition of catalyst. Only in the case of muffles possessing but a single door had special modifications to be introduced. In these circumstances air is drawn through the muffle either by connecting a water pump to a silica tube reaching to the back of the muffle, or by attaching a chimney to the door of the muffle also reaching to the back.

After examining various methods for the rapid determination of the sulphate ion, it was found that a modification of the classical method was the most suitable. Provided that sufficient excess of barium chloride solution is added, the precipitate may be filtered 30 minutes after precipitation. The addition of picric acid or agar-agar, which have been recommended for rapid granulation of barium sulphate, offered no advantage with the amounts of sulphate obtained from 1 g of coal. These two findings have been combined to provide a rapid Eschka method which has been included in the

* Similar conclusions have been reported to us by a large number of other laboratories.

list of recommended methods prepared by the Panel for the coking industry.*

As an alternative method, the rapid combustion method of Beet and Belcher[24] is recommended. In this method the sample contained in a boat is burnt in a rapid stream of oxygen in a tube at 1300–1350° C., the total time for combustion being 8–10 minutes. The sulphur oxides and chlorine are absorbed in hydrogen peroxide to form sulphuric and hydrochloric acids respectively. After having determined the total acidity by titrating with N/20 sodium hydroxide, a solution of mercuric oxycyanide is added to the neutral solution and the following reaction occurs :

$$NaCl + Hg(OH)CN \rightarrow NaOH + HgCl.CN.$$

The alkali liberated is titrated with standard sulphuric acid and gives the chlorine figure directly, and the sulphur figure is calculated from the difference between the two titres obtained.

Sulphur in solid fuels may also be determined by adding a catalyst mixture and gasifying at 1100–1150° C. in steam.[25] The whole of the sulphur is liberated as hydrogen sulphide which is absorbed in cadmium acetate solution and determined iodimetrically. This method, developed by Mantel and Schreiber, has been standardized by the German coking industry.

Methods for the Determination of 'Sulphate' and 'Pyritic' Sulphur

The methods described in B.S. 1016 are based on those of Powell and Parr. 'Sulphate' sulphur is removed by extracting 5 g of coal with dilute hydrochloric acid for 40 hours at 60° C., filtering and determining the sulphate gravimetrically in the filtrate. The extraction process may be shortened to 12 hours by shaking for 15 minute intervals every hour or so, but this has no advantage. 'Pyritic' sulphur is determined by extracting a 1g portion for 24 hours at room temperature with 4 N nitric acid, filtering and removing the excess nitric acid by evaporation and determining the sulphate gravimetrically. This procedure gives 'sulphate' sulphur plus 'pyritic' sulphur and the latter is obtained by deducting the 'sulphate' figure found by separate experiment. According to B.S. 1016 the extraction process may be shortened by shaking in a mechanical shaker for not less than 1 hour, but in our experience this is not the case.

The F.R.B. procedures differ in the methods of completing the determinations. Instead of employing the gravimetric finish the iron content of both extracts is determined by titration with

* B.C.R.A. *Technical Paper* No. 1, 1948.

titanous chloride, since it is claimed that nitric acid dissolves a small amount of organic sulphur and the resulting figure obtained gravimetrically is therefore too high. The 'pyritic' iron is obtained from the difference between the two figures, and the 'pyritic' sulphur calculated from the stoichiometric ratio. Alternatively the 'pyritic' iron may be determined on the residue after removal of 'sulphate' and 'non-pyritic' iron.

Mantel and Radmacher[26] have described an evolution method for the direct determination of pyritic sulphur which occupies 30 minutes. The coal is heated with zinc and hydrochloric acid and mercury catalyst, and the resulting hydrogen sulphide determined iodimetrically. Belcher and Spooner,[27] however, found the results were always low by this method. They investigated several alternative reducing agents, and found tin and hydrochloric acid without catalyst addition to be the best of those examined. Under these conditions fair results were obtained with coals containing small amounts of pyritic sulphur, but otherwise the results were still low. They were unable, therefore, to recommend an evolution method for the determination of pyritic sulphur. The same investigators developed a method similar to the F.R.B. modification of Powell-Parr extraction process, but in which the iron is determined by titration with standard mercurous nitrate solution, instead of titanous chloride since it has a number of advantages.

Other methods have been developed with the object of shortening these determinations* but, in general, this is achieved at the expense of accuracy. Recently, Teichmann[28] has recommended a rapid method for the determination of 'sulphate' sulphur which is of promise. The coal is extracted with 5N hydrochloric acid at the boiling point during 1 hour and the determination then completed in the conventional manner. The results compare favourably with the Powell-Parr method being, in general, slightly lower. The difference is, however, negligible for routine work and need only be considered where unusual accuracy is required. Teichmann claims that this difference is due to slight aerial oxidation of pyrites at 60 ° C. in dilute acid; under his conditions absorption of atmospheric oxygen is negligible and, therefore, the figure obtained is the correct value. Tests carried out in the authors' and other laboratories confirm Teichmann's conclusions and his method may, therefore, be recommended.

The 'sulphate' and 'pyritic' sulphur determinations might be accelerated by a suitable combination of the findings reported in the above discussion. The 'sulphate' sulphur and non-pyritic iron

* For example see *Chemistry of Coal Utilization*, H. H. Lowry (Editor), John Wiley (Chapman & Hall). 425, *et seq.*

may be extracted by Teichmann's procedure and the total iron by boiling nitric acid, the two extracts may then be titrated with standard mercurous nitrate solution. This would then enable both determinations to be completed within two hours.*

Methods for the Determination of Nitrogen

Nitrogen in coal is generally determined by the Kjeldahl method or one of its modifications. The figure obtained will always be lower than that given by the Dumas method since the latter will include occluded nitrogen. Various modifications of the Kjeldahl process have been recommended, mainly in the nature of the catalyst employed, but essentially it consists of decomposition of the coal by digestion with sulphuric acid, which converts the nitrogen to ammonium salts, followed by distillation of the ammonia liberated by treatment with excess alkali, into standard acid.

B.S. 1016 recommends the use of either mercuric sulphate or selenium as catalysts. Beet[29] found, however, that a mixture of the two is more efficient, a claim which is supported by the work of other investigators.[30] We have tried many of those recommended, but the mercuric sulphate-selenium catalyst appears to be the best.

To obtain complete conversion of nitrogen to ammonia it is essential to continue the digestion for some time after the solution has cleared. The reason for the need for this 'after-boil' period with coals has been established by Beet[29] from his extensive investigations of the Kjeldahl process. Part of the coal is converted to pyridine carboxylic acids which do not char with sulphuric acid and are extremely resistant to Kjeldahlization. When, therefore, the mixture becomes colourless or straw-coloured, an appreciable amount of these acids remains undecomposed. The 'after-boil' treatment is necessary to convert these compounds to ammonia. Beet[29] has actually isolated these and similar compounds from the digest after stopping the process at various stages.

Beet and Belcher[31] recommend a semi-micro method as a substitute for the macro method. The digestion using the mercuric sulphate-selenium catalyst occupies only a total time of 20 minutes and distillation is completed in 5 minutes. The ammonia is absorbed in saturated boric acid solution and titrated directly with N/100 hydrochloric acid.

A method based on gasification of the coal in superheated steam at 900° C. has been developed by Mantel and Schreiber.[32] The

* This has been actually proved since this section was prepared. See B.C.R.A. Panel No. 1, *Third Report*, 1949, for a rapid and accurate method for forms of sulphur.

coal is mixed with a catalyst consisting of soda-lime, Eschka mixture and molybdic oxide. The nitrogen is thus evolved completely as ammonia. A similar method was previously advanced by Beet[33] for the determination of nitrogen in cokes, since a protracted digestion is necessary by the Kjeldahl method. The coke is mixed with soda-lime as catalyst and gasified in steam at 900° C. The ammonia is absorbed in dilute sulphuric acid and subsequently distilled. The gasification occupies about 1 hour. Beet and Belcher[34] later developed a semi-micro method using 0·1 g of coke based on this principle. The gasification then takes 10 minutes and the total time is further reduced by distilling in the apparatus used in their semi-micro method for coals.

Chlorine

The B.S. method for chlorine consists of decomposing the coal with Eschka mixture at 500° C. and determining the chloride by Volhard's method. Although the method occupies comparatively little manipulative time, the ignition has to proceed for 24 hours to ensure complete decomposition.

Selvig and Gibson[35] recommend combustion of the sample in the calorimetric bomb, followed by argentometric titration of the chloride formed. The figures thus obtained were always higher than those given by the water extraction method.

Mantel and Schreiber[36] determine the chlorine by gasification of the fuel in steam in the presence of catalysts, as in their method for the determination of sulphur.

Belcher and Spooner[37] have described a method where the chlorine is determined simultaneously with carbon, hydrogen and sulphur (p. 565). However, only quali-quantitative accuracy is claimed and more care is required than in the determination of the other elements by this process. They recommend the titrimetric method (p. 561) in which sulphur is determined simultaneously if a more accurate assessment is required.†

Carbon and Hydrogen

Carbon and hydrogen in coals are usually determined by Liebig's classical method involving combustion in oxygen in a tube packed with copper oxide and lead chromate, the carbon dioxide and water produced being collected in weighed absorption vessels. This method demands high analytical proficiency before reliable results can be obtained. Moreover, it is unsuited for occasional determinations and is time-consuming.

† For an alternative rapid method see B.C.R.A. Panel No. 1, *Fourth Report*, 1950.

More suitable methods have been recommended, such as Dennstedt's method,[38] in which the products of decomposition are passed over a platinum catalyst and the combustion completed with the gaseous oxygen alone using both primary and secondary oxygen supplies. Interfering acid gases are retained in lead peroxide and red lead placed in boats near the outlet end of the combustion tube. Favourable reports have also been given of Ter Meulen's method,[39] in which manganese dioxide is used as the tube packing. One advantage of the method is that the tube need only be maintained at 450° C. Belcher and Smith[40] developed a semi-micro method similar in principle to that of Dennstedt in that a platinum catalyst is used, but eliminating the need for a secondary oxygen supply. The total time for a combustion takes 35 minutes using 50 mg. of coal.

More recently Belcher and Spooner[37] have described a method requiring a combustion time of only 10 minutes for a 0·5 g. sample, in which sulphur and chlorine may be determined simultaneously. The apparatus is the same as that used for the determination of sulphur and chlorine titrimetrically (p. 561), and the combustion is done in an empty tube at 1300–1350° C. using a rapid stream of oxygen. Sulphur oxides and chlorine are absorbed on a roll of silver gauze placed at the outlet end of the tube, forming silver sulphate and chloride respectively. Water and carbon dioxide are absorbed in Anhydrone (magnesium perchlorate) and soda asbestos.

Sulphur and chlorine may be determined by selective extraction of the silver sulphate and chloride with water and ammonia, and weighing the silver gauze roll after each stage. This method is only recommended if one or two samples have to be tested. For a series of determinations it is preferable to determine carbon and hydrogen only, and to use the titrimetric method for sulphur and chlorine. In this case the silver gauze should be cleaned after every two or three combustions (depending on the sulphur contents of the coals under examination) by immersing in ammonia for a few minutes. A duplicate silver gauze roll may be used so that combustions may be continued during this cleaning period.

Carbon, hydrogen and sulphur figures by this method agree with those obtained by the B.S. method. Chlorine figures are less satisfactory, possibly because of the small amount involved, but it is pointed out that quali-quantitative accuracy is often acceptable in this determination. Edwards and Vahrmann[41] of B.C.U.R.A. have subjected this method to critical examination and state that an accuracy for carbon, hydrogen and sulphur equivalent to the B.S. method was obtained. Chlorine figures

were less satisfactory, however, and they were unable to achieve the quali-quantitative accuracy of the originators.

Belcher and Spooner[42] in a later study of this technique developed micro and macro methods for the determination of carbon, hydrogen, sulphur and halogens in pure organic compounds and various other industrial materials besides coal. In the determination of carbon and hydrogen in organic compounds, either on the micro or macro scale, the combustion is carried out at 800° C. if the sulphur figure is also required. Certain compounds (such as the alkali sulphonates) do not liberate all the sulphur at this temperature. The procedure is similar to that for coals except that a nichrome-wire-wound furnace may be used.

More recently[43] a method has been described in which the sulphur after fixation on the silver gauze, is determined titrimetrically. This modification effects a considerable saving in time.

The Determination of Carbonate

It is necessary to determine carbonate in coals to calculate the organic carbon, since combustion methods give the sum of these two forms. In certain coals this correction may be ignored because of the small amount of carbonate present but other coals may contain as much as 1%. In the B.S. method carbon dioxide is liberated by treatment with acid and absorbed in excess of standard barium hydroxide. This solution is then back-titrated with standard hydrochloric acid, using phenolphthalein indicator. The F.R.B. publication describes the same method but also gives an alternative gravimetric method, the carbon dioxide being absorbed in soda-lime.

A rapid and simple method has been described by Beet,[44] in which the pressure at constant volume of the liberated carbon dioxide is measured. Results comparing favourably with the standard method were obtained, the total time for the determination requiring only about 5 minutes.

Methods for the Determination of Other Elements

Oxygen.—Oxygen is usually determined by difference, thus having to bear the burden of the accumulated errors from other determinations. Methods are available for the determination, but have not come into regular use. Amongst these may be mentioned Ter Meulen's hydrogenation method[39] or one of its modifications and Dolch and Will's method[45] where the coal is decomposed in a known quantity of oxygen and the residual oxygen measured; both of these, however, are liable to error owing to reactions of the ash. More recently Schütze[46] has devised a method for pure

organic compounds in which the compound is decomposed in nitrogen and the products of decomposition passed over heated carbon. The oxygen is thus converted to carbon monoxide, which is allowed to react with iodine pentoxide. Either the liberated iodine is then determined titrimetrically, or the carbon dioxide produced is absorbed in soda asbestos and weighed. Spooner[47] has made an extensive study of this process and by suitable modification has developed a method applicable to coals which requires only 20 minutes for its completion.

Phosphorus.—Phosphorus is determined in coal or coke ash when the fuel is required for metallurgical operations. Only one satisfactory method is known, that due to Marson, Edwards and Briscoe,[48] recommended in B.S. 1016. After decomposition of the ash with nitric and hydrofluoric acids the phosphorus is precipitated as the yellow phospho-molybdate and determined alkalimetrically.*

Arsenic.—Two methods are listed in B.S. 1016 for the determination of arsenic. The coal is heated with heavy magnesium oxide until decomposition is complete and the arsenic is determined by the Gutzeit procedure in one method, or electrolytically in the other method. This determination need only be carried out on coke used for malting purposes, when the amount of arsenic present should not exceed $\frac{1}{50}$ grain per lb. (2·84 p.p.m.).

Analysis of Ash

The methods used for analysis of ash recommended in B.S. 1016 follow closely classical methods used for the analysis of silicates. There is undoubtedly room for the development of more convenient methods as in the case of the determination of phosphorus and arsenic. Possibly the advances made in absorptiometry might be applied to these determinations with some hope of reducing the time required.

For the determination of alkalis the methods of Haslam and Beeley,[49] developed for the examination of refractories, appear to be applicable to ash analysis and would shorten the present procedure considerably. After decomposition by the Lawrence Smith method, potassium is precipitated as the cobaltinitrite in one aliquot, and sodium as zinc uranyl acetate in another. Similar methods[50] based on the opening out procedure of Berzelius have also been described.

Calorific Value

The calorific value of a fuel may be expressed either as the gross

* A rapid method has been since described, Belcher, *Fuel*, 1950, **29**, 232.

calorific value or the net calorific value. The difference between these two values is the heat liberated when the water vapour in excess of that necessary to saturate the gaseous products of combustion condenses to the liquid form at 60° F., and the gross exceeds the net by the amount of heat which is liberated by the latent heat of condensation of this water vapour reckoned at 1,055 B.T.U./lb. in British practice. The calorific value may also be defined at constant pressure or at constant volume, and the definition of the net calorific value at constant volume is the number of heat units liberated when the unit of the fuel is burned to constant volume in oxygen saturated with water vapour, the original and final materials being at 60° F. and the residual products being carbon dioxide, water vapour, sulphur dioxide and nitrogen. The definitions under other conditions are similar and are given in B.S. 1016[6] together with the definitions of the standard units used.

The determination should always be carried out in a high pressure bomb of the Berthelot type, of such a capacity that it shall contain, when filled under pressure, at least two and a half times the amount of oxygen required for the combustion. Full details of the apparatus and method of carrying out a determination are given in B.S. 1016,[6] together with the method for the determination of the water equivalent, for which purpose benzoic acid is used.

With the conventional type of apparatus it is necessary to make a correction for the fact that the temperature of the bomb, either before or after firing is not the same as the room temperature and, consequently, it is gaining or losing heat relative to its surroundings. The necessity for this correction lengthens the time of the test and also the calculation of the result, and for these reasons the Parr adiabatic bomb is to be preferred. In this apparatus the bomb is surrounded with a water jacket provided with its own hot and cold water supply, stirrer and thermometer, and during the test the temperature of the outer jacket is maintained at that of the calorimeter containing the bomb, thus ensuring no gain or loss of heat from the surroundings.*

The determination is invariably carried out in oxygen and the nitrogen and sulphur in the sample are, therefore, oxidized to a greater extent than occurs in air. The corrections necessary for these reactions are given in B.S. 1016[6] and in the Fuel Research Board Publication[3] on methods of analysis, and should be applied to all determinations.

*For a detailed account of this apparatus see the paper by Beet, *Chemistry in Commerce*, p. 1190, George Newnes, Ltd., London.

The Swelling Power of Coal

Several methods have been proposed as a measure of the swelling power of coal both at a rapid and slow rate of heating. In addition a number of agglutinating tests have been developed in which the coal sample is mixed with increasing amounts of inert material until it just fails to give an agglomerated residue. The idea behind these agglutinating tests is to measure the amount of tar and oils produced during the thermal decomposition of the coal, but owing to the time taken for the test and the variability of the results, such tests are little used at the present time. Of the tests for the determination of swelling power at a rapid rate of heating, the one which has been most widely adopted is that developed in the laboratories of the Woodall-Duckham Company. This test has now been standardized by the British Standards Institution and is described in B.S. 1016.[6] Its chief advantages are that only simple apparatus is required and a test can be completed in 3 minutes.*

The disadvantage of the B.S. swelling test is that all the highly swelling coals give the maximum swelling number, thus preventing the test from distinguishing between such coals. In such cases a swelling test at a slow rate of heating is necessary, and the one which has been developed in this country is the Sheffield Laboratory Coking Test described by Mott and Spooner.[51] In this a 6 g sample of coal crushed through 72 B.S. mesh is heated in a special retort under a load of 100 g at a rate of rise of temperature of 1° C./min. The swelling power of bright coal in this test is influenced by the presence of durain and fusain, and a method for the determination of durain has been developed on this basis and is given later. The same phenomenon is not present in the B.S. swelling test, for in this case, the swelling power of bright coal is not affected by the presence of durain and fusain in proportions less than 50%.

The Gray-King assay test[53] has been adopted as a method of measuring the swelling power of coal, but its chief use is in assessing the yield of by-products from coal which can be done either under standard conditions, or the conditions can be adapted to correspond with those encountered in any particular distillation plant. The test is of no value in assessing the quality of coke obtained from a particular coal and for this purpose no satisfactory laboratory test exists at the present time.

Determination of Fusion Temperature of Ash

The temperature at which a coal ash fuses is dependent on the

*A useful account of the applications of the B.S. Swelling Test has been given by Mott, *Coke and Smokeless Fuel Age*, 1943, **5**, 165.

chemical constituents of the ash, the degree of segregation, and the conditions under which the ash is produced. Because of these variables the determination of the fusion temperature of coal ash is only empirical, and the results obtained can only be used as a rough guide to what to expect in practice. As mildly reducing conditions are the ones most frequently met with in practice, the test is usually carried out under such conditions and at a rate of rise of temperature of 4–5° C./min. Other conditions may of course be used, but the exact conditions should always be specified in the report.

Details of the method of carrying out the test and the apparatus used are given in B.S. 1016.[6] Briefly the method consists of moulding a pyramid of the ash with the help of dextrin and observing the effect on this of a gradual increase of temperature. The temperature can either be measured with an optical pyrometer or with a bare thermocouple placed at the side of the pyramid. The temperatures usually recorded are the temperature at which the tip of the pyramid shows signs of rounding, known as the initial deformation temperature, and that at which the ash completely fuses to a blob, known as the fusion temperature.

The Determination or Durain and Fusain

An estimation of the quantities of these banded constituents of coal is sometimes useful in assessing the value of coals for industrial uses. Such a case is the assessment of the coking properties of coals and these are influenced by the presence of both durain and fusain.

Belcher and Goodbert[52] examined several methods for the determination of fusain and concluded that the only satisfactory method is that of Fuchs, Gauger, Hsiao and Wright. Three 1 g samples are digested for 2, 3 and 4 hours respectively with 8 N nitric acid, filtered, and after removing the alkali soluble material, the residues which consist of fusain are dried and weighed. The weights are plotted against time and extrapolated to zero time to allow for the slight attack on the fusain by the nitric acid.

Durain is best determined in the Sheffield Laboratory Coking Test where use is made of the fact that durain progressively reduces the swelling power of bright coal. The test evolved by Mott and Spooner[3] is carried out on samples of 5–20 IMM mesh size to ensure the absence of fusain which has a similar effect to durain. In assessing the durain content of a sample of coal, pieces of bright coal and durain are hand picked from part of the sample and crushed to 5–20 IMM mesh size. The swelling power of the bright coal and mixtures of known percentage of durain are determined, and the results plotted on a graph between swelling

power and durain content. From the straight line thus obtained the durain content of the sample is read off after determining the swelling power of the original coal sample also crushed to 5–20 IMM mesh size.

Correlation of Properties with the Analysis

Although details and references have been given for all the usual determinations carried out on coal and coke it is not always convenient or even possible to carry all of them out on any particular sample. Under such conditions it is advantageous to be able to carry out several of these determinations and assess the others. To achieve this with any accuracy, well established relationships must be used; those between carbon and hydrogen on the one hand, and volatile matter and calorific value on the other, are the most useful.

Several relationships have been given relating the carbon and hydrogen contents of a coal to its volatile matter, the most recent and comprehensive being that advanced by Spooner.[54] Besides relating the total volatile matter with the carbon and hydrogen, the yields of each of the constituents of the volatile are given as proportional to one of the chemical elements. The most important of these constituents is tar, and the yield of this is assessed as proportional to the hydrogen content on the pure coal basis in excess of 4·20% i.e. tar = K(H − 4·20) where K is a constant depending on the condition under which the thermal decomposition is carried out. The relationship for the total volatile matter of bright bituminous coal is V = 11·2H — 1·2C + 106 and is slightly different for durains and fusains.

The most recent work on the relationship between calorific value and carbon and hydrogen is that by Mott and Spooner[55] to which reference should be made for the earlier work. The equation they developed for coal of less than 15% oxygen is:

$$\text{Cal. Val} = 115\ \text{C} + 374\ \text{H} - 3420\ \text{Cal/gm.}$$

For coals containing more than 15% oxygen this relationship is modified.

These two relationships are the most important, and by means of them the calorific value and volatile matter can be calculated from the carbon and hydrogen, or alternatively can be determined, and from these the carbon and hydrogen contents can be calculated. Other relationships have been deduced between the swelling power of coal and the carbon and hydrogen* and other special properties and for these the original publications should be consulted.[56, 57]

* See "The Swelling Power of Coal" by C. E. Spooner, *Fuel*, 1951, **30**, 193.

TABLE IX

The Suitability of Coals for Industrial Purposes

PLANT	GRADE OF COAL	USE	DESIRABLE PROPERTIES						
			Moisture	Ash	Ash Fusion Point	Volatile Matter	Sulphur	B.S. Swelling Index	Calorific Value
Pulverized Fuel Plant	Washed Singles or Washed Slack	Reheating for Forging and Cogging. Annealing of Castings	8% Max.	6% Max.	Over 1300° C.	30 to 35%	Not more than 1·0%	1½ to 4½	12,500 B.Th.U.
Underfeed Stokers	Singles, Peas or Beans	Reheating furnaces and Boilers for heating apparatus	10% Max.	8% Max.	1200–1250° C.	35%	Not above 10%	1½ to 4½	12,000 B.Th.U.
Gas Producers (Static)	Trebles and Doubles	Gas for Acid Open Hearth Furnaces	6% Max.	8% Max.	1300–1350° C.	30 to 35%	Not above 1·0%	1½ to 4½	12,500 B.Th.U.
Mechanically Fired Boilers	Washed Singles or Slack	Steam Supply for Presses and Hammers	10% Max.	5 to 8%	Over 1300° C.	About 30%	Not above 1·0%	1½ to 4½	11,500 to 12,500 B.Th.U.
Hand-fired Lancashire Boilers	Washed Slack	Steam raising for Hammers, Process Work, Space Heating etc.	10%	5 to 8%	Over 1300° C.	20 to 25%	Less than 2·0% Preferably less than 1.5%	1½ to 4½	11,500 to 12,500 B.Th.U.
Hand-fired Furnaces	Trebles or 'Hards'	Reheating for Forges and Rolling Mills	6% Max.	6% Max.	Over 1300° C.	30 to 35%	Not above 1·0%	1½ to 4½	13,000 B.Th.U.

Composition of Coals for Industrial Purposes

The desirable composition of coals and cokes for industrial purposes will naturally vary according to the use for which they are required. Coals for making blast-furnace coke should be sufficiently low in sulphur so that the resultant coke has a sulphur content of not more than 1·0%, although for lean ores a somewhat higher figure may be tolerated. For foundry work the sulphur figure should not exceed 0·8%. Phosphorus should not exceed 0·01 to 0·02%.

The limits for moisture and ash in a coal used for coke-making will depend on the purpose for which the coke is to be used. For example, a moisture content of 7% is suitable for most purposes, and the ash should always be as low as is economically possible.

No limits for the chlorine content appear to have been laid down. It will be obvious that it should be as low as possible for it will have a corrosive action on metal parts wherever the coal is burnt. A high chlorine content usually indicates a high inorganic chloride content, and in coking practice such coals are liable to have a deleterious effect on coke oven walls, particularly if they are not of silica brick.

Other desirable properties of coals are shown in Table IX which has been compiled from the paper by Banks.[58]

REFERENCES

1 *A.S.T.M. Standards on Coal and Coke,* American Society for Testing Materials, 260, S. Broad St., Philadelphia, Pa.
2 B.S.1016, 1942, *British Standard Methods for the Analysis and Testing of Coal and Coke.*
3 F.R.B., *Methods of Analysis of Coal and Coke,* H.M.S.O., London, 1940.
4 *Sampling and Analysis of Coal, Coke and By-products,* U.S. Steel Corporation, Carnegie Steel Co., Pittsburgh, Pa.
5 B.C.R.A. Sampling, Analysis and Testing Panel.
6 B.S.1017, 1942, *British Standard Methods for the Sampling of Coal and Coke*
7 Brown and Bean, *J. Inst. Fuel.* 1939, **12,** 305.
8 Greenfield and Dummett, *Fuel,* 1937. **16.** 183.
9 Belcher and Spooner (unpublished work).
10 Belcher and Spooner, *Fuel,* 1944. **23.** 46.
11 Schmidt and Seymour, U.S. Bureau of Mines, 1945, R.I. 3811.
12 Mott and Spooner, *Fuel,* 1944. **23.** 42.
13 Belcher, *Analyst,* 1946. **71.** 236.
14 Dolch, Pochmuller and David, *Chem. App.,* 1929. **16.** 137, 151.
Dolch and Strube, *Z. Oberschles. Berg. u. Hutt,* 1929. **68.** 349.
Dolch, *Brennstoff Chem.,* 1930. **11.** 429.
15 Mannheimer, *Ind. Eng. Chem.,* Anal. Ed., 1929. **1.** 154.
16 Piatschek, *Braunkohle,* 1929. **27.** 49.
17 Lategan, *Fuel,* 1927. **6.** 447.
18 Gross and Abramsky, *Fuel,* 1932. **11.** 154.
19 Moran, *Iron and Coal Tr. Rev.,* 1942, March 27th.

[20] Radmacher, *Brennstoff Chem.*, 1939. **20.** 121.
[21] Brunjes and Manning, *Ind. Eng. Chem.*, Anal. Ed., 1940. **12.** 718.
[22] Tompkins, Ibid., 1942. **14.** 141.
[23] Mantel and Schreiber, *Gluckauf*, 1942. **78.** 185, 220.
[24] Beet and Belcher, *Fuel*, 1940. **19.** 92.
[25] Mantel and Schreiber, *Gluckauf*, 1940. **76.** 479.
[26] Mantel and Radmacher, Ibid., 1938. **74.** 989.
[27] Belcher and Spooner, *Fuel*, 1941. **20.** 172.
[28] Teichmann, Fuel Research Inst. (S. Africa), Bulletin No. 22.
[29] Beet, *Fuel*, 1932. **11.** 196, 406; Ibid., 1934. **13.** 343; Ibid., 1940. **19.** 108.
[30] Sreenivasan and Sadasivan, *Ind. Eng. Chem.*, Anal. Ed., 1939. **11.** 314.
[31] Beet and Belcher, *Fuel*, 1938. **17.** 53; *Mikrochemie*, 1938. **24.** 145.
[32] Mantel and Schreiber, *Gluckauf*, 1938. **74.** 777.
[33] Beet, *Fuel*, 1932. **11.** 304.
[34] Beet and Belcher, Ibid., 1938. **17.** 175.
[35] Selvig and Gibson, *Ind. Eng. Chem.*, Anal. Ed., 1933. **5.** 189.
[36] Mantel and Schreiber, *Gluckhauf*, 1940. **76.** 397.
[37] Belcher and Spooner. *Fuel*, 1941. **20.** 130.
[38] Dennstedt, *Z. Anal. Chem.*, 1903. **92.** 417.
[39] Ter Meulen and Heslinga, *Neue Metheden der organisch Chemischen Analyse.*
[40] Belcher and Smith, *Fuel*, 1940. **19.** 183.
[41] Edwards and Vahrmann.
[42] Belcher and Spooner, *J.C.S.*, 1943. 313; *Ind. Chem.*, 1943. **19.** 653.
[43] Belcher and Spooner, *Fuel*, 1950. **29.** 188.
[44] Beet, *Fuel*, 1944. **23.** 58.
[45] Dolch and Will, *Brennstoff Chemie*, 1931. **12.** 141, 166.
[46] Schutz, *Z. Anal. Chem.*, 1939. **118.** 241, 245; *Naturwissch*, 1939. **27.** 822.
[47] Spooner, *Fuel*, 1947, **26.** 15.
[48] Edwards, Marson and Briscoe, *J.S.C.I.*, 1932. **51.** 179.
[49] Haslam and Beeley, *Analyst*, 1941. **66.** 185.
[50] Cornes, *Analyst*, 1944. **69.** 237.
[51] Mott and Spooner, *Fuel*, 1937. **16.** 4.
[52] Belcher and Godbert, *Fuel*, 1939. **18.** 270.
[53] Mott and Spooner, *Fuel*, 1937. **16.** 96.
[54] Spooner, *Fuel*, 1943. **22.** 13, 39.
[55] Mott and Spooner, *Fuel*, 1940. **19.** 226, 242.
[56] Mott and Spooner, *Oil, Shale and Cannel Coal*, Inst. of Pet., 1938.
[57] Mott and Spooner, *Gas World*, 1940 (Coking Sect., June). **28.** 47.
[58] Banks, *Chemistry in Industrial Fuel Control*, Paper to S. York Sect. of Royal Inst. of Chemistry, April 5th, 1946.

PART SIX

Modern Physico-chemical Methods of Analysis

CHAPTER XII

MODERN PHYSICO-CHEMICAL METHODS OF ANALYSIS

INTRODUCTION

Apart from the so-called 'classical' methods of analysis may be grouped those which partially depend upon the use of instruments of a physical nature. Many such instruments are used as a means to an end and do not include techniques based on spectrography and X-ray crystallography, etc., which are purely physical. This section, therefore, will deal with some of the more useful analytical aids and will include electrolysis, electrometric titrations, absorptiometry, colorimetry, and polarography. It should be borne in mind, however, that the field of application of the above methods is vast indeed and it is the main purpose of the succeeding section to give the reader some idea of the functions that these instruments can be made to perform.

Frequently, the amounts of material involved are very small and great care must be exercised in order to avoid unsuspected errors. In absorptiometric and polarographic work in particular, blank determinations must often be made on reagents, etc., and precautions taken to eliminate any possibility of contamination from dirty glassware and from other sources. It has been stated that a good analyst is a man who is capable of transferring small amounts of material from one place to another without loss. In the field of physical chemistry one might add—or gain!

Finally, it cannot be stressed too strongly at this stage that no single instrument is a cure-all for the analyst's troubles but that properly used, they may together form a very useful means of overcoming some of the difficulties that frequently beset him.

I. ELECTROLYSIS

(i) General Discussion

Much work has been done on the electrolytic determination of metals and the method is now in common use in most laboratories. Apart from its application to the direct determination of metals it

may also be made to perform the useful function of removing unwanted or interfering elements prior to the determination by other means of certain constituents of an alloy. Electrolysis as such is usually carried out in a suitable medium using platinum electrodes, the latter item frequently being the most expensive part of the apparatus. Recent work, however, has centred on the use of apparatus designed to maintain accurate control of the potential during the course of electrolysis as with this system certain elements may be selectively plated from a mixed solution each at its own deposition potential. Normally, of course, as a metal is deposited, a corresponding amount of anion is liberated, usually in the form of free acid, and this results in a change of potential due to the electrical resistance of the solution changing. With the simple apparatus required for electrolysis it is not possible to maintain an accurate potential control. However it is not the purpose of this book to discuss the latest developments along these lines and accordingly we shall confine ourselves to simple electrolysis.

Another branch of this work which must be mentioned is that dealing with mercury cathode electrolysis which, as its name indicates, uses mercury as the cathode in place of platinum. The benefits of this system are that many metals, in fact nearly all the heavy metals, are deposited in solution in the mercury and serve as a convenient way of separating aluminium, the alkaline earth and alkali metals, which remain in solution, from most others. Thus quite small amounts of these metals may be separated from fairly large quantities of the heavy metals. The mercury of course may be purified subsequently by distillation, etc.

(ii) Simple Electrolysis

Fig. 8 shows the type of apparatus required for ordinary electrolysis, provision being made for stirring the solution. Some types of apparatus are equipped with a small hotplate to maintain the solution at any desired temperature during the electrolysis. This is occasionally useful but seldom essential. Many workers have claimed that better deposits are obtained more quickly by electrolysis from hot solutions but in the writer's experience, where time is not of prime importance, it is far better to conduct the electrolysis, say overnight, using a low current density. This of course applies to cases in which the deposit is required for accurate quantitative determination. Electrolysis from hot solutions and with a high current density often leads to oxidation of the deposit and consequent high results.

For certain determinations, electrolysis is far superior to other

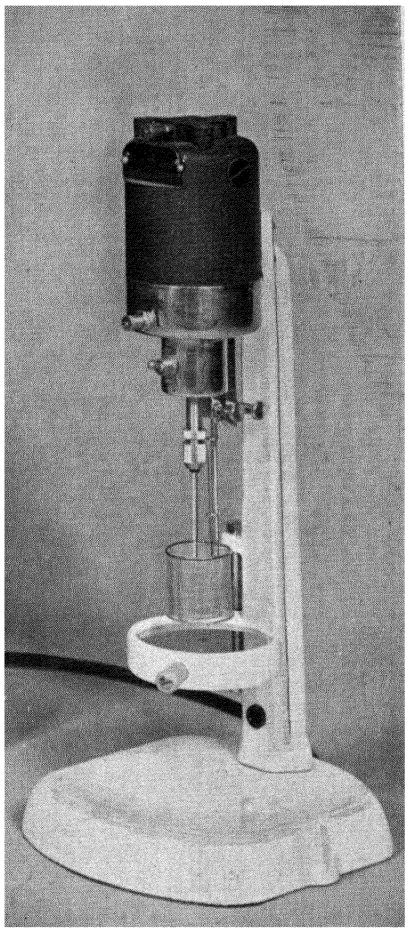


FIGURE 8. G. and T. electro-chemical analysis apparatus. Single-unit model (Griffin and Tatlock, Ltd.).

[*Facing p. 578.*

methods and this is especially true for the determination of copper in brass and similar alloys. With care, an accuracy to within 0·01% of the content may be achieved using a sample of from 1 to 5 g. Iron, if present to the extent of more than 1%, interferes by causing incomplete deposition and should be removed before electrolysing the solution. Nitrous acid also interferes by inhibiting deposition and in other ways, and this should also be removed, either by introducing a small quantity of urea or preferably by boiling the solution well before starting the electrolysis. Chlorides should be entirely absent of course or the platinum anode will be attacked. A suitable method for the determination of copper in brass is given below:

Dissolve 2 g of brass in 25 ml. of (1 : 1) nitric acid and when reaction has ceased add 2·5 ml. of sulphuric acid (sp. gr. 1·84) *slowly* and evaporate the solution until fumes of sulphuric acid appear. Care should be taken to avoid spitting of the solution. Fume for 5 minutes then allow to cool. Cautiously add 150 ml. of distilled water and dissolve the deposit. Finally add 0·5 ml. of nitric acid (sp. gr. 1·42), free from nitrous acid, and electrolyse using platinum electrodes and a current of 0·2 amps overnight or 1 amp for 3 hours. Rinse down the sides of the beaker and electrolyse for a further 30 minutes. Finally siphon off the liquid with the current still on and refill the beaker with distilled water. Continue siphoning and refilling until the current drops to a negligible value then remove the cathode, giving it another rinse with distilled water. Finally immerse the electrode in redistilled industrial spirit or acetone and dry by the aid of a fan. Avoid the use of heat unless accompanied by a good draught such as is given by a hair dryer. The increase in weight of the electrode is due to the copper present in the original alloy.

Many such methods are available and reference should be made to the literature for further details.

(iii) Mercury Cathode Electrolysis

Mercury cathode electrolysis is normally carried out in a sulphuric acid solution of about 3%. Unlike simple electrolysis its sole function is to remove unwanted metals, those left in solution being aluminium, magnesium, alkaline earth, alkali, and rare earth elements, phosphorus, vanadium and beryllium. It therefore forms a very useful way of separating even traces of the above metals from practically all others. Manganese is sometimes only partially separated due to oxidation to permanganate or manganese dioxide but this may be minimized by keeping the size of the anode as small as possible. No special apparatus is required beyond a vessel for the electrolyte and some means

of making contact with the mercury. A suitable set-up is shown in Fig. 9. Stirring is unnecessary unless a rapid separation is required and a current of from one to three amps is suitable for normal purposes. Metals which form insoluble sulphates such as lead are removed by mercury cathode electrolysis although the procedure may be somewhat slow. Lead sulphate is of course slightly soluble, as are all other 'insoluble' salts to a greater or lesser extent, and the small amount of substance actually in solution is removed by the electrolysis. This means that more of the substance dissolves to take its place until all the insoluble salt present has been removed. The rate of removal and dissolution therefore

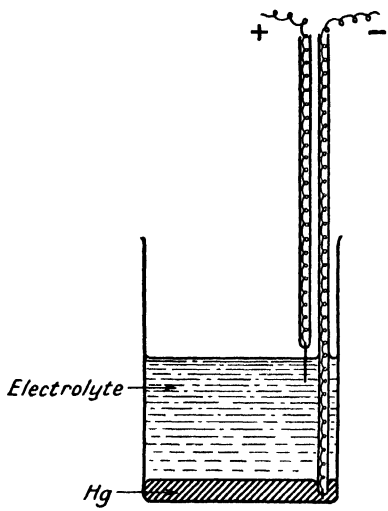


FIGURE 9.

depends partially upon the solubility of the particular substance. If a large quantity of insoluble material is present it is better to remove it by filtration prior to the electrolysis. Other mineral acids must be removed before electrolysis and this is best accomplished by adding sufficient sulphuric acid to the solution of the sample to convert everything present to sulphates and then an excess to give a final concentration of 3% free acid. The solution is then evaporated to fumes of sulphuric acid and finally diluted to the predetermined volume. Electrolysis is carried out for from three to five hours for each 1 g of metal to be removed using about 50 ml. of mercury and a current of about three amps. When the mercury contains more than about 2% of impurities it should be

redistilled as further deposition is then retarded and there may be a danger that some of the dissolved material will redissolve if the current is allowed to fall.

At the completion of electrolysis the electrolyte is removed by siphoning and washing or by decantation.

An excellent paper on mercury cathode electrolysis and its application to the determination of aluminium in certain non-ferrous materials has been published by Scherrer and Mogerman[1] and reference to this should be made for further details.

II. ELECTROMETRIC TITRATIONS, ETC.

Electrometric titrations may be divided into three sections (i) Potentiometric, (ii) Conductometric, and (iii) Amperometric and although a brief description of each is given here, only the first named will be dealt with in any detail as it is with potentiometric methods that the analyst will most often be concerned.

(i) Potentiometric Titrations

If a pair of suitable electrodes are immersed in a solution of unknown strength and readings of E.M.F. are taken at intervals against volume of titrating liquid, an abrupt change in E.M.F. will take place at the analytical end-point. One electrode is usually a calomel or other reference electrode whilst the other is one that depends upon the particular reaction involved. Generally speaking the end-point is reached when a maximum change in E.M.F. is noted for a minimum addition of titrating solution.

(ii) Conductometric Titrations

Whereas in potentiometric titrations the system may be compared with an ordinary titration inasmuch as the electrode replaces the indicator normally used, conductometric work depends on the fact that all the ions present affect the electrical conductivity of the solution. Thus if the product of reaction is an insoluble substance the conductivity of the solution will decrease due to the reduction of ion concentration. Similar results will occur when the total ion concentration changes due to a reduction or oxidation process. The end of the titration, therefore, is shown by the intersection of two straight lines, giving the conductance before and after the point of equivalence.

(iii) Amperometric Titrations

In amperometric titrations the current is measured at a suitable

E.M.F. between the indicator electrode and a depolarized reference electrode. The end-point again is usually indicated by the intersection of two lines showing the current before and after the point of equivalence.

Potentiometric Titrations

A typical form of potentiometric titration apparatus is shown in Fig. 10 which is that of the Cambridge Instrument Co. It comprises an electrode system with a stirrer motor, a potentiometer and a galvanometer. The standard electrode system includes platinum and calomel electrodes, and two burettes provide means for back titrating, etc. The potentiometer is of high resistance to eliminate drift due to falling battery voltage and the current is supplied by two dry cells. A dial covers the range of 0 to 2·0 volts in steps of 0·4 volt whilst fine adjustment is obtained by a separate control knob. The battery switch has three positions—'Normal', 'Off', and 'Reverse' enabling the operator to use the apparatus in alkaline solutions without the necessity for reversing any connections.

The end-point of the titration is determined either by a sudden deflection of the galvanometer spot or by a return of the spot to zero.

As an example of the use of this instrument the following method has been chosen :

The Determination of Chloride

For this titration the electrodes are one of silver chloride and the other of mercurous sulphate and are prepared as follows :

Immerse a piece of silver foil in 50% nitric acid for a few seconds, then rinse and immerse in a saturated solution of potassium chloride. Connect to the positive terminal of a 4 volt accumulator, and with a piece of platinum wire connected to the negative terminal allow the current to flow for about two minutes. Remove the electrode and rinse well. The silver will have become coated with silver chloride and this should be allowed to stand in water for half an hour before use. After use it should be kept in distilled water until again required. If allowed to become dry it should be soaked for half an hour before use. It may be used until it becomes sluggish in action when it may be cleaned in ammonia solution and then recoated.

The reference electrode is made in exactly the same way as a calomel electrode but using mercurous sulphate and 10% sulphuric acid in place of the calomel and potassium chloride.

In order to avoid the effect of changes in acidity the instrument

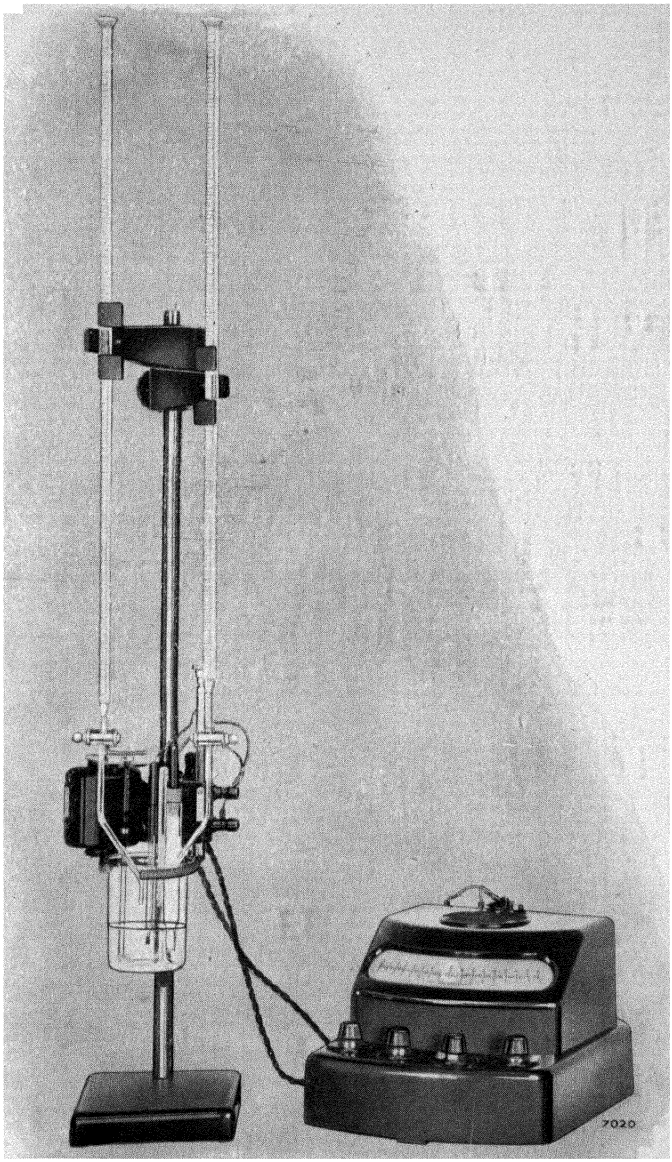


FIGURE 10. Cambridge titration apparatus. (Potentiometric pattern.)
(*By courtesy of the Cambridge Instrument Co. Ltd.*)

[*Facing p. 582.*

is standardized with a buffer solution and the titration of the test solution is also carried out in a similar medium. The most convenient buffer solution is approximately M/5 sodium acetate-acetic acid solution. A convenient quantity of M/5 acetic acid is divided into two equal volumes, one of which is just neutralized with sodium hydroxide. The two volumes are then mixed and are ready for use.

About 75 ml. of the buffer solution are placed in the beaker and the stirrer set in motion. Fix the silver chloride and reference electrodes in their clips and connect the silver chloride electrode to the positive terminal and the reference electrode to the negative terminal of the titration apparatus. Add to the beaker 1 *drop* of the titrating liquid (silver nitrate) and after turning the battery switch to 'Normal', operate the coarse and fine potential knobs to bring the galvanometer spot to the centre of the scale.

Allow the apparatus to run for a few minutes to permit the battery to settle down, adjusting the fine potential knob if necessary. Now run in the solution to be titrated which will cause the galvanometer spot to move to one end of the scale. The titrating liquid is now run in until the galvanometer spot is brought back to zero, the last few drops being added slowly to avoid overshooting the end-point. The volume of titrating liquid plus one drop (already added) is the quantity required for the titration.

For further titrations it is only necessary to add 75 ml. of buffer solution and to pour in the liquid to be titrated. The remainder of the titration being as before except that the one drop is not now added to the reading of the volume run out from the burette.

III. ABSORPTIOMETRY AND COLORIMETRY

(i) General Discussion

In recent years many excellent instruments have been developed to enable the chemist to make accurate measurements of the intensity of coloured solutions, etc., and the older method of visual matching of colours has now been largely superseded by the use of such instruments.

Absorptiometry is the measurement of the absorption by a given solution, of certain wavelengths of light and instruments exist which are designed to measure the absorption at any particular wavelength or over any given range of wavelengths. In the former case light from a suitable source (usually a tungsten lamp for the visible region) is broken down into its spectrum colours by means of a quartz prism and a narrow band is selected by means of a slit.

Light of the selected wavelength is then passed through the solution whose absorption is required and the intensity of the emergent beam is measured by means of a photoelectric cell. This intensity is compared with that obtained when no solution (or water) is present and the ratio of the two readings is a measure of the absorption of that solution. In the second case the waveband is chosen by passing the light from the lamp through an appropriate colour filter and then through the solution, etc. Whilst this is frequently sufficiently satisfactory, selectivity is limited by the fact that colour filters have a transmission covering rather a wide range of wavelengths and accurate measurements are not possible when a solution contains a substance whose colour is similar to that which one wishes to measure.

An instrument which measures the absorption of a given solution at any particular place in the spectrum is called a spectrophotometer, whilst those in the second category are known as absorptiometers.

Colorimetry depends upon the matching of colours by either the obsolete visual method using Nessler tubes and comparing the solution in question with a standard containing a known amount of the substance, or by using an instrument which contains coloured glass slides of increasing depth of colour for each of the primary colours, i.e., RED, YELLOW and BLUE. By superimposing the slides a match may be obtained for almost all colours, the instrument being constructed so that the standards and the solution are viewed side by side. Permanent calibrations may of course be made by the use of synthetic standards containing known amounts of the substance being determined.

Before proceeding with an account of the uses of each type of instrument, something of the theoretical principles involved should be discussed:

The proportion of light absorbed by a coloured solution is independent of the intensity of the incident light and may be expressed by the equation :

$$I = I_0 \, e^{-al}$$

where I is the intensity of the transmitted light, I_0 the intensity of the incident light, l the thickness of the absorbing solution and a is the absorption coefficient of the particular substance. This is known as Lambert's law. Bunsen and Roscoe modified the law, however, by introducing the 'extinction coefficient' in place of the absorption coefficient and this is represented by the equation :

$$I = I_0 \, 10^{-Kl}$$

where K is a constant known as the extinction coefficient and depends upon the medium in question and l the thickness of the medium expressed in centimetres. It will be seen that K therefore is the reciprocal of the thickness of the medium necessary to weaken the light to one-tenth of its original value. Its relation to a the absorption coefficient is therefore :

$$K = \frac{a}{\log_e 10} = \frac{a}{2{\cdot}3026}$$

Beer's law on the other hand states that the absorption of a solution is proportional to the number of molecules of the absorbing medium in the solution through which the light passes. Where the solvent is a non-absorbing substance the absorption is proportional to the concentration of the absorbing medium. This is conveniently expressed by the equation :

$$I = I_0 \, \alpha^{-cl}$$

where α is a constant for the absorbing solution and therefore is the ratio between the transmitted and incident light for unit thickness and unit concentration.

It has been found that Beer's law holds over a wide range of concentrations and for a great variety of substances.

In practical work the term 'density' of the solution is most frequently used and is $\log_{10} (I_0/I)$. Where a solution obeys Beer's law therefore the density is proportional to concentration and is thus the basis upon which most absorptiometric determinations are made.

(ii) Colorimeters

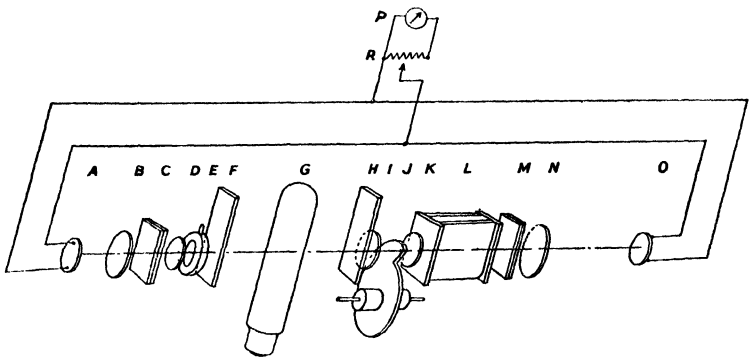
The subject of colorimetry is being dealt with first because these instruments depend to a large extent upon visual matching of colours and may therefore be regarded as the simplest means of obtaining a measure of the colour reflected or absorbed by a given substance. They suffer from the common defect, however, in being dependent upon the human eye, the precision of which is, unfortunately, not very high. They are useful of course in the textile or paint industry where opaque materials are used and a close match to a given tint is required, but have limited application in the analytical field where greater precision is essential. Such instruments will not be dealt with in detail therefore but passed over in favour of the more universally applied absorptiometers.

(iii) Absorptiometers

As has already been stated, absorptiometers are designed to

measure the absorption or density of a given solution over a restricted waveband, the choice of wavelength being made by means of coloured filters. One such instrument which has become very popular during recent years is the Hilger 'Spekker' absorptiometer and it is to this one that the present discussion will be confined (Fig. 11).

The Spekker absorptiometer is shown diagrammatically in Fig. 12 and consists of a light source (either a tungsten lamp or a mercury



(By courtesy of Messrs. Hilger & Watts, Ltd.)

FIGURE. 12. Simplified diagram of Spekker Absorptiometer optical system and photocell circuit.

A and O,	Photocells.	I,	Window.
B,	Lens.	J,	Measuring disc.
C,	Spectrum filter.	K,	Lens.
D,	Window.	L,	Cell for liquids.
E,	Iris diaphragm.	M,	Spectrum filter.
F,	Heat-absorbing filter.	N,	Lens.
G,	Lamp.	P,	Spot galvanometer.
H,	Heat-absorbing filter.	R,	Sensitivity control.

vapour lamp) mounted more or less centrally. To the right the light passes through a filter so that the resulting beam is of such a colour as to be most highly absorbed by the liquid medium under examination. This serves to increase the sensitivity of the instrument as well as being useful for eliminating interference from other coloured ions in the solution. The coloured beam then passes through a calibrated variable aperture (the drum) to a lens which yields a parallel beam. This in turn passes through the solution of the sample contained in a glass cell and thence through

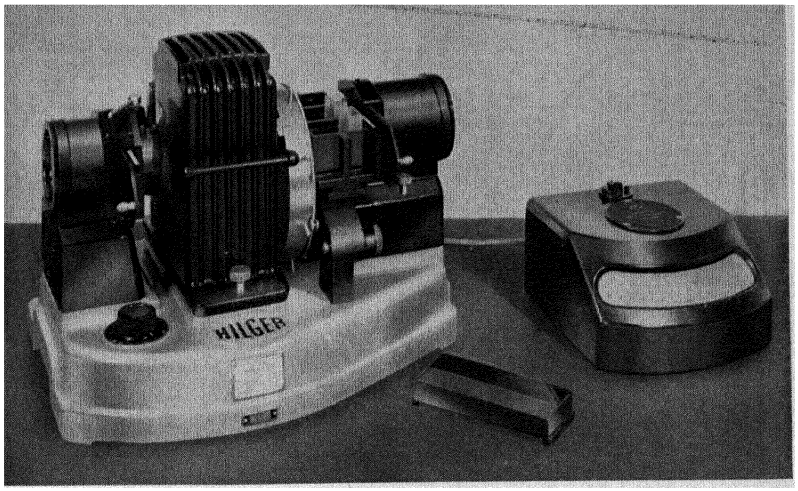


FIGURE 11. The Spekker Absorptiometer, Model H760.
(By courtesy of Messrs. Hilger & Watts, Ltd.)

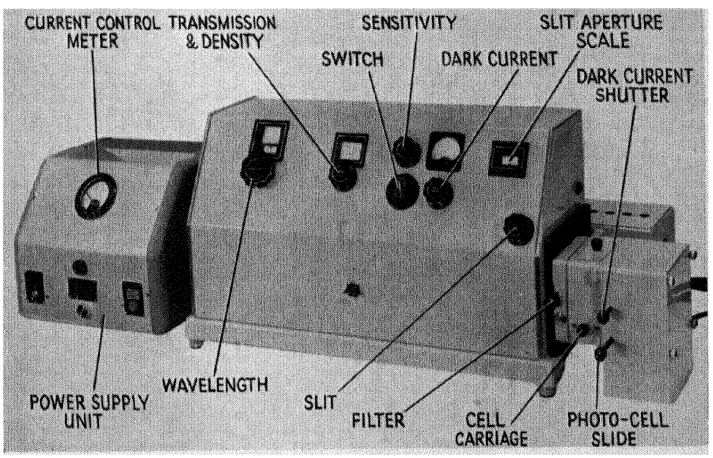


FIGURE 13. Unicam SP500 Visible and Ultraviolet Quartz Spectrophotometer.
(By courtesy of Unicam Instruments (Cambridge), Ltd.).

(See p. 590)

[*Facing p. 586.*

another lens which forms an image of the lamp on the indicating photocell.

To the left of the lamp the light passes through a cell containing water, a filter of the same colour as on the right-hand side, an iris diaphragm and on to a compensating photocell. The two photocells are connected in opposition across a galvanometer so that zero deflection is obtained when the photoelectric currents are equal. A sensitivity control is fitted.

The drum is calibrated logarithmically and results in the obtained reading being proportional to concentration of the substance in solution. It also means, however, that readings of high density cannot be made with such great accuracy as those of low density and the instrument is normally used in such a way that density readings above 1·0 are not made. Should a solution be obtained on which no reading can be made owing to high colour density, it should be either diluted by a known amount or a smaller aliquot and/or weight of sample taken. There are several reasons why certain solutions cannot be diluted however without altering the proportionality factor and they are those which (*a*) do not obey Beer's law, (*b*) react according to the amount of excess acid or alkali present and (*c*) react according to the amount of excess reagent. For these reasons therefore it is better to vary the weight or aliquot but in any case the calibration curve should be produced using the same amount of sample and reagents, etc., as in the actual assay.

Apart from three points it is not proposed to elaborate on the care etc., of the instrument as there are many publications [2, 3] dealing very thoroughly with this side of the question but attention is drawn to the following as these are of such paramount importance to the production of accurate results :

(i) It is vitally important that the solution cells are absolutely clean and free from smears or finger marks, etc.

(ii) Readings should be made as rapidly as is consistent with the care necessary to obtain a null deflection, i.e. the light beam should be allowed to fall on the photocells only as long as is absolutely necessary, the lamphouse shutter being closed immediately a balance has been obtained.

(iii) Make sure that the protective filters and water-cells are in place before the instrument is used or damage may be done to the photocells or almost certainly to the right-hand gelatin filter if this type of filter is being used. To measure the absorption of a solution, therefore, using the 'Spekker' absorptiometer, proceed as follows :

Fill the water cells with water and place in position, insert the

appropriate filters,* set the drum to 1·0 and close the left-hand iris diaphragm. Switch on the lamp (if a mercury vapour lamp is used it should be allowed to warm up for about ten minutes before use and once alight must not be switched off again until all the readings have been made, as it will not relight until it has cooled down) and open the lamphouse shutter. With the sample cell in position and filled with water, rotate the sensitivity control until full scale deflection is obtained, then return to zero reading by opening the left-hand iris, using the fine adjustment as necessary. Close the lamphouse shutter. The instrument is now set WATER TO WATER—1·0. Replace the water in the sample cell by the solution to be measured, or alternatively use another cell whose absorption is known to be identical. Open the lamphouse shutter and note that the galvanometer spot has deflected. Return it to zero by rotating the drum. 1·0 minus the reading obtained is a measure of the absorption of the solution in terms of density.

In normal analytical work where a blank determination is carried out, it is usual to read the blank absorption in the same way as the sample and deduct. If however a mercury vapour lamp is used, the blank due to interfering elements (as distinct from true blank) is often of such small proportions that it can be ignored, but owing to the small number of spectrum lines available with this lamp its application is somewhat limited.

Calibration is carried out by taking density readings over a convenient range of concentrations, using synthetic standards which have been processed in the same way as the sample. A graph is then prepared showing density or drum-readings against percentage of the element in question. Once made, a calibration curve should remain permanent providing all operating conditions remain constant. An alteration will usually be caused when one of the following things occur :

(*a*) A new lamp is fitted (not in the case of a mercury vapour lamp).
(*b*) A new set of filters is used.
(*c*) A photocell is damaged, either by omission of the use of protective filters or a water cell.

* Unless specific instructions are given with the method being followed as to which filters should be used, it will be necessary to have a complete spectrum curve made for the solution under investigation in order that filters may be selected whose transmitted light is most highly absorbed by the solution. As a rough guide the colour of the filters should be approximately complementary to the solution and may of course be found by trial and error ; they will be those which (usually) give the highest absorption reading. Where substances are present which absorb almost in the same region as the substance being measured it may be necessary to sacrifice a certain amount of sensitivity in order to eliminate interference.

(*d*) A photocell is removed and replaced or renewed.

(*e*) The drum is worn or renewed.

Frequent checking of the calibration is therefore desirable in order to maintain consistent accuracy, but with normal care, any variations from week to week should be very slight. Many methods involving the use of the Spekker have been published[2, 3, etc.], but a typical one is given below as an example :

The Absorptiometric Determination of Manganese in Copper Alloys

Weigh 0·5 g of alloy into a 200 ml. conical wide-mouth beaker and introduce 20 ml. of water followed by 15 ml. of sulphuric acid (sp. gr. 1·84) and 3 ml. of nitric acid (sp. gr. 1·42). When reaction has ceased boil to expel nitrous fumes, add 15 ml. of water and bring to boil again. Add two 0·3 g ANALOID pellets of potassium periodate and boil gently until the colour is developed. Allow a further two minutes boiling then cool and dilute to 100 ml. Measure the absorption of this solution as described above then add two drops of a 5% solution of potassium or sodium nitrite to the cell and stir well. The absorption of this 'blank' solution is then measured again and the difference in drum readings converted to percentage manganese by reference to the calibration curve.

Instrument conditions for above :

Lamp—Mercury Vapour	*Cell*—½ cm.
Drum setting—WATER TO WATER—1·0	*Filters*—Protective H.503 and Ilford 604

The calibration curve is made by adding standard manganese solution* in quantities varying from 0 to 5 ml. (representing 0–1·0% Mn) to a series of 0·5 g samples of pure copper, and then treating in the same way as for the sample.

(iv) Spectrophotometry

As mentioned previously, a spectrophotometer is an absorptiometer in which the absorption is measured at clearly defined wavelengths rather than over a given wave-band. In practice, of course, it is difficult, if not impossible, to obtain light of a given absolute wavelength and the nearest approach is to restrict the waveband to very narrow limits. This is achieved by the use of a slit of variable dimensions, and by such means, selection to within a few Ångstroms is normally obtained with commercially

* Made by dissolving 0·5 g of 'Specpure' manganese in 5 ml. of nitric acid and diluting to 500 ml. (1 ml. = 1 mgm. Mn).

available instruments. One such instrument is shown in Fig. 13 which is the UNICAM quartz spectrophotometer. (See p. 586.)

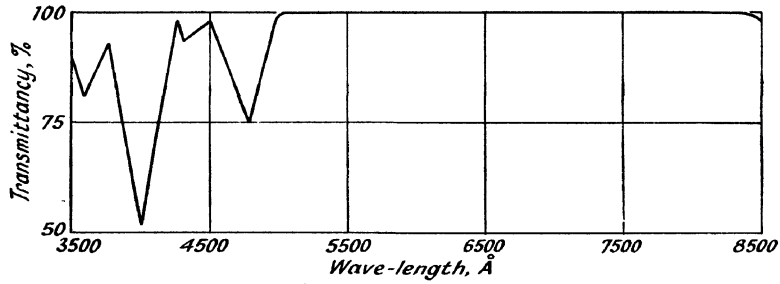
Methods suitable for use with the spectrophotometer are similar to those using the 'Spekker' but from the above description it will be seen that, due to the higher resolving power, the spectrophotometer may be employed preferentially when substances give complicated absorption curves. This is especially true in the case of the rare-earth elements where, for instance, samarium and praseodymium may be determined in a sample of neodymium and vice-versa. Fig. 14 shows a comparison of the absorption curves of these three substances and it will be seen that samarium may be determined at a wavelength of 4014 Å, praseodymium at 4433 Å and neodymium at 7950 Å at which wavelengths interference from each of the others is negligible.

IV. POLAROGRAPHY

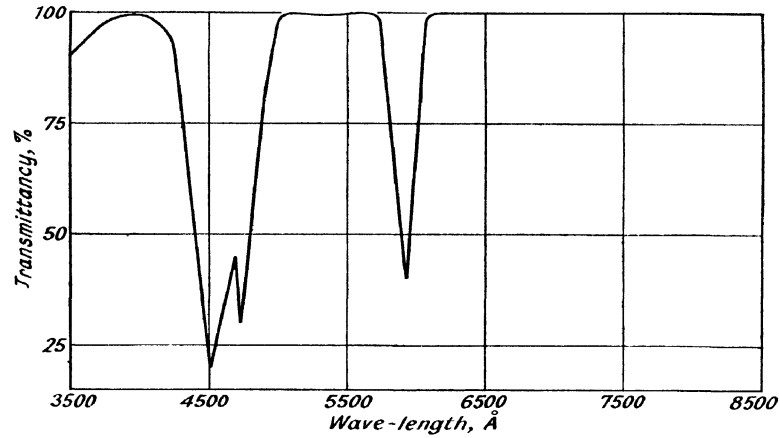
(i) General Considerations

The use of the polarograph in the analysis of alloys, etc., has many advantages and by no means the least of these is its sensitivity to traces of impurities. Its use, therefore, for the most part, is limited to fairly small percentages of alloying constituents and in many cases, methods are confined to alloys whose individual impurities are less than about 1%. With such a specialized field as polarography, it is quite impossible to do justice to the subject in the small amount of space devoted here and discussion will be confined to the elementary principles. More detailed information may be readily obtained however from any of the standard works on polarography.[4]

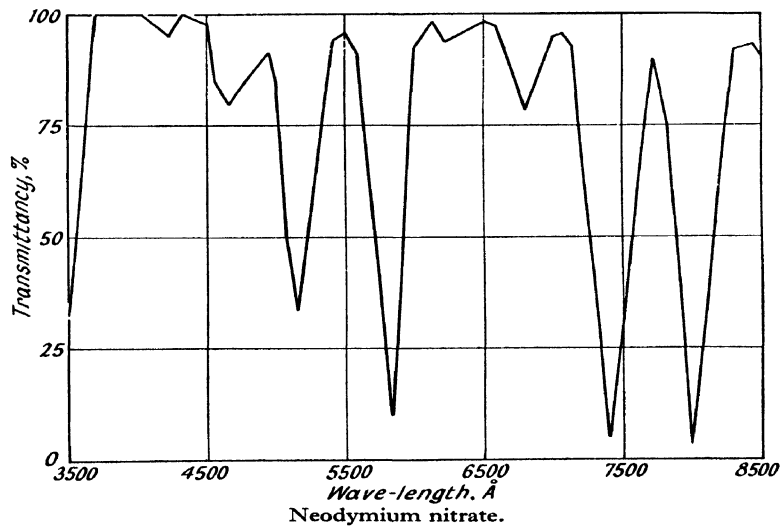
The polarograph is designed to obtain an automatic current/voltage curve on the solution being analysed. When a solution containing reducible ions is subjected to a steadily increasing potential by electrodes of suitable design, little current flows until the reduction potential of the ion in question is reached. At this stage the current increases rapidly until the rate of diffusion of the ions from the solution to the cathode balances the rate at which they are deposited on the cathode and no further increase in current will occur until the reduction potential of another ion is reached. Hence the current/voltage relationship will take the form of a series of waves, the potential at the mid-point of each being characteristic of the particular ion. The height of such a wave is a direct measure of concentration, all other conditions being constant, because the rate of diffusion to the cathode is a function



Samarium nitrate.



Praseodymium nitrate.



Neodymium nitrate.

FIGURE 14.

of concentration. This is shown graphically in Fig. 15 the height of the wave at the half wave potential ($E\frac{1}{2}$) being shown by AB.

In the apparatus used for polarographic analysis the anode is usually a stationary unpolarized mercury pool, whilst the cathode consists of a capillary through which mercury is dropping at a constant rate. The maximum current due to the ion reduction depends upon the size of the mercury drop and varies as the drop grows, reaching a maximum, then diminishing again as the drop falls and a new one starts. These fluctuations are suppressed to some extent by the use of a long period galvanometer and by certain other means, but the significant current value is the *average* of these variations and is known as the diffusion current.

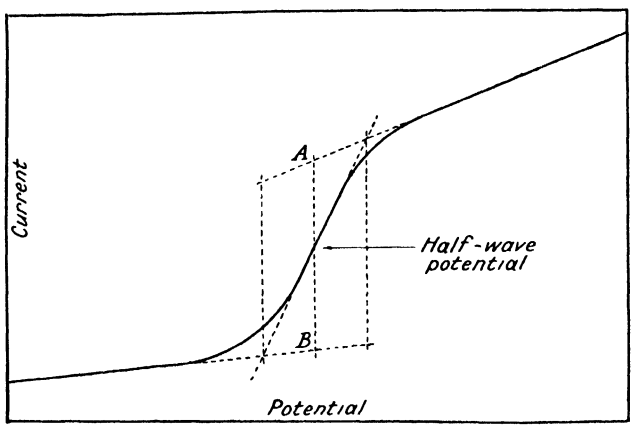


FIGURE 15.

The value of the diffusion current is given by the ILKOVIC equation:

$$i_d = 605nD^{\frac{1}{2}}\,\mathrm{Cm}^{2/3}\,t^{1/6}$$

where i_d is the average current in micro-amperes, n the number of faradays of electricity required per mole of the electrode reaction, D the diffusion coefficient of the reducible substance in cm.^{2} . sec.$^{-1}$ and t the drop time in seconds.

For practical reasons the drop time is usually arranged so that one drop falls every two to six seconds (in N . KCl) and in order to minimize the oscillation in current referred to above the nearer to two seconds the better. This is achieved by cutting back the capillary as required. The drop time is, of course, a function of the viscosity of the medium in which the mercury is dropping and the time must be checked using a standard medium, usually

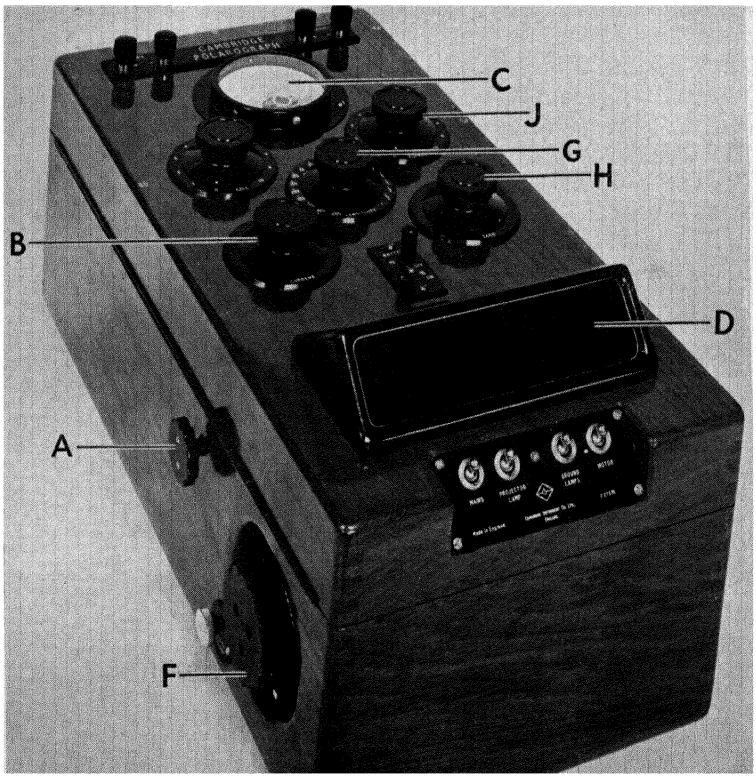


FIGURE 16. Cambridge Polarograph : Photographic Type
(*By courtesy of the Cambridge Instrument Co. Ltd.*)

A. Potentiometer knob
B. Rheostat
C. Milli-ammeter
D. Scale-viewing window
F. Camera drum knob
G. Galvanometer switch
H. Galvanometer potentiometer
J. Counter-current device

(The dropping mercury electrode assembly used with the polarograph is not shown in the above figure.)

[*Facing p. 593.*

normal potassium chloride. Irregularity of drop time is almost always a sign of a dirty capillary but more will be mentioned about that later.

(ii) Apparatus

Fig. 16 shows the Cambridge polarograph and dropping mercury electrode assembly. In this instrument a fine vertical line of light is reflected from the galvanometer mirror through a horizontal slit and on to a cylinder on which a piece of photographic paper is fixed. A point of light is therefore focused on the cylinder and is able to move in a horizontal plane. The cylinder on the other hand is rotated vertically past the spot by means of a geared synchronous motor and covers one revolution in about ten minutes. As this cylinder is directly coupled to a potentiometer its position determines the potential being applied to the electrodes whilst the spot of course varies according to the current flowing through the solution. Thus a complete current/voltage curve may be built up automatically for any given solution. The potentiometer covers a range from +0·3 volts to − 3·0 volts and is graduated in steps of 0·1 volt. The speed of the recording cylinder is arranged so that the potential increases at the rate of 0·1 volt every 20 seconds.

A small pilot lamp is also arranged so that a small amount of fogging of the photographic paper takes place as the cylinder rotates. This lamp cuts out momentarily as each 0·1 volt division is passed which results in a white line on a grey background being produced when the paper is developed. Similarly a graticule is placed over the horizontal slit which produces a white line along the current axis every 1 mm. with a slightly thicker one every 5 mm. Thus a complete knowledge of the current/voltage relationship may be obtained at a glance.

Before proceeding further, a description of the various controls is called for, for which reference should be made to Fig. 16.

To ensure that the correct potential is being applied to the electrodes according to that indicated on the potentiometer scale it is necessary to maintain a check on the current flowing through the potentiometer and this is accomplished by keeping the meter reading at full scale deflection (C) by means of the control knob (B).

A sensitivity range from·1 (full sensitivity) to $\frac{1}{1000}$ is controlled by knob (G) whilst the galvanometer spot zero adjustment is controlled by (H). This latter has a flexible range and may be used also for small scale compensation of unwanted waves (see later). Variable galvanometer damping may be employed in order to suppress the oscillations caused by the dropping mercury

electrode and this is governed by the adjustment (E). Control (J) is known as the counter-current adjustment and its purpose is to counter-balance the 'condenser' current which, though present in all cases, is most troublesome at high sensitivity. Condenser current increases with increasing potential and therefore a measure of compensation may be obtained by passing a small current through the galvanometer in the reverse direction and proportional to the applied potential. The amount of current passed may be varied by means of knob (J) and its effect on the shape of the wave may be seen in Fig. 17. The reasons for the presence of this 'condenser' current will not be discussed here but may be found by reference to the standard works[4] on the subject.

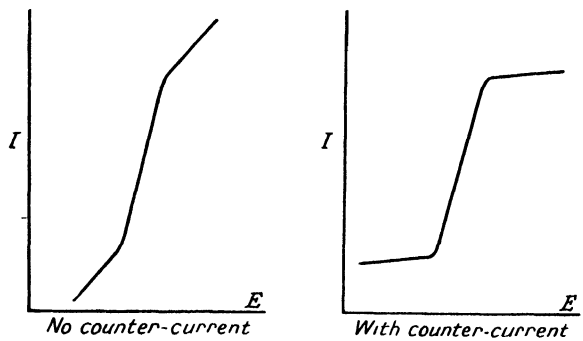


FIGURE 17.

The potential setting is controlled by means of a knob (A) so that records may be made at any position on the potential scale and the actual potential and galvanometer spot may be viewed on their respective scales through the aperture (D). This enables the operator to arrange the correct sensitivity, etc., prior to recording the actual wave. Records may be made repeatedly on the same solution, as the minute amount of substance actually plated out is of course redissolved immediately the potential is returned to its starting point or immediately a mercury drop falls so that the concentration remains constant for all practical purposes.

Finally, for accurate work it is necessary to maintain the solution being polarographed at a constant temperature as the magnitude of the diffusion current is affected by changes of temperature. Roughly speaking each 1° C. change causes a variation of about 2% in the wave height obtained and to minimize any errors due to this cause a thermostat is available to maintain the temperature at 25° C.

(iii) Polarographic Technique

Owing to the characteristic shape of a polarographic wave it is necessary to establish a means of identification with reference to the voltage axis and the system employed uses a point half-way through the reduction of a particular ion. This point is known as the half-wave potential and is characteristic of the ion in question for a given solution. The method of locating the half-wave potential ($E_{\frac{1}{2}}$) is shown in Fig. 15 and the height of the wave at this point (AB) is the measure taken for analytical purposes. A given element will have a half-wave potential which may vary according to the concentration of the solution in which it is dissolved, but more so according to the particular nature of that solution. For the purposes of identification therefore, a chart of half-wave potentials has been drawn up and is shown in Fig. 18. The potentials shown are with reference to the saturated calomel electrode and if a mercury pool anode is used it will be necessary to adjust them accordingly. It should be borne in mind, however, that any shift of potential according to the anode in use is constant for all elements when using a given base solution. It is therefore necessary only to find the half-wave potential of one element in a given base solution to enable the others to be charted, by reference to the appropriate series.

In practical work it is usual to prepare a standard containing a known quantity of the element being determined and using the same base solution as for the assay. It is quite common to divide the assay solution into two equal portions and to add the standard solution to one of them and an equal amount of water to the other. The difference in wave heights is then a measure of the standard addition whilst the smaller wave is a measure of the assay.

The polarograph is sensitive to quite small amounts of substances and a solution containing about 0·1 gm./litre is usually of ample concentration, so that aliquots and dilutions, etc., should be arranged to contain about that amount, although as little as 1 mgm./litre may often be detected, depending upon the substance in question. Almost invariably, oxygen is to be found dissolved in solutions and as this is reduced polarographically and causes a long drawn out wave covering a large potential range, it must be removed before attempting to determine other elements. This is usually accomplished by bubbling oxygen-free nitrogen or hydrogen through the solution for about 10 minutes immediately before polarographing. In many alkaline solutions oxygen may be removed by introducing a small quantity of sodium sulphite and this is to be recommended where the solution contains ammonia or other volatile substances, as gassing with hydrogen will, of course, remove the ammonia, etc., as well as the oxygen. Sodium sulphite,

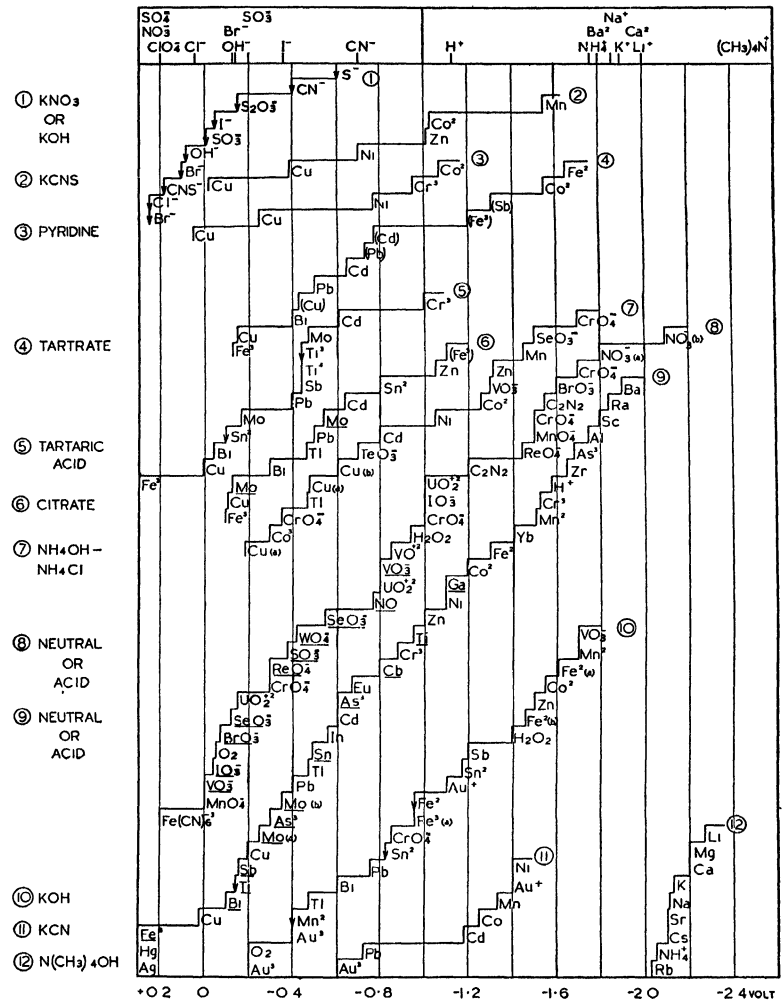


FIGURE 18. Chart of half-wave potentials.

Notes:

The potentials are with reference to the Saturated Calomel Electrode.

All Potentials are approximate.

A line under the symbol indicates a strongly acid solution.

Brackets enclosing the symbol indicate a strongly alkaline solution.

Anodic steps are shown by an arrow.

The values on the top line give the potential of a mercury pool against a normal solution of the anion, and the approximate upper working limit for a normal solution of the cathion.

Letters (*a*) or (*b*) against a symbol indicate the same step in somewhat different base solutions, otherwise a symbol occurring more than once in one series shows that more than one step is obtained in a single base solution.

however, cannot be used in acid solution as it is reducible at the dropping mercury cathode.

(iv) A Typical Polarographic Method

As an example of the kind of method which illustrates the advantages of the polarograph, the following has been selected :

Determination of Cadmium in Copper Alloys

This method is applicable to copper, brass and bronze and is divided into four sections according to the amounts of cadmium and manganese present :

(*a*) *Cd* > 1% (*Mn* < 1%)

Dissolve 1 gm. of alloy in 4 ml. of hydrochloric acid (sp. gr. 1·18) and 1·5 ml. of nitric acid (sp. gr. 1·42). When reaction has ceased add 25 ml. of water and boil off nitrous fumes, cool, and make up to 50 ml. Take 10 ml. and transfer to a 50 ml. graduated flask. Introduce 10 ml. of sodium sulphite solution (50 gm. of Na_2SO_3 *crystals* in 100 ml. of water) followed by 8 ml. of 13% potassium cyanide and 10 ml. of 10N. sodium hydroxide in that order. Finally add 1 ml. of 0·1% gelatin solution and dilute to 50 ml. Polarograph over a range of — 0·15 v to — 0·65 v using a mercury pool anode. $E_{\frac{1}{2}}$ for Cd = — 0·39 v.

(*b*) *Cd* < 1% (*Mn* < 1%)

Dissolve 2 g of alloy in 8 ml. of hydrochloric acid (sp. gr. 1·18) and 3 ml. of nitric acid (sp. gr. 1·42). When in solution add 25 ml. of water and boil off nitrous fumes, cool and make up to 50 ml. Take 10 ml. and transfer to a 50 ml. graduated flask. Introduce 10 ml. of sodium sulphite solution (see above), followed by 16 ml. of 13% potassium cyanide and 10 ml. of 10N. sodium hydroxide in that order. Finally add 1 ml. of 0·1% gelatin solution and dilute to 50 ml. Polarograph over a range — 0·15 v. to — 0·65 v.

(*c*) *Cd* > 1% (*Mn* > 1%)

Proceed as for (*a*) but after adding 10 ml. of sodium sulphite solution add 2 ml. of ammonium citrate solution* before the remainder of the reagents.

(*d*) *Cd* < 1% (*Mn* > 1%)

Proceed as for (*b*) but after adding 10 ml. of sodium sulphite solution add 2 ml. of ammonium citrate solution* before the remainder of the reagents.

* Made by just covering 500 g of citric acid A.R. with water and adding 500 ml. of NH_4OH (0·880) slowly and with constant stirring, cooling as the addition is being made. Finally make up to 1 litre and bring to boil for a minute or two. Filter through a Buchner funnel containing a Whatman No. 540 paper.

A standard determination should be run through as for a sample using A.R. copper plus a known addition of cadmium in the form of a solution of its nitrate in which 1 ml. ≡ 1 mgm. Cd.

Lead if present will give a wave at about − 0·2 v. and may be determined at the same time if required.

REFERENCES

[1] Scherrer, J. A., and Mogerman, W. D., *J. Res. Nat. Bur. Stds.* **21.** 105–111. July, 1938.

[2] Vaughan, E. J., *The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis*, Inst. of Chem. Monograph, 1941 ; *Further Advances in the Use of the Spekker Photoelectric Absorptiometer in Metallurgical Analysis*, Inst. of Chem. Monograph, 1942.

[3] Haywood, F. W., and Wood, A. A. R., *Metallurgical Analysis by Means of the Spekker Photoelectric Absorptiometer*, Adam Hilger Ltd., 1944.

[4] Kolthoff, I. M., and Lingane, J. J., *Polarography*, Interscience Publishers Inc., N.Y., 1941.

IV SPECTROSCOPIC ANALYSIS

Introduction

In his introduction to the first edition of this book, Sir Harold Carpenter wrote ' It is satisfactory that the authors have included a chapter on spectroscopic analysis. This is a somewhat recent development, but it seems likely that it will take its place as a useful aid to the analyst in many directions.' In the twenty-four years that have passed since this was written, spectrographic analysis has been developed to an extent that has placed it so far beyond being a 'useful aid' that it has become a recognized method for the analysis of a wide variety of materials, notable for the simplicity of its manipulative technique and its speed and cheapness.

In general, spectrographic analysis may be used to determine the metallic elements and the non-metals P, Si, C, B, and As in amounts up to several per cent of the sample. It is thus suitable for a great deal of the metallurgical analysis necessary for control purposes, and is particularly effective in dealing with large batches of samples of essentially similar composition. It is also a very sensitive method and for the determination of small traces is commonly more effective than purely chemical analysis. Spectrographic examination may also be employed to considerable advantage both as a guide and as a supplement to chemical analysis, in the one case affording useful data regarding all the elements present in a sample (thus ensuring that the analyst neither misses

an important element nor wastes time looking for one which is absent) and in the other serving as a convenient means of determining the purity of precipitates.

Although the spectroscope as we know it to-day has been evolved only during the last 130 years, the origin of spectroscopy dates back to 1666 when Newton observed that white light in passing through a prism was dispersed into an orderly arrangement of colours resembling a rainbow. We call this a spectrum, a term which also includes other arrangements of non-visible radiation. Later, rays outside the visible region were discovered, infra-red rays by Herschel[1] and ultra-violet rays by Ritter.[2] Newton's technique was improved by Wollaston[3] and especially by Fraunhofer[4] who developed an instrument which is basically the same as the spectroscope in use to-day. It is not proposed to trace the development of spectrographic methods in detail but the interested reader is referred to the important work of Sir John Herschel,[5] Kirchhoff and Bunsen,[6] Hartley,[7] Pollak and Leonard[8] and de Gramont.[9] Quantitative spectrographic methods of analysis of importance in industry were first described by Meggers, Kiess and Stimson[10] in 1922 and then followed the important series of papers by D. M. Smith[11] from 1930 onwards. The technique of the internal standard devised by Gerlach and Schweitzer[12] greatly increased the accuracy obtainable, and with the development of the microphotometer for measuring the density of spectrum lines, spectrographic analysis became firmly established as a method warranting the serious attention of chemists in many fields. The extent of this attention in recent years may be seen by reference to the literature.[13, 14, 15]

Briefly, the method depends on the fact that a substance can be made to emit a spectrum containing lines characteristic of the metallic elements present in the substance, and that the intensity of a spectrum line, under suitable conditions, is a function of the concentration of the emitting element. In practice, the relationship is determined from standards of known composition, the intensity of a spectrum line being measured by the density of its image on a photographic plate.

Equipment

(1) *Spectrograph and optical system*

A spectroscope is an instrument designed for the visual observation of spectra; when equipped with a scale for measuring wavelengths it becomes a spectrometer. A spectrograph is a spectroscope carrying a plate-holder for photographically recording spectra.

Light may be dispersed either by refraction in passing through a prism, or by diffraction from a ruled grating. Spectrographs employing both principles are in general use. The prism may be of either glass or quartz but since most industrial spectrography necessitates the use of lines in the ultra-violet, a quartz spectrograph is essential for serious work in this field.

There are four types of prism spectrograph in common use, usually designated as follows :

Designation	*Focal length* cm.	*Spectrum length* 2000–8000 A cm.	*Length of photographic plate* in.
Small	20	7·5	4·25
Intermediate	40	14	7
Medium	60	22	10
Large (Littrow)	170	67	10 (4x)

The choice of spectrograph depends upon the nature of the work to be done. For ferrous alloys and other materials giving complex spectra (Cr, Co, W, Ti, Mo, U, Zr) a large spectrograph is indispensable, since a high dispersion is required to obtain spectrum lines free from interference while still of a sufficient width for accurate density measurement. A disadvantage of this type of instrument is that to cover the wave-length range necessary for the complete examination of a sample, two or three photographs may be required at different settings of the instrument. The dispersion of the medium spectrograph being only about one-third that of the Littrow, the whole range is covered by one photograph. For this reason, it is very convenient for the examination of samples giving fairly simple spectra, e.g. light alloys and a number of other non-ferrous metals.

The intermediate and small spectrographs are limited in scope owing to their low dispersion. The small instrument has been used for the analysis of brass, lead alloys and zinc, while the intermediate size has been found satisfactory for analysis by means of the flame method. For the detection of certain metals—notably the alkali group—it is desirable to have a higher dispersion in the visible region than is given by the ordinary quartz system. To this end, some spectrographs are supplied with optical trains of both glass and quartz which may be substituted the one for the other.

Slit widths of 0·01 to 0·04 mm. are commonly used. Generally a narrow slit is advisable for qualitative work and a wider one for quantitative analysis with the microphotometer. In the latter base, the slit should not be so wide as to introduce undesirable background.

Condensing lenses.—In registering a spectrum, the slit is illuminated with the light source under examination. When the slit is illuminated directly by the source, the intensity is generally low; it is therefore a common practice to use a condensing lens between the source and the slit. The lens may be chosen either to form an image of the source on the slit or to illuminate the slit uniformly by all points of the source. The first method is useful in searching for all the elements present in a sample, or in observing the radiation from each part of the source; the second is essential for quantitative analysis. By a method described by Twyman and Simeon,[16] it is possible to obtain lines of uniform intensity from any selected part of the source. Catalogues of spectrograph manufacturers usually give details of suitable condensing lenses for use with their instruments.

The dispersion of the prism spectrograph decreases noticeably with increasing wave-length, whereas for a diffraction grating the dispersion is very nearly uniform. Though this is an advantage, the possibility of mistaking the ghosts of strong lines for impurity lines and the danger of confusing lines from the different orders are drawbacks to the use of grating spectrographs in industrial laboratories. Gratings appear to be favoured in the U.S.A. but at the present time the majority of spectrographs in use in this country are prism instruments. An excellent discussion of the different types of spectrograph and the techniques of their use is given by Sawyer.[17]

(2) *The spectrum and its production*

In the space available in this chapter it is not possible to give any account of the physical theories concerning the production of spectra. It must suffice to mention the different types of spectrum obtainable and to refer the reader to one of a number of text-books on the subject[18] and to Chapter 2 of Brode's invaluable *Chemical Spectroscopy*.[19]

All optical spectra are of two types:

(1) Emission spectra resulting from the dispersion of light emitted by a radiating source.
(2) Absorption spectra resulting from the absorption of light from another source by the medium in question.

Emission spectra are classified according to their origin:

(*a*) Continuous spectra characterized by an uninterrupted band of light, and produced by incandescent solids and discharge tubes operated under certain conditions.

(*b*) Discontinuous spectra, in general peculiar to luminous gases, and either *band spectra* of molecular origin or *line spectra* arising from gaseous atoms and ions.

Emission line spectra are of the most importance in spectrographic analysis (i.e. chemical analysis by spectrographic methods) and when, in the following pages, the word 'spectrum' is used without qualification, a spectrum of this kind should be understood.

Spectra are excited by means of the flame, the arc discharge, the spark discharge and the vacuum tube discharge, the latter having no important uses in metallurgical analysis.

Excitation by the flame.—The flame spectrum of a substance is easily excited by introducing a sample into the flame of a bunsen or acetylene burner. It is deficient in ultra-violet rays, contains only a few lines and little background. In addition to atomic lines, some bands may appear from compounds of the elements present, either with oxygen or nitrogen or other elements with which the sample was introduced into the flame.

In most cases the metals should be in the form of their chlorides as these salts are relatively volatile. Samples are conveniently introduced into the flame either directly on a loop of platinum wire, or by heating pumice or porous graphite which has been previously impregnated with a solution of the sample. Ramage[20] uses a filter paper moistened with a solution of the sample and slowly feeds it into an oxy-acetylene flame.

Flame spectra have been extensively employed by Lundegardh,[21] using a burner specially designed to produce a steady flame of pure acetylene and spraying a solution of the sample into the flame through a silver nozzle. Under these conditions a very steady and sensitive source is obtained; its exciting energy is higher than the bunsen flame but lower than the electric arc. The construction and use of the Lundegardh apparatus are described by McClelland and Whalley.[22] Both Lundegardh, and Cholak and Hubbard[23] claim that over thirty elements may be determined from flame spectra particularly in the case of biological materials. In metallurgical analysis however, flame sources are usually suitable only for the detection and determination of the alkali and alkaline-earth metals as well as indium, gallium and thallium. For other flame spectrum procedures see Torok;[24] Mitchell;[25] Waibel;[26] Bossuet;[27] Ramage, Sheldon and Sheldon;[28] and Steward and Harrison.[29]

Excitation by the arc.—The low voltage D.C. arc requires little equipment, is simple to operate, and is capable of exciting the

spectra of all the metals as well as As, B, C, P and Si, even when they are present in only minute amounts. Compared with the spark source to be discussed later, the arc has the advantage of giving a spectrum which is more representative of the sample, but the disadvantage of being less reproducible—an important drawback for quantitative analysis.

Voltages of 80 to 200 D.C. are generally used—the pulsating current from a half-wave rectifier is quite suitable—with some reactance in the circuit to increase the steadiness of the arc. Currents may vary from 2 to 10 amp. when using metal electrodes, and up to 20 amp. for non-volatile materials such as alumina and zirconia. The gap is usually from 5 to 10 mm. in width. It is most convenient to strike the arc between solid electrodes cut from the sample; for easily fusible metals however, this method is not satisfactory and it is preferable to place a small piece of the sample in a cavity in the lower of a pair of electrodes of some other material, between which the arc is struck. This method is also commonly used when the sample is small, or in the form of powder or solution.

The carrier electrodes may be of any suitable material, carbon, graphite, copper and silver being frequently used. Graphite electrodes can usually be purchased in a very pure state, but further purification is sometimes necessary and methods for this purpose have been devised.[30, 31, 32] Graphite has the advantage of introducing only a few lines in the medium ultra-violet, but the great objection of giving rise to much background, particularly in the violet and near ultra-violet where the intense band spectrum of cyanogen is found. High purity copper and silver may be used only when there is no danger of their lines masking important lines from the sample. Milbourn[33] has made a study of the copper arc and its application to the analysis of copper alloys, while Foster[34] and Rollwagen[35] have considered in detail the general mechanism of the arcing process.

When using a carrier electrode, it is usually recommended that the sample should be the anode as this is the hotter electrode. Smith[36] however, after investigating the question of polarity, concluded that when only one electrode is from the sample under investigation, this should be the cathode as the impurity lines are then more nearly like those obtained when both electrodes are from the sample. For copper and copper-rich alloys, Milbourn has shown that the sample should be negative with a rod of pure copper positive.

Many different types of graphite electrode have been described. Lower electrodes vary from 0·125 to 0·5 inches in diameter with

designs ranging from a plain rod with a small cavity in the tip, to elaborate types providing a platform or annular space for the sample, and constrictions to reduce heat losses. These different types are largely occasioned by the needs of particular analytical problems.

The greatest disadvantage of the arc as a source for quantitative analysis is its instability, and the mere insertion of a small sample in a crater in graphite does not always ensure a satisfactory spectrum on arcing. Since the excitation is almost wholly thermal, variations in gap spacing, electrode form and matrix composition will all affect the amount of heat produced in the arc, with consequent variations in the spectrum line intensities. In addition, the selective volatilization of the various constituents of the sample and the formation of oxide crusts both tend to make the discharge erratic.

To reduce these objectionable effects, various special types of electrode have been devised, and fluxes and 'buffers' added to the sample. It has also been recommended to rotate the lower electrode, deflect the arc to the front of the graphite by means of a magnet, and to draw a current of air through a hollow upper electrode.

To obtain extremely rapid volatilization and thereby use larger weights of sample (up to 75 mg.) Hasler[37] recommends mixing the sample intimately with a volatile carrier such as ammonium chloride (graphite dust and metal carbonates may also be used), and placing it in an annular space in the lower graphite electrode. It is claimed that with this type of arc the carbon band background is much reduced.

For samples that tend to decompose violently and blow out of open arcs, a 'boiler' type has been devised in which the sample in the crater in the lower electrode is covered with a graphite cap drilled with a small hole through which the sample volatilizes slowly into the gap. The chief limitation of this type of arc appears to be its inability to reach a temperature high enough to volatilize refractory oxides. Judd Lewis[38] recommends pressing the sample into a small pellet before placing in the crater.

Solutions may be examined in a similar manner by evaporating them on to the surface of graphite previously rendered non-absorbent by dipping in kerosene or collodion, and drying off at 105 to 110° C. before striking the arc. For the determination of very small amounts of impurities, an electrolytic concentration procedure such as that described by Bayle and Amy[39] may be necessary.

Gerlach and Gerlach[40] have described an arc which is repeatedly interrupted by bringing the electrodes into contact and separating

them, a method which secures more uniform burning, increased current strength and greater sensitivity. The resulting spectrum was rather weak but since the electrodes kept sufficiently cool to prevent any considerable oxidation, there was little continuous background. The method was much improved by Pfeilsticker[41, 42] who obtained a low voltage A.C. arc without moving the electrodes.

Refinements to the Pfeilsticker method have been introduced by Hasler and Dietert[43] and Walsh[44] who have designed multi-source generators whose characteristics may be varied over a wide range to give any type of discharge from an arc to a highly condensed spark. Other methods for electrically igniting arcs have been described by Brockman and Hochgesang.[45]

Duffendack and Wolfe[46, 47] use a high voltage (2000 v.) A.C. arc which they state has all the advantages of the low voltage D.C. arc and is very much steadier. Excellent results are obtainable if the separation of the electrodes (0·5 to 1·5 mm.), the voltage and the current are all carefully controlled.

The potential gradient in the arc is highest in the neighbourhood of the cathode and it has been found experimentally, that the intensities of spectrum lines of most of the metals are from five to twenty times as great in this region as in the positive column. This fact has been used by Mannkopff and Peters in developing the cathode layer or 'Glimmschicht' method described by Strock.[48] The enhancement of the lines is most pronounced for small weights (1 to 3 mg.) of sample and has been found of considerable practical use in a number of trace analyses, particularly in the case of poorly conducting samples. A possible disadvantage of the method is the necessity of keeping a short length (1 to 2 mm.) of the arc sharply focused on the slit of the spectrograph during the exposure.

Excitation by the spark discharge.—The spark discharge is the most convenient form of excitation for solid samples of some size and is widely used for the quantitative determination of alloying elements.

In comparison with the arc, the exciting energy is higher and thus predominantly ionic spectra are produced. The ultimate sensitivity is usually less than that of the arc though lines of some of the non-metals may be brought out more strongly because of the higher energy. Although the temperatures attained in the vapour column are high, the electrodes remain comparatively cold, thus making it possible to spark between electrodes of low melting point metals. Only a very small amount of the sample is consumed, a point which must be remembered when analysing alloys which are prone to segregate. The most noteworthy features

of the spark as a source of excitation are its reproducibility and stability, in both of which respects it is much superior to the simple arc. In the study of light excitation in spark sources many problems are involved; Kaiser[49] has reviewed the more important of these.

For most quantitative analysis, a simple condensed spark is used with a transformer of 10,000 to 15,000 v. and 1/4 kw., a condenser of 0·003 to 0·005 mfd. and an inductance of 0·05 to 0·25 mH. The uncondensed spark without use of condenser or inductance is claimed to have greater sensitivity but the heavy background is usually objectionable. The spark gap is usually maintained at 2 to 5 mm.

To obtain greater accuracy in spectrographic analysis, various modifications of the simple condensed spark have been devised. In the Feussner spark,[50] a rotating interrupter synchronized with the mains allows the discharge to take place only at the peak voltage of the cycle. Greater reproducibility is claimed for this arrangement but in practice it has not been found advantageous for all types of material, Frommer[51] and others, finding no improvement in results when using the Feussner spark for the analysis of aluminium alloys. An electronically controlled spark generator has been described by Malpica and Berry[52] but it does not appear to be widely used.

The literature shows little convincing evidence of the general superiority of controlled over uncontrolled sparks; indeed, Callon and Burgener[53] using both the Hilger spark unit (uncontrolled) and the ARL-Dietert heavy-duty spark unit (controlled) for the analysis of aluminium alloys state that "In most cases where careful tests have been made, no appreciable difference in accuracy has been obtained with these two types of source unit." The results so far published for the source units designed by Walsh[44], and Braudo and Clayton[54] are promising, but it is clear that, in the hands of a competent spectrographer, the simple uncontrolled condensed spark is adequate for a great deal of metallurgical analysis.

For the analysis of massive samples, a pair of electrodes may be machined from the sample, or the sample used as one electrode with a rod of suitable material such as graphite as the other. Powders and small turnings or drillings may be compressed into pellets and inserted in a hole drilled in a suitable carrier electrode. This procedure has been used by Neuhas[55] for the analysis of nickel alloys with good results.

Because of the low electrode temperature in the spark, it is a most convenient source for the direct analysis of solutions. These

may be run into the spark gap through the lower electrode (Twyman and Hitchen[56]) or through the upper (Keirs and Englis[57]), the electrodes being of gold or graphite.

The high-frequency spark of Gerlach and Gerlach,[40] originally developed for the analysis of biological tissues, may be used for thin films such as electrodeposited layers and also for moist filter papers. The set-up is simple and the discharge predominantly arc-like.

Arc and spark sources each have their particular uses in spectrographic analysis as has been seen ; both should be available in any well-equipped laboratory.

(3) *The microphotometer*

Quantitative spectrographic analysis involves the comparison of the intensities of spectrum lines in the sample being analysed with the intensities of corresponding lines in a sample of known composition. In practice, the intensities of the lines are measured by their densities in a photographed spectrum, usually by means of the microphotometer. The non-recording type of instrument is suitable for most work, though recording types are available. Details of their construction and use may be obtained from makers' catalogues and they are referred to in the section on quantitative analysis.

(4) *Viewing the spectrum*

For adequately viewing the spectrum, a magnification of about twenty diameters is necessary and a suitable instrument for obtaining this enlargement is an essential feature of a spectrographic laboratory. One such instrument is the Judd Lewis Comparator. This is designed so that by means of a double, low-power microscope two spectrum negatives may be viewed simultaneously and selected spectra—one from each negative—brought into close juxtaposition. In this way spectra from different plates can be quickly compared with each other, and by means of a short scale the wave-lengths of selected lines can be determined accurately enough for most identification purposes.

Another type of viewer projects an enlarged image of a portion of the plate (about 1·5 cm. diameter) on to a white screen. This makes for very easy examination of spectra, but two plates cannot be simply compared as with the Judd Lewis Comparator. However, since spectrographic laboratories soon acquire a collection of standard samples and spectrum charts, this limitation is not a very serious one, and this type of instrument is generally to be preferred.

Qualitative Analysis

A qualitative spectrographic examination of a substance is made either to determine all the elements present, or to determine if the substance contains one or more specified elements.

Determination of all the elements present in a sample.—For this purpose, the spectrum of the sample must be recorded and every line accounted for. To produce the spectrum the arc is generally preferable to the spark because of its greater sensitivity ; the latter may, however, be used when more suited to the nature of the sample or when the test must be non-destructive, or if experience has shown it to be satisfactory for the examination in question.

To facilitate the identification of spectrum lines, it is advisable to photograph immediately adjacent to the sample the spectrum of a known element or compound. Spectroscopically pure iron is particularly suitable for this purpose since its complex spectrum affords reference lines wherever they may be required. If the main element or elements present in the sample are known, it is an advantage to record their spectra adjacent to the sample on the side away from the iron. In the subsequent examination of the spectra, the lines from these elements can be ignored, leaving only those from the minor elements to be identified.

While recording these spectra, it is essential that the plate holder should not be moved since this will spoil the alignment ; the spectra must be correctly placed by movements of the diaphragm at the slit of the spectrograph. If the instrument has a printable wave-length scale, this should be recorded to complete the plate. Slit widths of 0·005 to 0·020 mm. are commonly used for qualitative examinations.

To estimate the wave-length of a spectrum line, its position must be determined in relation to neighbouring known lines in the same spectrum or an adjacent one. The simplified Hartmann formula gives

$$\lambda = \lambda_0 + \frac{C}{S + S_0}$$

where λ is the required wave-length ; λ_0 the wave-length of a known line ; S, S_0 the corresponding distances of the lines from the same point, and C a constant. This can be solved by measuring together with the unknown line three known lines which should not all be on the same side of the unknown.

In practice it is usually quite sufficient to plot the known wave-lengths against their measurements and to interpolate for the unknown wave-length. When the lines are close together a linear interpolation may be assumed and the required wave-length

rapidly estimated. As noted above a sufficiency of close lines is ensured when an iron spectrum is immediately adjacent to the spectrum of the sample.

Having estimated the wave-length of the line, it must next be identified.

On referring to a table of spectrum lines, it will probably be found that several different elements have lines at the estimated wave-length ; all those which have not previously been detected should be noted. As the examination proceeds, evidence should be found which will eliminate all but one of these elements, and to this the line can be finally assigned.

For the certain identification of a particular element in a sample, at least three of its most important lines should be found in the spectrum. This is a good working principle, though certain relaxations are unavoidable when the most important lines are masked by other elements or when they lie outside the useful range of the spectrograph and less important lines have to be used ; in such cases, experience alone will enable the spectrographer to make the correct interpretation of the spectrum.

Examination of a substance for the presence of a particular element.—Spectra of the sample and of a suitable reference material should be recorded as before ; also, whenever possible, a spectrum of the element sought.

The most important lines of this element are found from tables and identified in its spectrum. If the sample is observed to contain no lines at these wave-lengths, the element should be reported as 'not detected' rather than 'absent' since it may be present in an amount below the limiting sensitivity of the method. If lines are observed at the selected wave-lengths, it is essential to confirm that they could not be due to other elements in the sample before finally reporting the presence of the element in question.

In the absence of a spectrum of the element sought the position of the selected lines must be found from suitable lines in the spectrum of the reference materials or of the sample itself, or from suitable charts.

Spectrum charts and tables.—For viewing spectra, the comparator has the advantage of enabling selected comparison spectra from previous plates to be exactly aligned with and observed together with the spectrum under examination. The simple open enlarger is to be preferred however when suitable spectrum charts are available. These are enlarged photographs in which the wave-lengths and identities of lines are clearly indicated. They may be purchased but are best prepared by the spectrographer himself from his own equipment. Charts of the iron spectrum which also

show the position of important lines of other elements will be found of the greatest use in qualitative work. Charts of other pure metals or typical alloys may also be prepared with advantage.

The most comprehensive list of spectrum lines at present obtainable is found in the '100,000 *Line Tables*' of the Massachusetts Institute of Technology.[58] The lines are arranged in order of wave-length, and in addition 500 of the most sensitive lines of the elements are tabled both in order of wave-length and under the elements themselves. Brode's *Chemical Spectroscopy*[19] contains 35 plates of the iron spectrum in addition to useful tables of spectrum lines. Kayser's *Tabelle der Hauptlinien*[59] contains a selection of about 25,000 lines arranged in order of wave-length only, while shorter lists are available in Twyman and Smith's *Wave-length Tables for Spectrum Analysis*,[60] and in the tables published by Gerlach and Riedl as the third volume of *Die Chemische Emissions-spektralanalyse*.[61]

QUANTITATIVE ANALYSIS BY MEANS OF THE SPARK DISCHARGE

As previously noted, quantitative spectrographic analysis entails a comparison of the spectrum of the sample with that of a standard of similar known composition. The comparison is made through measurements of the intensities of selected lines, the standards providing a relationship between intensity and concentration under specific operating conditions. The direct quantitative evaluation of a spectrum by photoelectric means has been described and is in use to a limited extent.[62, 63] At present, however, the great majority of quantitative spectrographic techniques are based on the measurement of the densities of lines in a photographed spectrum.

For a given light intensity, the density produced may vary noticeably from one photographic plate to another; each plate must therefore be calibrated (see later). In addition, it is found that even under well controlled conditions, the total emission of radiation is not constant from spectrum to spectrum. An evaluation of line intensities based only on the intensity of a line of the element sought does not, therefore, generally give results of much accuracy. The 'internal standard' method first proposed by Gerlach and Schweitzer[12] affords an empirical correction for this variation.

In this procedure, the parameter related to element concentration is not the intensity of a line of the element but its intensity as

compared with a line of the basis metal. By hypothesis, both lines follow changes in total emission while the basis line is substantially unaffected by small changes in composition of the sample. Hence the ratio of intensities of the two lines may be taken as varying only with the concentration of the minor element.

Procedure

(1) Standards

In a spark source, the spectral response appears to be influenced by the following factors concerning the sample: composition of matrix, physical form, oxidation effects, states of combination of the elements present and the particle size of dispersed constituents, previous metallurgical treatment. It is a first essential therefore that the dimensions, form and metallurgical treatment of the sample for analysis should be exactly reproduced in the standards. Most spectrographers use samples in the 'as cast' condition though a few recommend giving them a heat-treatment prior to analysis.

Where special samples are cast for spectrographic analysis, the standards should be cast in the same mould and under the same conditions of temperature, speed of pouring, etc. They should be checked both chemically and spectrographically before being accepted as satisfactory. Since the line intensities are affected to varying extents by the nature and the amount of other elements present, the standards should be as nearly similar in composition to the sample being analysed as is possible in practice.

(2) Type of Sample

Two systems are commonly used for directly applying the spark discharge to the sample being analysed. In the first rod-shaped specimens are used as self-electrodes; in the second, a machined flat surface of the sample is used in conjunction with a counter-electrode of graphite or other suitable material. In accuracy of results achieved there is probably little to choose between the two systems. When standard samples are used to calibrate each plate, rods are generally rather more convenient and economical in use, while for simplicity of manipulation, specially cast flat discs are preferable.

These are commonly cast about 2·5 inches in diameter and 0·25 inches thick, while rods may be 5 to 10 mm. in diameter and about 70 mm. long. Both kinds of sample are usually cast in an iron mould giving a heavy chill, though Averbach[64] recommends a sand-cast disc for magnesium-base alloys. The rod-type casting used by Frommer is illustrated in Plate 36, *J. Inst. Metals*, 1939. 64.

(3) Sparking Surface

This should be smoothly finished without tool marks and is best prepared in a lathe. Rods are generally machined to a plane cylindrical tip of 3 to 5 mm. diameter and about 5 mm. deep, though some spectrographers prefer conical or wedge-shaped ends. The best dimensions have generally to be determined by experiment, and the permissible tolerance for accurate analyses is generally quite small.

Discs are usually positioned on the sparking stand so that the spark falls about 0·5 inches from the edge of the sample, the area adjacent to the pouring sprue being avoided.

Samples may be used repeatedly, a fresh surface being prepared for each sparking. Generally speaking a poor finish to the sparking surface leads to unsatisfactory results in analysis.

(4) Excitation of the Spectrum

The character of the condensed spark may be varied considerably by altering the values of capacity and inductance in the circuit.

With increasing capacity, the oscillations become slower, the energy dissipated in the gap is increased, and the electrodes become hotter. When the self-induction is small, little metallic vapour is present in the gap, excitation is of a high degree, and air lines are present in the spectrum.

With increasing self-induction, the oscillations become slower and the temperature of the electrodes rises; as a consequence the quantity of metallic vapour increases, the excitation becomes of a lower degree, and the number of air lines diminishes.

In this country spark units consisting of a $\frac{1}{4}$-kVa transformer of 15,000 volts peak, a condenser of 0·003–0·005 mfd. capacity and an inductance of from 0·005 to 0·25 mH are usually employed. In the United States, much more powerful sets are in use; Churchill,[65] for example, uses a spark unit of 2kVa nominal power with a capacity of 0·021 mfd. and an inductance of 1·44 mH. In practice, it does not appear that the size of the condenser affects the accuracy of results to any great degree, though for any particular size of condenser there are limiting values of inductance for optimum results.

Variations in the width of the spark gap may have noticeable effects on the line intensity ratios. The working gap should be so chosen that slight variations in width produce the minimum errors in results taking into account all the elements that are to be determined; gap widths of 2 to 5 mm. are in most common use. The gap is set to the correct width either by a gauge or by projecting an image of the electrodes on to a marked screen.

(5) Pre-sparking and Exposure Times

During the running of the spark, there is a more or less continuous change in the spectrum line intensities due to a rise in temperature of the electrodes, an accumulation of vapours in the spark gap, oxidation of the sparking surfaces and the depletion of the more volatile constituents of the sample. Different elements behave in a different manner, depending on their physical and chemical properties. As the sparking proceeds, a quasi-equilibrium may be obtained, after which pitting and oxide encrustation cause the spark to become erratic.

With the purpose of allowing some sort of equilibrium to be established (as evidenced by approximately constant line intensity ratios) it was customary a few years ago to find long pre-sparking times up to several minutes recommended for the analysis of aluminium and magnesium-base alloys. In practice, however, as has been pointed out by Frommer,[51] what matters most is not whether the ratio remains constant over a period, but how accurately it is reproduced during a given interval of time, and how far its value differs for two elements with different concentrations of the element being determined.

These are the important factors, since on the first depends the accuracy and on the second the sensitivity of the method. Experience shows that with long pre-sparking times, there is generally speaking a loss in sensitivity which more than offsets the advantage of working with constant line intensity ratios. Considerations of speed and economy in operating a spectrographic laboratory also preclude the use of long sparking times.

Some pre-sparking is generally conceded to be advantageous if only to remove accidental contamination of the sample after preparing the surface; periods of 10 to 30 seconds are commonly found in published procedures and are often arbitrarily chosen.

Care should be taken to time the interval accurately, particularly when the line intensities are known to be changing considerably. In routine analysis electrical timing devices for operating the exposure shutter and switching the spark on and off are decidedly advantageous.

The exposure time is selected in full consideration of the properties of the photographic plate and the speed demanded in the analysis. It should be such that the density of the lines used falls within the limits of the linear portion of the plate characteristic, and is not too great for reliable measurement in the microphotometer; exposure times of 10 to 40 seconds are most commonly used.

(6) Spectrograph

The slit must be illuminated by the source in such a way that the intensity of the spectrum lines is uniform along their length. This may be obtained by focusing an image of the source on to the collimator by means of an appropriate spherical lens between the source and the slit. The various modes of illumination of spectrograph slits have been studied by Stockbarger and Burns,[66] while Breckpot and Lialine[67] discuss the errors introduced by unsatisfactory illumination.

The slit should be from 1 to 2 mm. in height and 0·015 to 0·04 mm. in width ; it must be sufficiently narrow for adequate resolution of the lines to be measured, but wide enough to allow them to be measured rapidly in the microphotometer. The wider the slit, the greater is the amount of undesirable background in the spectrum.

Since the slit width is one of the factors which may influence the relative intensities of the lines, it should be accurately adjusted and maintained at a constant width for a particular analysis or run of analyses.

(7) Photography of the Spectrum

The factors governing the choice of a photographic emulsion for a particular analysis are : speed in the spectrum range being used ; contrast ; change in contrast with wave-length ; grain size ; speed of processing. Plates widely used for spectrographic analysis in this country are Ilford Thin Film Half-tone and Ordinary, and Kodak B10, B20 and L15. The speed of the plate must be such that it allows a suitable exposure time to be used, the grain size should be small to permit of accurate density measurements, while ease and speed of processing are conducive to the efficient working of the spectrographic laboratory.

For quantitative work, high contrast is generally desirable since this makes density measurement less critical, but if a very wide range of concentration has to be covered by the same pair of lines, a lower contrast may be preferable.

Ideally the emulsion should have the same contrast over the whole wave-length range used in the analysis, but most of the plates at present available (including those mentioned above) are reasonably uniform only in the range 2500 to 3100A, and thereafter show a noticeable rise in contrast with increasing wave-length.[68] The Uniform Gamma Plate introduced by Messrs. Kodak Ltd.[69] is, however, much improved in this respect and shows a high degree of uniformity of contrast in the range 2500 to 4000A.

In processing, the object must be to secure maximum uniformity

over the plate. In the light of both experience and experiment, recommendations have been put forward by the Photographic Panel of the British Non-Ferrous Metals Research Association.[70] These include dish development with agitation of the developer either by rocking or by means of a rubber squeegee or brush, the use of an acid stop bath and a hardening fixer.

Plates are preferably dried at room temperature, and should be developed as soon as possible after exposure. The properties desirable in photographic materials for quantitative spectrography are discussed in some detail by Barber.[71]

(8) Measurement of Line Densities

In the measurement of densities by means of the microphotometer, the following points should be noted :

The microphotometer and particularly the galvanometer should be free from vibration, and the former shielded from direct illumination.

The plate should be carefully focused in accordance with the instructions supplied with the microphotometer, and set so that the projected image of the line is parallel with the slit.

The width of the slit should be rather less than that of the line image. For the Hilger instrument it should be ten times the width of the spectrograph slit. The height of the slit should be about two-thirds that of the line image.

The spectrum line should be traversed slowly in order that the minimum galvanometer deflection may be accurately determined.

The constancy of the light source should be frequently checked by measurement of the clear glass deflection at the same spot on the plate.

Ideally, all the required lines in one spectrum should be measured before passing on to the next. This, however, necessitates much manipulation of the plate and tends to make measurement very slow. In practice it should be found that the light source remains sufficiently steady for quite a number of lines to be measured before attention to the light is required. It then becomes advantageous to measure one line throughout a suitable group of spectra, followed by the next line, and so on to the end of the group.

(9) Evaluation of Spectra

The various factors involved in photographic photometry—on which the quantitative interpretation of spectra is based—have been discussed by Dobson, Griffith and Harrison,[72] Pierce and Nachtrieb[73] and Smith and Liddiard.[74]

For the internal standard method of analysis, the basic assumption may be expressed as

$$\frac{I_1}{I_2} = aC^n \qquad \ldots\ldots\ldots\ldots(1)$$

where I_1 and I_2 are the intensities of a line of a minor element and the internal standard line, C, is the concentration of the minor element, and a and n are constants depending on the line pair and he sparking conditions used. In its more usual form this becomes:

$$\log \frac{I_1}{I_2} = n \log C + \log a \qquad \ldots\ldots\ldots\ldots(2)$$

In practice, the intensities of the lines are not directly determined but only the blackening produced by the lines on the photographic plate, as represented by microphotometer galvanometer deflections. The density D produced on a photographic plate by an intensity of illumination I in time t is closely expressed by the equation :

$$D = \gamma \log (It^p) - i \qquad \ldots\ldots\ldots(3)$$

where p, γ and i are approximately constant, and provided the plate is neither under- nor over-exposed.

The difference in density of two lines in the same spectrum may therefore be expressed as :

$$D_1 - D_2 = \gamma \log \frac{I_1}{I_2} \qquad \ldots\ldots\ldots(4)$$

where I_1 and I_2 are the intensities of the lines in the source, and D_1 and D_2 the corresponding densities of the lines on the photographic plate.

In measuring the densities in a microphotometer, if d_1 and d_2 are galvanometer deflections for the lines, and g the deflection for the clear plate, then

$$D_1 = \log \frac{g}{d_1} \text{ and } D_2 = \log \frac{g}{d_2} \qquad \ldots\ldots\ldots(5)$$

$$D_1 - D_2 = \log \frac{d_2}{d_1} \qquad \ldots\ldots\ldots\ldots\ldots(6)$$

Equating the two expressions for $D_1 - D_2$ we have

$$\log \frac{I_1}{I_2} = \frac{I}{\gamma} \log \frac{d_2}{d_1} \qquad \ldots\ldots\ldots\ldots\ldots(7)$$

and by substitution in equation (2)

$$\log C = \frac{K_1}{\gamma} \log \frac{d_2}{d_1} + K_2 \qquad \ldots\ldots\ldots\ldots (8)$$

where K_1 and K_2 are constants.

Thus, for constant γ, a simple linear relation holds between log concentration and log galvanometer deflection ratio. To ensure that γ is constant, the two lines should lie in the same wave-length region, and their densities should fall within the linear portion of the plate characteristic. For the type of plate normally used for spectrographic analysis, the density of a line to be measured in the microphotometer should be not less than about 0·4, i.e. the galvanometer deflection should be not greater than about 200 for a clear plate deflection of 500. The upper working density is usually limited by the accuracy with which a small galvanometer deflection can be read.

These safeguards only ensure that on any individual plate one is working in a region of approximately constant γ. In practice it is found that, even under closely controlled conditions of development, γ varies from plate to plate. Each plate, therefore, has to be calibrated separately; there are several ways of doing this.

The use of analysed standards.—In this method a calibration curve for each plate is obtained from spectra of three or more standards covering the range required, preferably with one standard of the average composition of the samples to be analysed. Values of log d_1/d_2 ('log ratios') are plotted against the known log concentrations to give a straight line from which values of 'log ratio' for the unknowns can be read off as percentages of element present.

At least 12 spectra in all from the set of three or more standards should be recorded on each plate, preferably at intervals down the plate to minimize the effect of plate irregularities. Each standard spectrum should be obtained from a different disc or pair of pencils.

This method, while simple to apply, has certain disadvantages. The high proportion of standard spectra is wasteful, especially when only a few samples have to be analysed. Moreover, when used repeatedly, the standards are soon consumed and fresh sets have to be prepared and carefully analysed. In addition, it is probably less exact, as a means of plate calibration, than the following methods.

The use of relative intensities.—From equation (3) it will be seen that, by varying the intensity I in a known manner, a relation

can be established between I and density D, and hence between I and galvanometer deflection d. There is also the fundamental relation :

$$\log \frac{I_1}{I_2} = n \log C + \log b$$

This provides a means for determining the 'calibration curve' for a particular element, and the curve does not have to be determined afresh for each plate. In practice, n is found to be substantially constant for a particular determination, but b to vary somewhat over a period of time. Since a change in b shifts the calibration curve without changing its slope, the position of the curve may be checked by sparking one known sample at suitable intervals.

It is possible therefore to calibrate each plate by varying I in a known manner to establish the density curve relating I and d, and from this curve to express values of d_1/d_2 in terms of I_1/I_2. These values may either be used to construct the basic 'calibration curve' from standard samples or be read off as percentages of element present once this curve has been constructed. By this means, the repeated use of standards on each plate is avoided. To determine the concentration, however, an additional calculation is required, namely the conversion of densities to relative intensities. When using the method of relative intensities it is usual therefore to use a mechanical calculator to speed up the conversion of galvanometer deflections into concentrations (see later note).

The methods available for calibrating photographic plates have been discussed by Harrison[75] and most of them studied in detail.[76] The stepped sector, stepped wedge, and internal-line group methods have all been used and found satisfactory.

Stepped sector.—By rotating a suitably cut sector close to the spectograph slit, known variations of exposure are produced across the width of the spectrum. The slit should be evenly illuminated and the sector rotated at a speed which avoids the stroboscopic effects which may arise with an intermittent source such as the spark. Basically, the sector varies the time of exposure and not the intensity of illumination, thus allowing possible errors to be introduced through the photographic intermittency effect if the speed of rotation is not constant. Silberstein and Webb[77] have shown that these errors are avoided if the sector is rotated at a speed above the so-called 'fusion frequency'. To obtain the calibration curve, the different steps of the selected line are measured in the microphotometer, and the readings plotted against the known relative exposures.

Stepped optical wedge.—This device produces a stepped

spectrum in which the intensities are varied in a known way depending on the densities across the wedge. The method is free from the two defects of the rotating sector and is very convenient in use. Since the absorbing medium is seldom optically neutral it is theoretically necessary to calibrate the wedge for the particular wave-length used. In practice, however, it is possible to obtain reproducible results by assuming a single calibration for the range of wave-lengths used in most spectrographic procedures. The exposure for the calibration spectrum should be of the same order as that for the samples being analysed. The calibration curve is obtained by plotting the galvanometer readings for the different steps of the spectrum against the known relative densities of the steps of the wedge.

Internal-line group.—In this method which has been used by Vincent and Sawyer[78] and other workers, the relative intensities of a selected group of lines in a suitable spectrum are determined and thereafter used as a source of known relative intensities. It is essential that the lines should not vary in relative intensity due to electrical effects and hence they should be selected with care. Dieke and Crosswhite[79] have examined the iron spectrum and found suitable lines for this purpose. The method is simple and requires no special apparatus ; it is not, however, considered to be as reliable as the previous methods.

Other methods of plate calibration are by the use of a stepped diaphragm and continuous source (Hansen,[80] Thomson and Duffendack[81]), the three-line method of Scheibe and Schnettler,[82] and a two-line method described by Levy[83] and used by Churchill.[65] Whichever method is used, the operating conditions, once established, should be rigidly adhered to.

(10) Choice of Line Pairs for Measurement

It is generally recommended that both the internal standard line and the minor element line should be of the same kind, i.e. both arc lines or both spark lines, since an arc/spark line pair is expected to vary in intensity with slight changes in the electrical conditions of the spark. This limitation, which in practice is often very undesirable, is not found to be absolutely essential, many dissimilar pairs of lines giving satisfactory results. Other considerations governing the selection of the lines are that they should be sufficiently sensitive, of a suitable intensity, free from interference and not too far apart in wave-length. The most satisfactory method of assessing the suitability of a line pair for a particular analysis is to determine both its sensitivity and its reproducibility by repeatedly sparking samples of known composition. A list of

line pairs taken from published procedures up to 1939 is given by Smith.[84]

(11) Calculators

The conversion of microphotometer readings into the required percentages of element present may be simplified by the use of graphical calculators; devices of this sort have been described and discussed by Owens,[85] King,[86] and Brommelle and Clayton.[87]

(12) Accuracy

The accuracy obtainable in quantitative determinations depends to some extent on the material being analysed and on the element and percentage being determined. Standard errors of 2 to 6% of the amount present may be expected in the range 0·1 to 4·0% though better results have been reported in favourable cases. To obtain the greatest accuracy the importance of strictly adhering to the details of a given procedure cannot be too strongly emphasized.

(13) Semi-quantitative Analysis

In cases where only approximate quantitative results are required, or where it is merely desired to know if an element is present within certain limits, a visual examination of the spectrum may often be adequate. It is generally possible to find pairs of lines which are equal in intensity at different known percentages of the element in question; by observing visually the intensities of these lines in the spectrum of the sample, a fair estimate of the amount of the element present can be made.

(14) Establishing a Quantitative Procedure

From the now very considerable bulk of available literature, much valuable information may be obtained, and the spectrographer faced with a particular analytical problem will do well to study what has been done by previous workers on the same subject. To determine the best operating conditions for a particular analysis all the factors which can influence the results should be examined experimentally. These have been indicated by the various headings, e.g. standards, type of sample, sparking surface, etc. Excellent accounts of the experimental results obtained in establishing analytical procedures for steels and aluminium alloys have been contributed by Barker[88] and the laboratories of the British Aluminium Company, Ltd.[89] respectively. Churchill[65] discusses quantitative techniques in some detail, while Smith[84] gives a valuable review of published information on specific

aspects of spectrographic analysis as well as a summary of published procedures. Twyman[90] can be confidently referred to for illumination on any matter pertaining to the spectrograph and its use in analysis, and for information regarding many practical applications of the method.

The following is a short list of some useful papers dealing with the spectrographic analysis of some common metals and alloys.

ALUMINIUM AND ITS ALLOYS

Collected Papers on Metallurgical Analysis by the Spectrograph, 23–8, 29–64, 65–81, 82–93. British Non-ferrous Metals Research Association, London, 1945.
Callon, R. W., and Burgener, J. E., *J. Opt. Soc. Amer.*, 1944. **34.** 543–9.
Wolbank, F., *Z. Metallkunde*, 1939. **31.** 257–61.
Moritz, H., *Aluminium*, 1943. **25.** 100–5.
Churchill, H. V., and Churchill, J. R., *J. Opt. Soc. Amer.*, 1941. **31.** 611–9.
Spectrochemical and Polarographic Analysis of Aluminium and Aluminium Alloys. London: British Aluminium Company Limited, Publication Number 401 (1943).

ZINC AND ITS ALLOYS

Zehden, W., *J. Soc. Chem. Ind.*, 1940. **59.** 236–8.
Wolbank, F., and Lueg, G., *Z. Metallkunde*, 1940. **32.** 430–6.
Balz, G., *Z. Metallkunde*, 1941. **33.** 260–7.
Collected Papers on Metallurgical Analysis by the Spectrograph. 116–29, British Non-ferrous Metals Research Association, London, 1945.
Winter, H., *Z. Metallkunde*, 1937. **29.** 341–51.
Polarographic and Spectrographic Analysis of High Purity Zinc and Zinc Alloys for Die Casting. London: H.M. Stationery Office, 1945.

FERROUS ALLOYS

Barker, F. G., *J. Iron Steel Inst.*, 1939. **139.** 211–55.
Vincent, H. B., and Sawyer, R. A., *Metal Progress*, 1939. **36.** 35–9.
Bardocz, A., *Spectrochim. Acta*, 1942. **2.** 350–60.
Cameron, J., *J. West Scot. Iron Steel Inst.*, 1943–44. **51.** 15–27.
Coulliette, J. H., *Ind. Eng. Chem.*, Anal. Ed., 1943. **15.** 732–4.
Guettel, C. L., *J. Opt. Soc. Amer.*, 1944. **34.** 41–6.
Young, L. G., *Engineer*, 1944. **178.** 116–8.
Ling, F. B., McPheat, J., and Arnott, J., *40th Ann. Conf. Inst. British Foundrymen*, Paper 771, 1943.
Shirley, H. T., and Elliott, E., *J. Iron Steel Inst.*, 1943. **147.** 299–323.
Steele, S. D., and Johnston, J. M., *J. Soc. Chem. Ind.*, 1945. **64.** 278–83.

COPPER AND ITS ALLOYS

Milbourn, M., *J. Inst. Metals*, 1943. **69.** 441–63.
Leichtle, P. A., *J. Opt. Soc. Amer.*, 1944. **34.** 454–63.
Jaycox, E. K., *J. Opt. Soc. Amer.*, 1945. **35.** 175–9.
Collected Papers on Metallurgical Analysis by the Spectrograph. 130–4, 135–9. British Non-ferrous Metals Research Association, London, 1945.

MAGNESIUM AND ITS ALLOYS

Averbach, B. L., *Ind. Eng. Chem.*, Anal. Ed., 1945. **17.** 341–8.
Carter, G. P., *Met. Ind.*, 1942. **60.** 140–3, 159–62.
Hess, T. M., and Reinhardt, L. G., *J. Opt. Soc. Amer.*, 1944. **34.** 104–9.
Fox, F. A., and Nelson, J., *J. Soc. Chem. Ind.*, 1941. **60.** 278–86.

LEAD AND ITS ALLOYS

Kaiser, H., *Z. Tech. Physik*, 1936. **17.** 227–39.
Kaiser, H., *Metallwirts*, 1937. **16.** 301–6.
Collected Papers on Metallurgical Analysis by the Spectrograph; 94–99, 100–9, 110–5. British Non-ferrous Metals Research Association, London, 1945.
Werner, O., and Rudolf, W., *Angew. Chem.*, 1938. **51.** 899–906.

BIBLIOGRAPHY

1 W. Herschel, *Phil. Trans.*, 1800. **90.** 255.
2 J. W. Ritter, *Gilbert's Ann.*, 1801. **7.** 527.
3 W. H. Wollaston, *Phil. Trans.*, 1802. **92.** 365.
4 J. Fraunhofer, *Gilbert's Ann.*, 1817. **56.** 264.
5 J. F. W. Herschel, *Trans. Roy. Soc. Edin.*, 1823. **9.** 445.
6 G. Kirchhoff and R. Bunsen, *Pogg. Ann.*, 1860. **110.** 161.
7 W. H. Hartley, *Phil. Trans.*, 1884. **175.** 326.
8 J. H. Pollak and A. G. G. Leonard, *Sci. Proc. Roy. Dublin Soc.*, 1907. **11.** 184.
9 A. De Gramont, *Compt. Rend.*, Series of papers, 1900–23.
10 W. F. Meggers, C. C. Kiess and F. J. Stimson, *U.S. Bur. Stand. Sci. Papers.* 1922. **18** (444). 235.
11 D. M. Smith, 'Metallurgical Analysis by the Spectrograph', *British Non-Ferrous Metals Research Association*, London, 1933; and other papers.
12 W. Gerlach and E. Schweitzer, *Die Chemische Emissionsspektralanalyse*, I, Leipzig, L. Voss, 1929; English translation *Foundations and Methods of Chemical Analysis by the Emission Spectrum*, London, Adam Hilger Ltd., 1931.
13 W. F. Meggers and B. F. Scribner, 'Index to the Literature on Spectrochemical Analysis, 1920–37', *American Society for Testing Materials*, Philadelphia, 1939.
14 F. Twyman, *Spectrochemical Abstracts*, 1933–37, Adam Hilger Ltd., London, 1938.
15 E. H. S. Van Someren, *Spectrochemical Abstracts*, 1938–39, Adam Hilger Ltd., London, 1941.
16 F. Twyman and F. Simeon, *Trans. Opt. Soc.*, 1929–30. **31.** 179.
17 R. A. Sawyer, *Experimental Spectroscopy.* Prentice-Hall, New York; Chapman & Hall Ltd., London, 1944.
18 H. E. White, *Introduction to Atomic Spectra*, McGraw-Hill Book Co. Inc., New York and London.
19 W. R. Brode, *Chemical Spectroscopy.* John Wiley & Sons Inc., New York; Chapman & Hall, Ltd., London, 1943.
20 H. Ramage, *Nature*, 1929. **123.** 601.
21 H. G. Lundegardh, *Die Quantitative Spektralanalyse der Elemente*, Gustav Fisher, Jena, 1929, 1934.
22 J. A. C. McClelland and H. K. Whalley, *J. Soc. Chem. Ind.*, 1941. **60.** 288.
23 J. Cholak and D. M. Hubbard, *Ind. Eng. Chem*, Anal. Ed., 1944. **16.** 729.
24 T. Torok, *Z. Anal. Chem.*, 1939. **116.** 29.
25 R. L. Mitchell, *J. Soc. Chem. Ind.*, 1936. **55.** 267.
26 F. Waibel, *Z. Techn. Physik*, 1934. **15.** 454.
27 R. Bossuet, *Compt. Rend.*, 1935. **200.** 1094.
28 H. Ramage, J. H. Sheldon and W. Sheldon, *Proc. Roy. Soc. B.*, 1933. **113.** 308.
29 F. C. Steward and J. A. Harrison, *Ann. Bot. Lond.*, 1939. **3.** 427.
30 J. S. Owens, *Metals and Alloys*, 1938. **9.** 15.
31 A. H. Staud and A. E. Ruehle, *Ind. Eng. Chem.*, Anal. Ed., 1938. **10.** 59.
32 G. W. Standen and L. Kovach, *Proc. Amer. Soc. Test. Mat.*, 1935. **35** (Part 2). 79.

[33] M. Milbourn, *J. Inst. Metals*. 1943. **69**. 441.
[34] E. W. Foster, *Proc. Phys. Soc.*, 1941. **53**. 299.
[35] W. Rollwagen, *Spectrochim. Acta*, 1939. **1**. 66.
[36] D. M. Smith, 'Metallurgical Analysis by the Spectrograph, *British Non-Ferrous Metals Research Association*, London, 1933.
[37] M. F. Hasler, *J. Opt. Soc. Amer.*, 1941. **31**. 140.
[38] B. Judd Lewis, *Spectroscopy in Science and Industry*, Blackie & Son Ltd., London, 1936.
[39] E. Bayle and L. Amy, *Compt. Rend.*, 1927. **185**. 268.
[40] W. Gerlach and W. Gerlach, *Die Chemische Emissionsspektralanalyse*, II, L. Voss, Leipzig, 1933 ; English translation, *Clinical and Pathological Applications of Spectrum Analysis*, Adam Hilger Ltd., London, 1934.
[41] K. Pfeilsticker, *Z. Electrochem.*, 1937. **43**. 719.
[42] K. Pfeilsticker, *Z. Metallkunde*, 1938. **30**. 211.
[43] M. F. Hasler and H. Dietert, *J. Opt. Soc. Amer.*, 1943. **33**. 218.
[44] A. Walsh, *Metal Ind.*, 1946. **68**. 243, 263, 293.
[45] F. G. Brockman and F. P. Hochgesang, *Ind. Eng. Chem.*, Anal. Ed., 1942. **14**. 796.
[46] O. S. Duffendack and R. A. Wolfe, *Proc. 5th Summer Conf. Spectroscopy, Mass., Inst. Techn.*, 1937, John Wiley & Sons Inc., New York ; Chapman & Hall Ltd., London, 1938.
[47] O. S. Duffendack, R. A. Wolfe and R. W. Smith, *Ind. Eng. Chem.*, Anal. Ed., 1933. **5**. 226.
[48] L. W. Strock, *Spectrum Analysis with the Carbon Arc Cathode Layer*, Adam Hilger Ltd., London, 1936.
[49] Kaiser, H., *Proc. 7th Summer Conf. Spectroscopy, Mass. Inst. Techn.*, 1939. John Wiley & Sons Inc., New York ; Chapman & Hall Ltd., London, 1940.
[50] O. Feussner, *Z Techn. Physik*, 1932. **13**. 573.
[51] L. Frommer, *J. Inst. Metals*, 1939. **64**. 396.
[52] J. T. M. Malpica and T. M. Berry, *Gen. Elect. Rev.*, 1941. **44**. 563.
[53] R. W. Callon and J. E. Burgener, *J. Opt. Soc. Amer.*, 1944. **34**. 543.
[54] C. Braudo and H. R. Clayton, *J. Soc. Chem. Ind.*, 1947. **66**. 259.
[55] C. J. Neuhas, *J. Opt. Soc. Amer.*, 1943. **33**. 167.
[56] F. Twyman and C. S. Hitchen, *Proc. Roy. Soc. A.*, 1931. **133**. 72.
[57] R. J. Keirs and D. T. Englis, *Ind. Eng. Chem.*, Anal. Ed., 1940. **12**. 275.
[58] Mass. Inst. Techn., *Wave Length Tables of More than* 100,000 *Spectrum Lines*. John Wiley & Sons Inc., New York. Chapman & Hall Ltd., London, 1939.
[59] H. Kayser and R. Ritschl, *Tabelle der Hauptlinien der Linienspektren aller Elemente*, Julius Springer, Berlin, 1939.
[60] F. Twyman and D. M. Smith, *Wavelength Tables for Spectrum Analysis*, Adam Hilger Ltd., London, 1931.
[61] W. Gerlach and E. Riedl, *Die Chemische Emissionsspektralanalyse*, III, L. Voss, Leipzig, 1936.
[62] M. F. Hasler, R. W. Lindhurst and J. W. Kemp, *J. Opt. Soc. Amer.*, 1948. **38**. 789.
[63] J. L. Saunderson and T. M. Hess, *Metal Progr.*, 1946. **49**. 947.
[64] B. L. Averbach, *Ind. Eng. Chem.*, Anal. Ed., 1945. **17**. 341.
[65] J. R. Churchill, *Ind. Eng. Chem.*, Anal. Ed., 1944. **16**. 653.
[66] D. C. Stockbarger and L. Burns, *J. Opt. Soc. Amer.*, 1933. **23**. 379.
[67] R. Breckpot and L. Lialine, *Ann. Soc. Sci. Bruxelles*, 1935. **B55**. 30.
[68] E. H. Amstein, *J. Soc. Chem. Ind.*, 1944. **63**. 172.
[69] E. P. Davey and M. D. Gauntlett, *J. Soc. Chem. Ind.*, 1945. **64**. 70.
[70] *Collected Papers on Metallurgical Analysis by the Spectrograph*, 1–10, British Non-Ferrous Metals Research Association, Lonson, 1945.
[71] D. R. Barber, *Engineering*, 1945. **160**. 257.
[72] G. M. B. Dobson, I. O. Griffith and D. N. Harrison, *Photographic Photometry*, Clarendon Press, Oxford, 1926.
[73] W. C. Pierce and N. H. Nachtrieb, *Ind. Eng. Chem.*, Anal. Ed., 1941. **13**. 774.

[74] D. M. Smith and E. A. G. Liddiard, *Photographic J.*, 1944. **84.** 293.
[75] G. R. Harrison, *J. Opt. Soc. Amer.*, 1934. **24.** 59.
[76] *Collected Papers on Metallurgical Analysis by the Spectrograph*, 50–64, British Non-Ferrous Metals Research Association, London, 1945.
[77] L. Silberstein and J. H. Webb, *Phil. Mag.*, 1934. **18.** 1.
[78] H. B. Vincent and R. A. Sawyer, *Metal Progr.*, 1939. **36.** 35.
[79] G. H. Dieke and H. M. Crosswhite, *J. Opt. Soc. Amer.*, 1943. **33.** 425.
[80] G. Hansen, *Z. Physik*, 1924. **29.** 356.
[81] K. B. Thompson and O. S. Duffendack, *J. Opt. Soc. Amer.*, 1933. **23.** 101.
[82] G. Scheibe and O. S. Schnettler, *Naturwiss.*, 1930. **18.** 753.
[83] S. Levy, *J. Opt. Soc. Amer.*, 1944. **34.** 447.
[84] D. M. Smith, *Quantitative Spectrographic Analysis with the Microphotometer*, Part 1, British Non-Ferrous Metals Research Association, London, 1939.
[85] J. S. Owens, *Ind. Eng. Chem.*, Anal. Ed., 1938. **10.** 64.
[86] C. King, *J. Opt. Soc. Amer.*, 1942. **32.** 112.
[87] N. S. Brommelle and H. R. Clayton, *J. Soc. Chem. Ind.*, 1944. **63.** 83.
[88] F. G. Barker, *J. Iron Steel Inst.*, 1939. **139.** 211.
[89] *Collected Papers on Metallurgical Analysis by the Spectrograph*, 30–64, British Non-Ferrous Metals Research Association, London, 1945.
[90] F. Twyman, *The Spectrochemical Analysis of Metals and Alloys*, Charles Griffin & Co. Ltd., London, 1941.

V. MICROCHEMICAL METHODS OF METALLURGICAL ANALYSIS

The scope of this brief section, is limited to indicating the possibilities of carrying out analysis on sample weights much lower than those normally employed. It is not intended to discuss methods in which trace elements are determined using large samples, although strictly speaking such cases do fall within the broader definitions of microchemical analysis.

Table X lists the usually accepted scales of working taking quantity of sample employed as the criterion. In practice some overlapping will frequently occur so that it is inadvisable to regard these ranges as being rigidly fixed.

TABLE X

Scale	Approx. Range of Sample Weights
Semimicro or Centigram	10–100 mg
Micro, Full Micro or Milligram	1–10 mg
Submicro, Ultramicro or Microgram	10–100 μg

It has been statistically shown that quantitative reproduction of chemical reactions should be possible using amounts of material as small as 10^{-16} g, provided that appropriate techniques of

manipulation, observation and measurement are employed.[3] As metallurgical samples—especially certain types of alloy—are subject to segregation it must be borne in mind, that in many cases, greater difficulties are likely to be encountered in obtaining a representative sample than would be solved through working on the smaller scale. It follows for this very reason that microchemical analysis should prove a powerful tool for investigating the occurrence of heterogeneity by taking minute samples from various parts of an ingot, billet or other metallic component. Microchemical analysis becomes essential when the quantity of sample is strictly limited or when the material itself is precious. Examples are tiny components from instruments or fine mechanisms; segregates or inclusions from castings or forgings; scrapings from archaeological specimens as well as corrosion products where the amount available is invariably very limited. An outstanding example of the fundamental chemical behaviour of an element being studied by microchemical methods is provided by that of element 94—plutonium. In this instance only tens of micrograms were in existence at the time. Yet, it has been stated that the knowledge of the chemistry of plutonium is—without exception—more complete than that of any other element in the periodic table.

Microchemical analysis is not recommended for routine procedure if sufficient sample is available. In these cases it is preferable that the intermediate semimicro scale should be used. Examples of this are to be found in other sections of this book—particularly methods employing absorptiometric finishes—and they are advocated because in general they offer greater possibilities of speed, precision and obviate the necessity for employing analysts highly skilled in micromanipulation.

In adapting an existing method to the micro scale the problems which arise are mainly those of reducing all important dimensions proportionately. Volumes, dimensions of apparatus, etc., should as far as possible be scaled down in similar ratio. Concentrations of solutions, however, should remain at the same strength as on the macro scale. Difficulties will arise in doing this, and there is always the temptation to avoid the issue by using more dilute solutions for, e.g., to obviate the necessity of having to measure very small volumes accurately. Different techniques have to be used for transfer of precipitates, and sources of contamination of reagents, glassware and sample exert a much greater influence. At the same time hazards due to adsorption and co-precipitation are considerably reduced.

The basic manipulative techniques were worked out by Emich

and Pregl of Graz, Austria, and are adequately described in standard text-books on the subject.[1, 2, 3, 4, 5] The treatises which deal with organic microanalysis provide much that is of benefit to the inorganic analyst and should consequently not be ignored.

Application to Metallurgical Analysis

The first suggestions for applying microchemical techniques to the analysis of metals were made by Benedicks and Treje[6] in 1936. These were mainly of a qualitative nature. Since that date an intensive study of spot tests has been made, particularly by Feigl[8] and such qualitative tests can often be used to excellent advantage for identification purposes. Excellent schemes for qualitative analysis on the micro scale have been described by Belcher and Wilson.[9] These, whilst based on the classical 'group' separations, have been in many cases modified to give 'short cut' methods of rapid identification.

The first quantitative metallurgical methods on the microchemical scale were published by LeRoy[10] in 1938 and comprise detailed procedures for the determination of manganese, phosphorus and chromium in steels using sample weights of 5 milligrams. LeRoy demonstrated that microvolumetric and colorimetric procedures were more sensitive and gave more reproducible results than gravimetric ones. In 1940, Klinger, Koch and Blaschzyk[11] of the firm of Krupp published a monograph describing micromethods for most of the common elements in steels as well as for certain of the specialized alloying elements. Absorptiometric, titrimetric, electrolytic and polarographic finishes were variously used. Many of the methods however required complicated chemical separations.

Vaughan[12] of the 'Bragg' Admiralty Laboratory perceiving the need for avoiding troublesome separations which were time-consuming, laid the foundations of modern absorptiometric methods of analysis employing a photo-electric absorptiometer. He also developed comprehensive schemes whereby more than one element could be determined on a single sample weighing with the precision and accuracy of the older classical methods.

Reduction and adaptation of many of these methods to the milligram scale was fully investigated by Vaughan and Whalley[13] and constituted a great advance over anything previously published.

For full details, the original publication[13] should be consulted. All methods are absorptiometric with the exception of those for carbon and sulphur. (See Table XI.) Chemical separations are avoided wherever possible. In addition to specific micromethods

for individual elements, several composite schemes are described for determining up to nine elements on a single sample weighing of 15 milligrams.

TABLE XI

MICROCHEMICAL METHODS AVAILABLE FOR STEEL ANALYSIS
(Vaughan and Whalley[13])

Element	Method	Finish	Sample Wt. mg	Range %
Carbon	Combustion CO_2	Gravimetric	50	0–3·0
Chromium	(1) NaOH Separation Diphenylcarbazide	Absorptiometric	0·8	0–6·0
,,	(2) Diphenylcarbazide (Direct)	,,	0·5	0–6·0
,,	(3) Dichromate	,,	4·0	0–30
Cobalt	(1) Nitroso R. Salt	,,	1·0	0–6
,,	(2) Nitroso R. Salt	,,	0·5	0–20
Copper	(1) Diethyldithiocarbamate (Direct)	,,	4·0	0–3·0
,,	(2) Diethyldithiocarbamate (Separation)	,,	4·0	0–6·0
Manganese	Permanganate	,,	4·0	0–12
Molybdenum	Thiocyanate	,,	1·6	0–9
Nickel	Oxidized Dimethylglyoxime	,,	0·4	0–30
Phosphorus	Molybdenum Blue	,,	5·0	0–1·0
Silicon	Molybdenum Blue	,,	1·0	0–6·0
Sulphur	(1) Titration of SO_2 with I_2	Volumetric	50	0–0·3
,,	(2) Diphenylcarbazide	Absorptiometric	10·0	0–0·15
Titanium	(1) Direct Thymol	,,	2·0	0–4·0
,,	(2) Thymol (Separation)	,,	2·0	0–4·0
Tungsten	Dithiol	,,	2·0	0–5·0
Vanadium	(1) Strychnine	,,	5·0	0–3·0
,,	(2) Diphenylamine	,,	1·0	0–4·0

The principles, techniques and apparatus described should serve as the basis for similar methods on almost any type of metal or

alloy. For example: Townend and Whalley[14] have described similar techniques for the microchemical determination of copper, nickel, iron, silicon, titanium and manganese in aluminium alloys, whilst Phillips and Holton[15] developed a microabsorptiometric method for the determination of zinc in aluminium or its alloys.

Ingram[16] has described the application of microcombustion methods to metallurgical analysis. Micro and semimicro analysis of fuels have been very fully dealt with by Belcher and Spooner,[17] Beet and Belcher[18] and by Belcher.[19]

Small-scale electrolytic methods should find future application in metallurgical analysis and these have been reviewed by Lindsay:[20] Lindsay[21] has also proposed an auxiliary electrode for the control of electrodeposition on the micro scale. A micro mercury cathode cell would seem to offer possibilities for removal of many interfering heavy metals, whilst micro polarographic cells should make possible many elegant techniques through application of the dropping electrode principle.

That micro methods employing gravimetric finishes are not being neglected is shown by recent papers by Miller and Curie[22] for the determination of lead in white metals, fusible alloys and tin-free copper base alloys. The separation is achieved as the lead nitrate thiourea complex; this is subsequently converted to weighable lead chromate. The same workers[23] also describe micro-determination of lead in bronzes by electrolytically depositing the lead as oxide followed by subsequent conversion to lead chromate for weighing.

An extensive field would seem to lie in the possibilities of isolation of sought elements and separation of interfering elements through complexation with organic reagents followed by extraction with immiscible solvents.

Chromatographic separations have been described by Linstead[24] of Chemical Research Laboratory.

Turning to purely physical techniques employing micro samples, the application of spectrographic methods to the analysis of segregates has been investigated by Barker, Convey and Oldfield[25, 26] of the 'Bragg' Admiralty Laboratory. They succeeded through the use of specially designed electrodes in determining silicon, manganese, nickel, chromium, molybdenum and vanadium by evaluation of the spectrograms obtained after a sparking of 15 seconds duration. The quantity of sample consumed was of the order of 5 micrograms. Very satisfactory reproducibility was obtained and the work is valuable as an example of non-destructive testing on the micro scale. Gatterer[27]

has devised a method for the spectrographic determination of the halogens, sulphur and selenium in small mineral samples using high frequency coil excitation in electrodeless vacuum tubes.

The method of von Ardenne and Bernhard[28] for the determination of carbon in iron and steel by a nuclear reaction is worthy of note as an example of application radiometric techniques to the micro scale. The sample is bombarded with protons or deuterons causing conversion of the carbon present into a radioactive isotope of nitrogen having a half-life of 9·93 minutes. The emissions are measured by a Geiger-Müller counter. It is claimed that carbon down to a level of 0·05% can be determined.

The above examples indicate the progress so far achieved in devising workable microchemical methods for metallurgical materials. It is hoped that they may stimulate others to develop such methods capable of dealing with the many specialized problems which arise in this field.

A few suggestions dealing with sampling and equipment requirements for carrying out of metallurgical microchemical investigations are now given.

Sampling

Especial care is necessary in the preparation of metallurgical samples for microanalysis. Small specimens may be reduced to the necessary fine state of division by turning down on a watchmaker's lathe or milling in a modelmaker's machine. Another method is to flatten the small specimen in a hardened steel mortar, after annealing to soften if necessary. The flattened specimen may then be snipped into small pieces. Removal of foreign matter should always be carried out, either by magneting, or by hand sorting using ivory-tipped forceps under a lens or low-power microscope. Samples must be degreased with ether and finally stored in stoppered sample tubes. Corrosion products or electrolytically plated films require special care in order to ensure that no contamination is introduced.

Accommodation

Microchemical analysis is preferably carried out in a room apart from the normal macro laboratory. It can usually be quite small, but should be well-lit, quiet and free from dust. The normal services of water, electricity and gas should of course be available. Fume extraction can usually be of a very simple nature, as when working with such small quantities of material no great volume of fumes is produced. Sometimes a glass or porcelain funnel connected to a filter pump will suffice for fume removal.

Design of microchemical laboratories has been discussed by Ingram.[29]

Weighing Techniques

The modern microchemical balance has a nominal sensitivity of 0·001 milligram, i.e. 1 microgram. From various studies which have been made of the performance of such balances it would appear that their precision (based on the standard deviation of a single weighing) is of the order ± 4–5 micrograms.

The order of the sample weights required by some of the above-mentioned methods is 0·4–5 milligrams and such amounts should preferentially be weighed on a microbalance. Such operations should be carried out with the precautions laid down by Emich and Pregl.[1, 2, 3, 4] A microbalance will certainly be required for weighing the absorption tubes used on a microcombustion train when determining carbon on a 50 milligram sample, as even with a 1% carbon content the increase in weight due to the CO_2 absorbed will only be 1·8 milligrams. Samples of 10–50 milligrams may be weighed on a semimicro balance which is nominally adjusted to have a sensitivity of 0·01 milligrams, i.e. 10 micrograms. It should also be noted that a good macro analytical balance, having a serrated beam and a nominal sensitivity of 0·1 milligrams can, by use of the method of swings as recommended by Belcher and Godbert,[5] be utilized to the limits of its sensitivity approaching 0·01 milligrams.

Special Apparatus

Provided that methods with absorptiometric finish only are to be used, the special apparatus required, in addition to a microbalance and a photo-electric absorptiometer with its specially designed cells and the adaptor which must be used to narrow the light beam[13], will consist of conical flasks of 10–25 ml. capacity, some tall-form 5 ml. beakers, and a few micropipettes for solution transfer of capacity, 0·1, 0·5, 1·0 and 2·0 ml. respectively. In addition graduated flasks of 5 and 10 ml. capacity will be required for making up of solutions to known volume. Vaughan and Whalley[13] describe a useful device for ensuring thorough mixing in such small capacity flasks. It consists of a 10 ml. boiling flask which can be attached inverted to the micro standard flask by means of a ground glass joint.

In cases where filtration becomes unavoidable many neat devices have been designed. These have been reviewed by Burton[30] and by Wyatt.[31]

Various types of apparatus for volumetric work on the micro

scale have been discussed by Masters.[32] The 1 ml. capacity burette described by Winteringham[33] having coarse and fine control has proved most useful, and can easily be constructed from generally available materials.

Miscellaneous gadgets and devices have been described by Stock and Fill,[34, 35] including suggestions for micro reagent bottles, ground joints for small bore tubing, clamps for objects of small diameter. Stock[36] has also described the various semi-automatic and time-saving devices as aids to microchemistry which were exhibited recently in London.

REFERENCES

1 Emich and Schneider, *Microchemical Laboratory Manual*, New York, 1932, Wiley.
2 Pregl and Grant, *Quantitative Organic Microanalysis*, 1945, Churchill.
3 Benedetti-Pichler, *Introduction to the Microtechnique of Inorganic Analysis*, New York, 1942, Wiley.
4 C. L. Wilson, *Introduction to Microchemical Methods*, 1938.
5 Belcher and Godbert, *Semimicro Quantitative Organic Analysis*, London, 1945, Longmans Green.
6 Belcher, *Microchemistry and its Applications*, Royal Institute of Chemistry Monograph, 1946.
7 Benedicks and Treje, *Revue de Metallurgie*, 1936. **33.** 203.
8 Feigl and Osper, *Quantitative Analysis by Spot Tests*, Amsterdam, 1947, Elsevier Publishing Co.
9 Belcher and Wilson, *Qualitative Inorganic Microanalysis*, London, 1946, Longmans Green.
10 LeRoy, *Revue de Metallurgie*, 1938. **35.** 104.
11 Klinger, Koch and Blaschzyk, *Iron and Steel Institute Translation No.* 169. (Original in *Angw. Chem.*, 1940. **53.** 537 and in *Tech. Mitt Krupp Forschung*, 1940. **3.** 255.)
12 Vaughan, 'The Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis' and 'Further Advances in the Use of the Spekker Photo-electric Absorptiometer in Metallurgical Analysis', *Institute of Chemistry Monographs*, 1941 and 1942.
13 Vaughan and Whalley, 'A New Scheme for the Microchemical Analysis of Ferrous Alloys', *J. Iron & Steel Inst.*, 1947. **155.** 535.
14 Townend and Whalley, *Metallurgia*, June, 1947. **36.** 104.
15 Phillips and Holton, *Metallurgia*, August, 1948. **38.**
16 Ingram, *Metallurgia*, 1945. **32.** 137–40, 237–9.
17 Belcher and Spooner, *Iron and Coal Trades Review*, 1944. **146.** 99, 134.
18 Beet and Belcher, *Fuel*, 1938. **17.** 175.
19 Belcher, Ibid. **20.** 185.
20 Lindsey, *Analyst*, 1948. **73.** 67–73.
21 Ibid, 1948. **73.** 99.
22 Miller and Curie, Ibid, September, 1950. **75.** 467–70.
23 Ibid., 471–3.
24 Linstead, *Nature*, 1948. **162.** 691.
25 Barker, Convey and Oldfield, 'The Application of Spectrographic Methods to the Analysis of Segregates', *J. Iron and Steel Inst.*, 1941. **11.** 183.
26 Barker, Ibid, 1939. **No. 1.** 211.
27 Gatterer, *Spectrochim Acta*, 1948. **3.** 214–32.
28 von Ardenne and Bernhard, Reproduced in B.I.O.S. Final Report, No. 1606, *Progress in Microchemistry in Germany*, Appendix 'E', London H.M. Stationery Office, 1948.

[29] Ingram, 'Microchemical Laboratory Design and Equipment', *Metallurgia*, 1947. **38.** 351–4.
[30] Burton, 'Methods of Microfiltration for Quantitative Analysis', *Metallurgia*, 1945. **32.** 285–8.
[31] Wyatt, 'Micro-Filtration—A Review', *Analyst*. **71.** 122–9.
[32] Masters, 'Apparatus in Microvolumetric Analysis', *Chem. Age*, 1943. **48.** 439–42.
[33] Winteringham, *Analyst*, May, 1945. **70.** 173.
[34] Stock and Fill, 'Microseparatory Device', *Metallurgia*, 1945. **33.** 44.
[35] 'Miscellaneous Microchemical Devices', Ibid, **33.** 323–4; 1947. **35.** 172; 1947. **36.** 225–6.
[36] Stock, 'New Aids to Microchemistry', *Chem. Age*, April 29th, 1950. 605–9.

APPENDIX

1. *Standard solutions*
2. *Atomic weights*
3. *Gravimetric factors*
4. *The use and care of platinum apparatus*

SECTION 1

STANDARD SOLUTIONS FOR VOLUMETRIC ANALYSIS

The following notes are intended to provide general guidance. The methods of standardization selected are straightforward and may be relied upon to be of adequate accuracy for analysis. While much of the information refers to 0·1 N solutions, it is principally a matter of individual preference whether the solutions are adjusted to have a definite normality or whether each has its own factor. In some circumstances the analyst will prefer to standardize stronger solutions (e.g. approximately 1·0 N) and prepare weaker solutions by accurate dilution.

Standardization, strictly speaking, involves reference of the solution either to a primary standard material or to a derived sub-standard.

The standard material (e.g. metallic silver) is a substance which can be prepared and maintained in a state of great and known purity.

A derived sub-standard is usually a material of inherently suitable qualities which has been assessed in terms of a primary standard by a method employing few intermediate steps.

In the metallurgical analytical laboratory however, it is often more convenient to assess reagents against 'standard' samples of material similar to the samples with which the reagent is to be used. Such samples (e.g. British Chemical Standards and Bureau of Standards of Analysed Samples) are usually issued accompanied by a certificate of analysis which is based on the results of work independently conducted by several laboratories.

Hydrochloric Acid, 0·1 N = 3·647 g of HCl per litre

Dilute 9 ml. of analytical reagent grade concentrated acid to 1 litre.

(*a*) Standardize with respect to pure anhydrous sodium carbonate which has been dried at 260° C., using screened methyl orange as indicator.

1 ml. 0·1 N acid = 0·0053 g Na_2CO_3

(*b*) Standardize against pure borax which is recrystallized at a temperature below 55° C. washed with alcohol and ether, and allowed to stand, spread into a thin layer, at room temperature overnight. Use screened methyl orange as indicator.

1 ml. 0·1 N acid = 0·01907 g of $Na_2B_4O_7 . 10H_2O$

Nitric Acid, 0·1 N = 6·302 g of HNO_3 per litre

Dilute 6·5 ml. of pure concentrated acid (sp. gr. 1·42) to 1 litre. Standardize against standard sodium hydroxide solution (using phenolphthalein as indicator) when the acid is for the volumetric determination of phosphorus.

1 ml. 0·1 N acid = 0·004 g NaOH

Sulphuric Acid, 0·1 N = 4·904 g of H_2SO_4 per litre

Dilute 2·7 ml. of pure concentrated acid to 1 litre. Standardize against pure anhydrous sodium carbonate, dried at 260° C., using screened methy lorange as indicator.

1 ml. 0·1 N acid = 0·0053 g Na_2CO_3

Sodium Hydroxide, 0·1 N = 4·001 g of NaOH per litre

Dissolve the pure sodium hydroxide in cold recently boiled distilled water, add 0·1 g of barium hydroxide (to precipitate any carbonate present), filter into

a litre flask and dilute to the correct volume with cold boiled distilled water.

(*a*) For use in titrating strong acids, standardize against standard hydrochloric acid, using screened methyl orange as indicator.

(*b*) For use with weak acids, standardize against pure potassium hydrogen phthalate, dried at 120° C., using phenolphthalein as indicator.

1 ml. 0·1 N NaOH = 0·02041 g $KHC_8H_4O_4$
= 0·000135 g P
= 0·003647 g HCl
= 0·006302 g HNO_3

Iodine, 0·1 N = 12·69 g of I_2 per litre

Shake 12·7 g of pure iodine with 25 g of pure potassium iodide and 150 ml. of water. When all the iodine is dissolved, dilute to 1 litre.

The normality of this reagent is usually determined, just prior to use, by one of the following methods ; since iodine is slowly lost from the solution and the concentration falls with time of keeping.

(*a*) Direct titration with standard sodium thiosulphate solution using starch solution as indicator.

(*b*) Using pure tin (see under 'Tin').

but more usually

(*c*) Titration against standard sodium arsenite solution.

For this, dissolve 0·2 g of pure arsenious oxide in about 10 ml. of 0·1 N NaOH solution by gentle warming. When dissolved, dilute to about 100 ml. with cold water, add three drops of phenolphthalein as indicator and make slightly acid with HCl. Cool to room temperature, add 5–10 g of sodium bicarbonate, 3 ml. of starch solution and titrate with the iodine solution to a permanent blue colour.

The weight of As_2O_3 used × 1·199 = equivalent weight of tin
The weight of As_2O_3 used × 0·7577 = equivalent weight of arsenic
then : 1 ml. 0·1 N iodine = 0·003747 g As
= 0·005935 g Sn

Potassium Dichromate, 0·1 N = 4·904 g of $K_2Cr_2O_7$ per litre

Dry the pure salt at 140° C., weigh off 4·904 g, dissolve in water and make up to 1 litre. This chemical is usually sufficiently pure (use 'Analytical Reagent' grade) to be used as an absolute standard.

If standardization is desired use pure iron wire, dissolve, reduce and titrate exactly as described under 'Iron'.

1 ml. 0·1 N $K_2Cr_2O_7$ = 0·005584 g Fe

Potassium Permanganate, 0·1 N = 3·161 g of $KMnO_4$ per litre

Dissolve 3·2 g of pure reagent in 1 litre of distilled water, filter if necessary through glass wool and keep in a dark glass-stoppered bottle.

Standardize against pure sodium oxalate dried at 120° C. (or oxalic acid) by dissolving 0·3 g of sodium oxalate in about 200 ml. of 5% sulphuric acid solution, warming to 70° C. and titrating with the potassium permanganate solution to a faint permanent pink end-point.

1 ml. 0·1 N $KMnO_4$ = 0·00609 g Sb
= 0·00558 g Fe
= 0·00110 g Mn (Bismuthate method)
= 0·00165 g Mn (Volhard method)
= 0·00173 g Cr (Iron reduction method)
= 0·00509 g V (Iron or SO_2 reduction method)
= 0·00280 g CaO

Silver Nitrate, 0·1 N = 16·99 g of $AgNO_3$ per litre
or 10·788 g of pure silver per litre

Dry pure silver nitrate at 150° C., weigh out 16·99 g, dissolve in distilled water and dilute to 1 litre. Alternatively dissolve 10·788 g of the pure metal in the minimum 50% nitric acid, gently evaporate most of the acid, dilute with water and when cold, make up to 1 litre. Store in a dark glass-stoppered bottle.

If standardization is desired, *either:*

(*a*) Titrate against solutions containing known weights of pure sodium chloride dried at 300° C.

or

(*b*) Precipitate silver chloride from a known volume of the silver nitrate solution, by means of hydrochloric acid. The precipitate is collected on a tared Gooch crucible, washed with 1% nitric acid and finally water. Dry at 105° C. to constant weight.

1 ml. 0·1 N $AgNO_3$ = 0·005845 g NaCl
= 0·003546 g Cl
= 0·007612 g NH_4CNS
= 0·009717 g KCNS

Sodium Arsenite, 0·1 N = 4·946 g of As_2O_3 per litre

Dissolve the above weight of pure crystalline arsenious oxide in 40 ml. of N sodium hydroxide. Add about 40 ml. of N hydrochloric or sulphuric acid so that the solution is neutral to litmus, and dilute to 1 litre.

Sodium Thiosulphate, 0·1 N = 24·82 g of $Na_2S_2O_3 . 5H_2O$ per litre

Dissolve about 24·9 g of the pure salt in water and dilute to 1 litre. It is preferable to use boiled, cooled distilled water. Slow decomposition of the dissolved salt may be caused by traces of acid (including CO_2) and by bacteria. The solution may be kept alkaline and sterile by adding about 0·1 g of sodium carbonate or 2 g of borax per litre. An alkaline solution is sometimes inconvenient and it may be preferred to preserve the solution by adding a crystal of phenol or a few drops of chloroform and using a rubber-stoppered bottle.

Standardize by one of the following methods :

(*a*) Titration of the iodine liberated from potassium iodide by a known weight of cupric salts—see under 'Copper'.

(*b*) To a solution containing about 2 g KI dissolved in 2% H_2SO_4, add a known volume (25 ml.) of standard 0·1 N $KMnO_4$. This will displace an equivalent volume of 0·1 N iodine solution which is titrated directly with the sodium thiosulphate solution using starch solution as indicator.

1 ml. 0·1 N $Na_2S_2O_3$ = 0·006357 g Cu
= 0·003161 g $KMnO_4$
= 0 004904 g $K_2Cr_2O_7$

Ammonium Molybdate, 4·26 g $(NH_4)_6 Mo_7O_{24} . 4H_2O$ per litre

1 ml. = 0·005 g Pb

Dissolve the above quantity in cold distilled water and standardize on pure lead foil (chemically pure) by dissolving 0·2 g of lead in 5 ml. 30% HNO_3, evaporate almost to dryness, dissolve in 30 ml. water, add 5 ml. conc. H_2SO_4, bring to the boil, cool, filter off $PbSO_4$, dissolve in ammonium acetate and titrate hot with ammonium molybdate solution exactly as described under 'Lead'.

Ferrous Ammonium Sulphate, 0·1 N

39·2 g . $FeSO_4$ $(NH_4)_2SO_4$. $6H_2O$ per litre

Dissolve the crystals in cold 5% H_2SO_4 solution to the required volume. This solution in theory should be exactly equivalent to the standard 0·1 N $KMnO_4$ solution, but as the crystals deteriorate with age, the solution loses strength and should be made up slightly stronger than the theoretical amount (e.g. 39·5 g of the salt per litre) and standardized against $KMnO_4$ immediately before use.

Potassium Ferrocyanide, 21·54 g $K_4Fe(CN)_6$. $3H_2O$ per litre

1 ml. = 0·005 g Zn

It is usually more convenient to make up the above potassium ferrocyanide solution to contain *also* 0·3 g $K_3Fe(CN)_6$ per litre as this solution will then be suitable for use with both external and internal indicators. Standardize on 0·25 g of chemically pure Zn by dissolving the metal in 10–15 ml. conc. HCl, diluting with water to 50 ml. and adjusting the acidity (using HCl and NH_4OH with litmus indicator) to give a total acidity of 1% when the final solution has been diluted to 250 ml. with hot water (i.e. 2–3 ml. conc. HCl present).

Titrate hot using internal or external indicator exactly as described under 'Zinc'.

INDICATOR SOLUTIONS

Ammonium Molybdate
Use a 2% aqueous solution.

Iron Alum (ferric ammonium sulphate)
Make a 10% aqueous solution and add sufficient nitric acid to bleach the brown colour and prevent hydrolysis.

Methyl Orange
A 0·1% solution in distilled water.

Methyl Red
A 0·2% solution in ethyl alcohol.

Phenolphthalein
0·5 g is dissolved in 50 ml. ethyl alcohol and diluted with water to 100 ml.

Potassium Chromate
A 5% solution in distilled water.

Potassium Ferricyanide
Use a freshly prepared 1% aqueous solution.

Starch
Mix 0·5–1 g of soluble starch (e.g. Lintner's) into a smooth paste with 10 ml. cold distilled water. Add the paste to 200–300 ml. of boiling distilled water, boil for a moment and use cold.

The addition of 0·5 g of salicylic acid or a few drops of chloroform or a crystal of phenol delays the formation of bacterial 'slime'.

Tannic Acid
Use a 1% aqueous solution freshly prepared.

Uranium Acetate or Nitrate
15% aqueous solutions.

SPECIAL REAGENTS

Ammonium Nitro-Molybdate (for Phosphorus)
Mix 100 g of molybdic acid (MoO_3) into a paste with 265 ml. of water, add 155 ml. of conc. NH_4OH and stir until all dissolved. To this solution stir in 66 ml. conc. HNO_3 and allow to stand 1 hour.
Make a second solution consisting of 395 ml. conc. HNO_3 and 1100 ml. water and pour the first solution into the second with constant stirring.
Stand 24 hours before use.

Magnesia Mixture (for Arsenic and Phosphorus)
Dissolve 260 g $MgCl_2 . 6H_2O$ and 200 g NH_4Cl in 750 ml. of warm water. Add NH_4OH until just alkaline, stand 1 hour and filter. To the filtrate add sufficient HCl until just acid to litmus paper. Dilute to 1 litre.

Standard Titanium Sulphate Solution (for Colorimetric Estimation)
(*a*) Dissolve 7·40 g potassium titanium oxalate in 50 ml. water, add 40 ml. conc. H_2SO_4 and evaporate just to fumes. Cool, dilute with 200 ml. water and warm to dissolve. Filter, wash with 10% H_2SO_4 and dilute filtrate to 1 litre with 10% H_2SO_4.

1 ml. = 0·001 g Ti

(*b*) Fuse 0·1 g of pure TiO_2 in a silica crucible with 5 g of potassium bisulphate taking care to prevent loss from spattering. Leach the melt and wash the crucible with 10% H_2SO_4 and dilute to 1 litre with 10% H_2SO_4:

1 ml. = 0·0001 g TiO_2
= 0·00006 g Ti

Standard Manganese Solution (for Colorimetric Estimation)
Dissolve 0·2877 g of pure $KMnO_4$ in distilled water and dilute to 1 litre. 1 ml. contains 0·0001 g Mn.

Standard Chromium Solution
Dissolve 0·2828 g of pure $K_2Cr_2O_7$ in distilled water and dilute to 1 litre.

1 ml. contains 0·0001 g Cr

SECTION 2

INTERNATIONAL ATOMIC WEIGHTS, 1949

[Reprinted from 15th Report of the Commission on Atomic Weights of the International Union of Pure and Applied Chemistry, and the Journal of the Chemical Society, 1951, p. 1.]

	Symbol	Atomic number	Atomic weight*
Actinium	Ac	89	227
Aluminium	Al	13	26·97
Americium	Am	95	[241]
Antimony	Sb	51	121·76
Argon	A	18	39·944
Arsenic	As	33	74·91
Astatine	At	85	[210]
Barium	Ba	56	137·36
Beryllium	Be	4	9·013
Bismuth	Bi	83	209·00
Boron	B	5	10·82
Bromine	Br	35	79·916
Cadmium	Cd	48	112·41
Calcium	Ca	20	40·08
Carbon	C	6	12·010
Cerium	Ce	58	140·13
Caesium	Cs	55	132·91
Chlorine	Cl	17	35·457
Chromium	Cr	24	52·01
Cobalt	Co	27	58·94
Copper	Cu	29	63·54
Curium	Cm	96	[242]
Dysprosium	Dy	66	162·46
Erbium	Er	68	167·2
Europium	Eu	63	152·0
Fluorine	F	9	19·00
Francium	Fr	87	[223]
Gadolinium	Gd	64	156·9
Gallium	Ga	31	69·72
Germanium	Ge	32	72·60
Gold	Au	79	197·2
Hafnium	Hf	72	178·6
Helium	He	2	4·003
Holmium	Ho	67	164·94
Hydrogen	H	1	1·0081
Indium	In	49	114·76
Iodine	I	53	126·92
Iridium	Ir	77	193·1
Iron	Fe	26	55·85
Krypton	Kr	36	83·7
Lanthanum	La	57	138·92
Lead	Pb	82	207·21

* A value given in brackets denotes the mass number of the most stable known isotope.

	Symbol	Atomic number	Atomic weight*
Lithium	Li	3	6·940
Lutetium	Lu	71	174·99
Magnesium	Mg	12	24·32
Manganese	Mn	25	54·93
Mercury	Hg	80	200·61
Molybdenum	Mo	42	95·95
Neodymium	Nd	60	144·27
Neptunium	Np	93	[237]
Neon	Ne	10	20·183
Nickel	Ni	28	58·69
Niobium	Nb	41	92·91
Nitrogen	N	7	14·008
Osmium	Os	76	190·2
Oxygen	O	8	16·0000
Palladium	Pd	46	106·7
Phosphorus	P	15	30·98
Platinum	Pt	78	195·23
Plutonium	Pu	94	[239]
Polonium	Po	84	210
Potassium	K	19	39·096
Praseodymium	Pr	59	140·92
Promethium	Pm	61	[147]
Protactinium	Pa	91	231
Radium	Ra	88	226·05
Radon	Rn	86	222
Rhenium	Re	75	186·31
Rhodium	Rh	45	102·91
Rubidium	Rb	37	85·48
Ruthenium	Ru	44	101·7
Samarium	Sm	62	150·43
Scandium	Sc	21	45·10
Selenium	Se	34	78·96
Silicon	Si	14	28·06
Silver	Ag	47	107·880
Sodium	Na	11	22·997
Strontium	Sr	38	87·63
Sulphur	S	16	32·066
Tantalum	Ta	73	180·88
Technetium	Tc	43	[99]
Tellurium	Te	52	127·61
Terbium	Tb	65	159·2
Thallium	Tl	81	204·39
Thorium	Th	90	232·12
Thulium	Tm	69	169·4
Tin	Sn	50	118·70
Titanium	Ti	22	47·90
Tungsten	W	74	183·92
Uranium	U	92	238·07
Vanadium	V	23	50·95
Xenon	Xe	54	131·3
Ytterbium	Yb	70	173·04
Yttrium	Y	39	88·92
Zinc	Zn	30	65·38
Zirconium	Zr	40	91·22

* A value given in brackets denotes the mass number of the most stable known isotope.

GRAVIMETRIC FACTORS

Determined	Required	Factor
ALUMINIUM		
Al_2O_3	Al	0·5291
$AlPO_4$	Al	0·2211
$Al(C_9H_6ON)_3$	Al	0·0587
AMMONIUM		
NH_4Cl	N	0·2619
ANTIMONY		
Sb_2O_4	Sb	0·7919
Sb_2S_3	Sb	0·7169
Sb_2S_5	Sb	0·6030
ARSENIC		
As_2S_3	As	0·6091
$Mg_2As_2O_7$	As	0·4826
As_2S_5	As	0·4832
BARIUM		
$BaCrO_4$	Ba	0·5421
$BaSO_4$	Ba	0·5885
BERYLLIUM		
BeO	Be	0·3605
BISMUTH		
Bi_2O_3	Bi	0·8970
BiOCl	Bi	0·8024
CADMIUM		
CdO	Cd	0·8754
CdS	Cd	0·7781
CALCIUM		
CaO	Ca	0·7147
CARBON		
CO_2	C	0·2727
CHLORINE		
AgCl	Cl	0·2474
KCl	Cl	0·4756
NaCl	Cl	0·6066
CHROMIUM		
$BaCrO_4$	Cr	0·2053
$PbCrO_4$	Cr	0·1609
Cr_2O_3	Cr	0·6843
K_2CrO_4	CrO_3	0·5150
$K_2Cr_2O_7$	Cr	0·3536
COBALT		
CoO	Co	0·7865
Co_3O_4	Co	0·7342
COLUMBIUM (NIOBIUM)		
Cb_2O_5	Cb	0·7000
COPPER		
CuO	Cu	0·7989
Cu_2O	Cu	0·8882
Cu_2S	Cu	0·7986
IRON		
FeO	Fe	0·7773
Fe_2O_3	Fe	0·6994
$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	Fe	0·1424
LEAD		
$PbCrO_4$	Pb	0·6411
PbO	Pb	0·9283
$PbSO_4$	Pb	0·6833
$PbMoO_4$	Pb	0·5643
MAGNESIUM		
MgO	Mg	0·6032
$Mg_2P_2O_7$	Mg	0·2184
MANGANESE		
MnO	Mn	0·7744
MnO_2	Mn	0·6319
Mn_2O_3	Mn	0·6959
$KMnO_4$	Mn	0·3476
Mn_3O_4	Mn	0·7203
MOLYBDENUM		
MoO_3	Mo	0·6665
MoS_3	Mo	0·4995
$PbMoO_4$	Mo	0·2613
NICKEL		
$Ni(C_4H_7N_2O_2)_2$	Ni	0·2032
NiO	Ni	0·7858
NITROGEN		
NH_4Cl	N	0·2619
PHOSPHORUS		
P_2O_5	P	0·4368
$AlPO_4$	P_2O_5	0·5822
$Mg_2P_2O_7$	P	0·2786
$(NH_4)_3PO_4 \cdot 12MoO_3$	P	0·0165
POTASSIUM		
KCl	K	0·5244
K_2O	K	0·8302
K_2PtCl_6	K	0·1608
SELENIUM		
H_2SeO_4	Se	0·5454

INDEX

INDEX TO DIAGRAMS AND PLATES

Fig. No.		*Page*
1.	Methyl Borate Distillation Apparatus	71
2.	Apparatus for Conversion of Methyl Borate to Boric Acid	73
3.	Distillation of Nitrogen as Ammonia	185
4.	Apparatus for Determination of Arsenic in Commercial Zinc (Gutzeit Method)	308
5.	Distillation Flask and Absorption Train for Determination of Osmium (Gilchrist and Wichers method)	395
6.	Combustion Apparatus for Total Carbon in Steel	418
7.	Complete Combustion and Absorption Train for Strohlein Apparatus	*facing* 419
8.	G and T Electro-Chemical Analysis Apparatus. Single-unit Model	*facing* 578
9.	Mercury Cathode	580
10.	Cambridge Titration Apparatus (Potentiometric pattern)	582
11.	The Spekker Absorptiometer, Model H760	*facing* 586
12.	Simplified Diagram of Spekker Absorptiometer optical system and photocell circuit	586
13.	Unicam SP500 Visible and Ultraviolet Quartz Spectrophotometer	*facing* 586
14.	Comparison of Absorption Curves using the Spectrophotometer	591
15.	Polarogram showing Half-wave potential	592
16.	Cambridge Polarograph: Photographic Type	*facing* 593
17.	Diagrams showing effect of counter-current on the Polarogram	594
18.	Chart of Half-wave Potentials	596

INDEX TO TABLES

Table		*Page*
I.	Typical Applications of Whatman Papers	23
II.	Comparative Speeds of Whatman Papers	23
III.	Pyrex Glass Porous Plates	24
IV.	Treatment of Iridosmine (Osmiridium)	398
V.	Separation of Platinium Metals in Ores	399
VI.	Quantitative Separation of Metals of Platinum Group (for Ores, Sweeps, Residues, etc.)	400
VII.	Summary of Separation of Metals of Platinum Group	404
VIII.	Some Typical Analyses of Steel and Cast Irons	406 and 407
IX.	The Suitability of Coals for Industrial Purposes	572
X.	Scales of working for Microchemical Analysis	624
XI	Microchemical Methods available for Steel Analysis	627

INDEX

	Page
ABSORPTIOMETERS	585–589
Absorptiometry	583–590
'Acid' Open-Hearth Slag, analysis of	523
Alkalis, estimation of, in aluminium ore	497
blast furnace slag	521–523
ceramics containing silicon carbide	549
copper slag	517
ironstones	508–509
refractories	534–535
Alloys, sampling of	9
Alumina, estimation of, in 'Acid' Open-Hearth slag	523
aluminium ore	497
'Basic' Open-Hearth slag	524
ceramics containing silicon carbide	549
chrome brick	547
chrome-magnesite	544–545
clays	536–540
dolomite	545
French chalk	552
lead slag	525
limestones	545
magnesite	546
refractories	532, 541
Aluminium, confirmatory tests for	28
determination of, colorimetrically	52–53
gravimetrically	46–51
volumetrically	51–52
estimation of, in aluminium (commercial metal)	276–283
aluminium (super-purity)	283–285
aluminium bronze	365–366
blast furnace slag	518
brass, etc.	370–371
calcium-hardened lead-base bearing metals	381
cast irons	410–412
copper ore	498
copper slag	516
iron alloys	413–415
iron ores	502–503
magnesium (commercial metal)	349–350
magnesium alloys	350–351
manganese ore	512
nickel alloys	470–471
steels	410–412
zinc (commercial metal)	311–312
zinc-base alloys	383
zinc ores	514
occurrence of	45
Aluminium Alloys, analysis of	323–348
bibliography of	353–355
Aluminium Ore, analysis of	497
Amperometric Titrations	581–582
Antifriction Metals, analysis of	372–382

	Page
Antimony, analysis of, commercial metal	285–286
confirmatory tests for	28
determination of, volumetrically	53–55
estimation of, in antimony metal	285
bronzes	363–364
calcium-hardened lead-base bearing metals	380–381
Gunmetal	363–364
lead (pigs)	294
phosphor-bronzes	363–364
tin (ingots)	302–303
White metals, etc	372–373, 376
White metal drosses	380
occurrence of	53
separation of, in lead (pigs)	293
lead ore	511
Aqua Regia, as solvent	276
Arc Discharge	602–605
Arsenic, confirmatory tests, for	28
determination of, colorimetrically	55
gravimetrically	56
volumetrically	56–57
estimation of, in antimony metal	286
coal and coke	567
copper (pure metal)	298–290
copper slag	516
manganese ore	513–514
steels	409–410
tin (ingots)	303–304
tin slag	527
White metals, etc.	378
zinc (commercial metal)	306–309
occurrence of	55
Asbestos, as filter	24
Ash, analysis of, from coal and coke	567
estimation of, in coal and coke	557–558
Atomic Weights, Table of, *see* Appendix	640–641
Barium, confirmatory tests for	28
determination of, gravimetrically	58–59
estimation of, in lead slag	525
occurrence of	57
Barium Oxide, estimation of, in manganese ore	511–512
'Basic' Open Hearth Slag, analysis of	524
Basic Refractories, analysis of	541–547
Bauxite, analysis of	497
Bearing metals, analysis of	372–382
Beryllium, confirmatory tests for	28
determination of, colorimetrically	63–64
volumetrically	60–63
occurrence of	60
Bismuth, confirmatory tests for	29
determination of, colorimetrically	68–70
gravimetrically	65–67
volumetrically	67–68
estimation of, in copper (pure metal)	287–288
lead (pigs)	294–295
tin (ingots)	298–299
occurrence of	64
separation of, in lead (pigs)	293

	Page
Blende, analysis of	514–515
Boron, determination of, colorimetrically	74
gravimetrically	70–72
volumetrically	72–74
occurrence of	70
Bullion Bars, analysis of	397–405
CADMIUM, confirmatory tests for	29
determination of, gravimetrically	78–79
volumetrically	79–81
estimation of, in copper alloys (polarographic)	597–198
copper-cadmium	371–372
tin (ingots)	301–302
zinc (commercial metal)	313–315
zinc-base alloys	384–486
White metals, etc.	374, 379
occurrence of	78
Calcination, total, in iron ores	506
Calcium, confirmatory tests for	29
determination of, gravimetrically	78–79
volumetrically	79–81
estimation of, in calcium-hardened lead-base bearing metals	374, 381–382
copper ore	499
occurrence of	78
Calculators, for spectrographic analysis	620
Calorific Value, of fuel	567–568
Cambridge Polarograph	593–594
Carbon, determination of, colorimetrically	84–85
gravimetrically	81–83
volumetrically	83–84
estimation of, in blast furnace flue dust and sinter (as coke)	509
cast irons (as graphite)	416–417
coal and coke	564–566
ferro-alloys	483–485
iron (as total C)	417–421
nickel (commercial metal)	322
pig iron (as graphite)	416–417
silicon carbide (as free C)	549
steel (by colour)	415–416
steel (as total C)	417–421
Stellite	482
occurrence of	81
Carbon Dioxide, estimation of, in dolomite and limestone	545
Carbonate, estimation of, in coal and coke	566
Cassiterite, analysis of	512–514
Cast irons, scheme for analysis of	408–409
Caustic Soda, as solvent	276
Cerium, confirmatory tests for	29
determination of, colorimetrically	89
gravimetrically	86–88
occurrence of	86
Ceramic Materials containing Silicon Carbide, analysis of	548
Chloride, determination of	582–583
Chlorine, estimation of, in coal and coke	564
Chromium, confirmatory tests for	30
determination of, colorimetrically	95–96
gravimetrically	89
volumetrically	89–95

	Page
Chromium, estimation of, in aluminium alloys	345–347
chrome brick	548
ferrochromium	485
steels	423–425
Stellite	480
occurrence of	88
Chromium Oxide, estimation of, in 'Basic' Open-Hearth slag	524
Chrome-magnesite	545
lead slag	525
Chrome Brick, analysis of	547–548
Chrome-Magnesite, analysis of	544–545
Coal, analysis of	553–573
bibliography of	573–574
composition of, for industrial purposes	572–573
properties of, correlation with analysis	571
Cobalt, confirmatory tests for	30
determination of, colorimetrically	99–100
electrolytically	100–101
gravimetrically	97–98
volumetrically	98–99
estimation of, in copper ore	498–499
nickel (commercial metal)	318–319
steel	421–423
Stellite	482
tin (ingots)	300
occurrence of	96
Coke, *see* Coal.	
Colorimeters	585
Colorimetry	583–590
Columbium, *see* Niobium.	
Combined Water, estimation of, in iron ores	509–510
Conductometric Titrations	581
Copper, analysis of, pure metal	287–292
confirmatory tests for	30
determination of, colorimetrically	112–113
electrolytically	113–114
gravimetrically	105–106
photometrically	113
volumetrically	107–112
estimation of, in aluminium (commercial metal)	277–279
aluminium (super-purity)	283
aluminium alloys	324–328
brass, etc.	364–365
bronzes	358–359
cast iron	433
copper-base alloys	357–358
copper ore	498
copper slag	516
Gunmetal	358–359
lead (pigs)	295
lead ore	510
lead slag	525
magnesium (commercial metal)	349
mild steel	433
nickel (commercial metal)	321
phosphor-bronzes	358–359
steel	430–432
tin (ingots)	296–297
tin ore	513
tin slag	526

	Page
Copper, estimation of, in White metal, etc.	373, 375–376, 379
zinc (commercial metal)	315–317
zinc-base alloys	383
occurrence of	104
sampling of	287
separation of, in lead (pigs)	293
Copper-base Alloys, analysis of, commercial grades	356–372
Copper Ore, analysis of	498–499
Copper Slag, analysis of	516–517
Corundum, analysis of	541
Cupels, porosity of	550
Cuprous Oxide, estimation of, in pure copper	291–292
Dolomite, analysis of	545–546
Dry Tests, for metals	25–27
Durain, estimation of, in coal	570–571
Electrometic Titrations	581–583
Electrolysis	577–581
Elements, selected methods for determination of	45–271
Excitation, of spectrum	612
Ferric Oxide, estimation of, in aluminium ore	497
ceramics containing silicon carbide	549
chrome-magnesite	544
clays	537–541
copper slag	516
French chalk	552
magnesite	546
refractories	533, 541–542
zinc ores	514
Zirconia	542–543
Ferro Alloys, analysis of	482–488
Filters, types of	22–24
Firebricks, porosity of	550
French Chalk, analysis of	552
Fusain, estimation of, in coal	570–571
Fused Alumina, analysis of	541
Fusion	13–15, 276
Fusion Temperature, of ash from coal	569–570
Galena, analysis of	510–511
Gallium, confirmatory tests for	30
determination of, electrolytically	117
gravimetrically	115–117
occurrence of	115
Germanium, confirmatory tests for	31
determination of, gravimetrically	118–119
occurrence of	117
Glucinum, *see* Beryllium.	
Gold, confirmatory tests for	31
determination of, colorimetrically	131
Fire Assaying	120–129
gravimetrically	129–131
estimation of, in bullion bars	397–405
lead slag	526
standard alloys	397–405
occurrence of	119
properties of	120

	Page
Graphite, estimation of, in cast iron	416–417
ferro alloys	483
pig iron	416–417
Gravimetric Factors, Table of, *see* Appendix	642–643
HYDROCHLORIC Acid, as solvent	275
Hydrogen, estimation of, in coal and coke	564–566
IGNITION, loss on, in aluminium ore	497
dolomite	545
French chalk	552
limestone	545
refractories	531
Iron, confirmatory tests for	32
determination of, colorimetrically	146–147
gravimetrically	135–138
volumetrically	138–146
estimation of, in 'Acid' Open-Hearth slag	523
aluminium (commercial metal)	279
aluminium (super-purity)	284
aluminium alloys	335–337
antimony metal	286
'Basic' Open-Hearth slag	524
brass, etc.	367
bronzes	364
ceramics	550–551
chrome brick	547
copper (pure metal)	287
copper ore	498
Gunmetal	364
iron ores (as ferrous iron)	501
iron ores (as total iron)	500–501
lead ore	511
magnesium (commercial metal)	349–350
manganese ore	512
nickel (commercial metal)	319–320
phosphor-bronzes	364
silicon carbide	549
Stellite	481–482
tin (ingots)	299–300
tin slag	527
titanium alloys	488
White metals, etc.	374, 377–379
zinc (commercial metal)	309–310
zinc-base alloys	383
occurrence of	134
Irons, analysis of	406–482
Iron Ores, analysis of	499–510
Iron Oxide, estimation of, in blast furnace slag	521
dolomite	545
lead slag	525
limestone	545
tin ore	513
Iron slags, analysis of	517–523
JUDD Lewis Comparator	607
LEAD, confirmatory tests for	32
determination of, colorimetrically	154–155
Dry assaying	156–157

		Page
Lead, determination of,	electrolytically	155–156
	gravimetrically	148–150
	volumetrically	150–154
estimation of, in	aluminium (commercial metal)	282
	aluminium alloys	347–348
	antimony metal	285–286
	bronzes	362–363
	copper (pure metal)	288–289
	Gunmetal	362–363
	lead slag	524–525
	phosphor-bronzes	362–363
	steel	433–435
	tin (ingots)	297–298
	tin slag	527
	White metals, etc.	377, 379
	zinc (commercial metal)	310–311
	zinc ores	514
	zinc-base alloys	383
occurrence of		147
Lead Ores, analysis of		510–511
Lead Pigs, analysis of		292–295
Lead Slag, analysis of		524–526
Lime, analysis of		545–546
estimation of, in	'Acid' Open-Hearth slag	523
	aluminium ore	497
	'Basic' Open-Hearth slag	524
	blast furnace slag	518–519
	ceramics containing silicon carbide	549
	chrome brick	547
	chrome-magnesite	545
	copper slag	516
	dolomite	545
	French chalk	552
	iron ores	503–504
	lead ores	510
	lead slag	525
	limestone	545
	magnesite	546
	manganese ores	512
	refractories	533, 541
	zinc ores	514
Limestone, analysis of		545–546
Line Densities		615
Line Pairs		619
MAGNESIA, estimation of, in	'Acid' Open-Hearth slag	523
	aluminium ore	497
	'Basic' Open-Hearth slag	524
	blast furnace slag	519–520
	ceramics containing silicon carbide	549
	chrome brick	547
	chrome-magnesite	545
	copper slag	516–517
	dolomite	545
	French chalk	552
	iron ores	504–506
	lead slag	526
	limestone	545
	magnesite	546
	refractories	533, 541

	Page
Magnesia, estimation of, in zinc ore	514–515
Magnesite, analysis of	546–547
Magnesium, analysis of, commercial metal	348–350
confirmatory tests for	32
determination of, colorimetrically	161
gravimetrically	158–161
estimation of, in aluminium alloys	328–331
calcium-hardened lead-base bearing metals	381–382
copper ore	499
zinc-base alloys	383–384
occurrence of	157
Magnesium Alloys, analysis of	350–353
bibliography of	353–355
Manganese, confirmatory tests for	32
determination of, colorimetrically	169
gravimetrically	162–163
volumetrically	163–169
estimation of, in aluminium (commercial metal)	283
aluminium alloys	341–343
brass, etc.	367–368
bronzes	364
cast iron	435–436
copper ore	498
ferro-alloys	483
Gunmetal	364
magnesium (commercial metal)	350
magnesium alloys	353
manganese ore	512
nickel (commercial metal)	320–321
phosphor-bronzes	364
steels	435–443
Stellite	482
occurrence of	161
Manganese Ore, analysis of	511–512
Manganese Oxide, estimation of, in 'Acid' Open-Hearth slag	523
aluminium ore	497
'Basic' Open-Hearth slag	524
blast furnace slag	520
chrome-magnesite	545
iron ores	508
magnesite	546
refractories	534
zinc ores	514
Mercury, confirmatory tests for	33
determination of, electrolytically	173
gravimetrically	170
volumetrically	171–173
estimation of, in calcium-hardened lead-base bearing metals	382
occurrence of	169
Mercury Cathode Electrolysis	579–581
Metallics, samples containing, sampling of	8
Metals, classification of	41
confirmatory tests for	28–41
sampling of	9
Metal Scrap, sampling of	9
Microchemical Analysis, accommodation for	629–630
apparatus for	630–631
bibliography of	631–632
methods of	624–631

	Page
Microchemical Analysis, weighing techniques for	630
Microphotometer	607
Moisture, estimation of, in coal and coke	554–557
iron alloys	500
lead ores	510
tin ores	512
Molybdenum, confirmatory tests for	33
determination of, colorimetrically	176–177
gravimetrically	174–176
estimation of, in cast iron	445–447
ferromolybdenum	486–487
steel	443–447
occurrence of	173
NICKEL, analysis of, commercial metal	317–322
confirmatory tests for	33
determination of, gravimetrically	178–179
volumetrically	179–181
estimation of, in aluminium alloys	333–335
brass, etc.	368–369
bronzes	359
copper (pure metal)	289
copper ore	499
Gunmetal	359
nickel (commercial metal)	317–318
phosphor-bronzes	359
steel	447–451
tin (ingots)	300
White metals, etc.	379–380
occurrence of	177
Niobium, confirmatory tests for	34
determination of, gravimetrically	101–104
estimation of, in steel	425–430
occurrence of	101
Nitric Acid, as solvent	275
Nitrogen, determination of, colorimetrically	187–188
gravimetrically	182–183
volumetrically	183–187
estimation of, bibliography	453
in coal and coke	563–564
iron and steel	451–452
occurrence of	181
Non-Metallic Inclusions, estimation of, in pure copper	291
ORES, analysis of	497–515
solution of	11
Osmium, confirmatory tests for	34
estimation of, in standard alloys and bullion bars	397–405
separation of, from metals and alloys of Platinum Group	386–396
from ores	397
Oxygen, determination of, gravimetrically	189
volumetrically	189–191
estimation of, in coal and coke	566–567
steel	453
occurrence of	188
PALLADIUM, confirmatory tests for	34
determination of, colorimetrically	193
gravimetrically	191–193
estimation of, in standard alloys and bullion bars	397–405

	Page
Palladium, occurrence of	191
separation of, from metals and alloys of Platinum Group	386–396
from ores	397
Particle Size, *see* Sampling.	
Phosphorus, determination of, gravimetrically	194–198
volumetrically	198–199
estimation of, in 'Acid' Open-Hearth slag	523
'Basic' Open-Hearth slag	524
bronzes	361–362
coal and coke	567
copper (pure metal)	290–291
copper ore	498
ferro alloys	483
Gunmetal	361–362
magnesite	546–547
manganese ore	512
phosphor-bronzes	361–362
steels	455–458
occurrence of	193
Phosphorus Pentoxide, estimation of, in iron ores	507–508
Physico-Chemical Methods of Analysis	577–632
Platinum, apparatus of, use and care of, *see* Appendix	644
confirmatory tests for	35
determination of, colorimetrically	202
gravimetrically	200–202
estimation of, in standard alloys and bullion bars	397–405
occurrence of	199
separation of, from metals and alloys of Platinum Group	386–396
from ores	397
standard alloys of	402–405
Platinum Group of Metals and Alloys, analysis of	386–405
Polarographic Analysis, bibliography of	598
methods of	590–598
Porosity, of firebricks, cupels and other burnt ceramic ware	550
Potassium, confirmatory tests for	35
determination of, gravimetrically	203–207
occurrence of	202
Potassium Silicate, analysis of	551
Potentiometric Titrations	581–583
Pre-Sparking and Exposure Times	613
Precipitates, drying and ignition of	21–22
Proximate Analysis, of coal and coke	554
Pyrolusite, analysis of	511–512
QUALITATIVE Analysis	25–41
Qualitative Spectrograph Analysis	608–610
Quantitative Spectrograph Analysis, by Spark Discharge	610–621
RARE Earths, detection of, in Zirconia	542–543
Refractories, analysis of	531–552
Rhodium, confirmatory tests for	35
determination of, gravimetrically	208–209
estimation of, in standard alloys and bullion bars	397–405
occurrence of	207
separation of, from metals and alloys of Platinum Group	386–396
from ores	397
Ruthenium, confirmatory tests for	35
estimation of, in standard alloys and bullion bars	397–405
separation of, from metals and alloys of Platinum Group	386–396
from ores	397

	Page
SAMPLES, for Spectrographic Analysis	611
Microanalysis	629
Sampling, general	3–10
of aluminium (commercial metal)	276–277
ceramics containing silicon carbide	548
coal and coke	553–554
copper (pure metal)	287
lead (pigs)	292
refractories	531, 541
sand	6
tin (ingots)	296
White metals	374
zinc (commercial metal)	306
Screens, I.M.M. Standard Laboratory, table of	6
Selenium, confirmatory tests for	36
determination of, gravimetrically	210–212
volumetrically	212
estimation of, in steels	458–460
occurrence of	209
Semi-Quantitative Spectrographic Analysis	620
Separation, metals of Platinum Group	386–396
wet methods of	16–20
Silica, estimation of, in 'Acid' Open-Hearth slag	523
aluminium ore	497
'Basic' Open-Hearth slag	524
blast furnace slag	517
ceramics containing silicon carbide	548–549
chrome brick	547
chrome-magnesite	544
copper ore	498
copper slag	517
dolomite	545
French chalk	552
iron ores	501–502
lead ores	510
lead slags	525
limestone	545
magnesite	546
manganese ore	511–512
potassium silicate	551
refractories	531, 541
silicon carbide	549
sodium silicate	551
Zirconia	542
Silicon, determination of, colorimetrically	217
gravimetrically	213–217
estimation of, in aluminium (commercial metal)	279–280
aluminium (super-purity)	284–285
aluminium alloys	331–333
brass, etc.	371
ferro-alloys	483–484
magnesium (commercial metal)	349
nickel (commercial metal)	319–320
silicon carbide	549
Staybrite steels	473
steels	460–462
Stellite	481
occurrence of	213
Silicon Carbide, estimation of, in ceramics	548–549
purity of	549

	Page
Silver, analysis of, standard alloys	397–401
confirmatory tests for	36
determination of, gravimetrically	218–220
volumetrically	220–221
estimation of, in copper ore	499
lead ore	510
lead slag	526
standard alloys and bullion bars	397–405
tin (ingots)	304–305
White metals, etc.	374, 376–377
occurrence of	217
Simple Electrolysis	578–579
Sintered Glass	24
Slags, analysis of	516–527
Sodium, determination of, gravimetrically	222–225
occurrence of	221
Sodium Silicate, analysis of	551
Solution, of lead (pigs)	292
standard methods of	11–15
of tin (ingots)	296
zinc (commercial metal)	306
Solvents, for non-ferrous alloys	275
Spark Discharge	605–607
Sparking Surface	612
Specific Gravity, of copper slag	517
Spectra, evaluation of	615–619
photography of	614–615
Spectrograph	599–601, 614
Spectrophotometry	589–590
Spectroscopic Analysis, bibliography of	621–624
methods of	598–621
Spectrum, production of	601–607
Standards, for spectrographic analysis	611
Standard Solutions, for ferrous analysis	488–493
refractories	536–537
general, *see* Appendix	635–639
Standardisation of, for White Metals, etc.	372–374
Steels, methods for analysis of	409–482
schemes for analysis of	406–409
Strohlein Apparatus, for total carbon in steels	419–421
Strontium, confirmatory tests for	36
Sulphate, estimation of, in coal and coke	561–562
Sulphur, determination of, gravimetrically	220–229
volumetrically	229–230
estimation of, in 'Acid' Open-Hearth slag	523
'Basic' Open-Hearth slag	524
blast furnace slag	521
coak and coke, pyritic	561–562
coal and coke, total	559–561
copper (pure metal)	291
copper ore	498
dolomite	546
ferro-alloys	483
iron ore	506–507
lead ore	511
lead slag	526
limestone	546
manganese ore	512
nickel (commercial metal)	321–322
steels	462–466

	Page
Sulphur, estimation of, in tin (ingots)	305–306
tin ore	513
occurrence of	225
Sulphuric Acid, as solvent	275
Swelling Power, of coal	569
Talc, analysis of	552
Tantalum, confirmatory tests for	37
determination of, gravimetrically	231–232
estimation of, in steel	425–430
occurrence of	231
Tellurium, confirmatory tests for	37
determination of, gravimetrically	233–234
volumetrically	234
estimation of, in copper (pure metal)	292
steels	458–460
occurrence of	232
Thallium, confirmatory tests for	37
determination of, gravimetrically	235–236
occurrence of	234
Thorium, confirmatory tests for	38
determination of, gravimetrically	236–238
occurrence of	236
Tin, confirmatory tests for	38
determination of, dry assaying	243–244
gravimetrically	239–240
volumetrically	240–243
estimation of, in aluminium alloys	344–345
bronzes	360–361
calcium-hardened lead-base bearing metals	380–381
Gunmetal	360–361
phosphor-bronzes	360–361
steels	466
tin slag	526
White metals, etc.	373, 375
White metal drosses	380
zinc (commercial metal)	312–313
zinc-base alloys	382–383
occurrence of	238
Tin Ingots, analysis of	296–306
Tin Ore, analysis of	512–514
Tin Oxide, estimation of, in tin ore	513
Tin Slag, analysis of	526–527
Titanium, confirmatory tests for	39
determination of, colorimetrically	247–249
gravimetrically	245–247
estimation of, in aluminium (commercial metal)	280–281
aluminium alloys	343–344
ferro-titanium	487–488
nickel alloys	470
steels	467–470
Staybrite steel	473
occurrence of	244
Titanium Oxide, estimation of, in aluminium ore	497
ceramics containing silicon carbide	549
chrome-magnesite	544
clays	536–540
French chalk	552
iron ores	503

	Page
Titanium Oxide, estimation of, in refractories	532–533, 541
Zirconia	542–543
Tungsten, confirmatory tests for	39
determination of, gravimetrically	250–252
estimation of, ferro-tungsten	484
in High-Speed steels	471–472
low tungsten steels	472–473
Staybrite steels	473
Stellite	481
tungsten carbide alloys	473–474
tungsten powder	473, 484
occurrence of	249
Tungstic Acid, estimation of, in tin ores	513
URANIUM, confirmatory tests for	39
detection of, gravimetrically	254–256
volumetrically	256–257
occurrence of	252
separation of	253–254
VANADIUM, confirmatory tests for	40
determination of, colorimetrically	260–261
gravimetrically	257–258
volumetrically	259–260
estimation of, ferro-vanadium	485–486
in steels	474–477
occurrence of	257
Volatile Matter, estimation of, in coal and coke	558–559
WHATMAN Papers, application of	23
White Metals, analysis of	372–382
ZINC, analysis of commercial metal	306–317
confirmatory tests for	40
determination of, gravimetrically	262–265
volumetrically	265–267
estimation of, in aluminium (commercial metal)	281–282
aluminium alloys	337–341
brass, etc.	369–370
bronzes	359–360
copper ore	499
Gunmetal	359–360
lead (pigs)	295
lead ores	511
magnesium alloys	351–353
phosphor-bronzes	359–360
tin (ingots)	300–301
White metals, etc.	378–379
zinc ores	515
occurrence of	261
Zinc-Base Alloys, analysis of	382–386
Zinc Ores, analysis of	514–515
Zinc Oxide, estimation of, in lead slag	525
Zircon, analysis of	543
Zirconia, analysis of	541–542
Zirconium, confirmatory tests for	41
determination of, gravimetrically	270–271
estimation of, in steels	477–480
occurrence of	267
separation of	267–269