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REAGENTS FOR QUALITATIVE INORGANIC ANALYSIS

SECOND REPORT

OF THE INTERNATIONAL COMMITTEE ON NEW ANALYTICAL REACTIONS AND REAGENTS OF THE INTERNATIONAL UNION OF CHEMISTRY

REAGENTS FOR QUALITATIVE INORGANIC ANALYSIS

EDITORS :

P. E. WENGER, Geneva
R. DUCKERT, Geneva

JOINT-AUTHORS :

C. J. VAN NIEUWENBURG, Delft
J. GILLIS, Ghent

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PREFACE TO THE FRENCH EDITION

The authors of the First Report of the " International Committee on New Analytical Reactions and Reagents " indicated in what spirit the Section for Analytical Chemistry of the 9th Congress for Pure and Applied Chemistry acted, when it requested the International Union of Chemistry to establish a Committee on Analytical Reagents.

There were, even in those days, an enormous number of reagents but critical, analytical studies of any extent were not available. Matters have even been worse since. Therefore it was highly necessary that the members of the International Committee on New Analytical Reagents should shoulder the task that had been assigned to them.

The First Report (1938) contained some suggestions for future work. The work had to be done as quickly as possible, although the questions asked could not all be answered speedily.

As the table of reagents was given as completely as possible in this First Report of the Committee on Reagents, the immediate object in view, it seemed to us, was to make a selection of definite reagents and at the same time to take into account any discoveries of new reagents, as well as the numerous publications of chemical studies (1937-1943).

We were therefore compelled, in compiling the Second Report, to study particularly the reagents that can be safely used in qualitative analysis and to ignore other numerous reagents that are only of documentary value for inorganic analysis. However, we have not been able to undertake the studies mentioned in the Preface of the First Report bearing more strictly on the analytical process. That task would have been much too heavy, as the events in world politics brought any number of difficulties with them for all members of the Committee.

It seems useful to recall few decisions that have been taken in the course of the last few years.

Because the task set to the Committee on Reagents appeared to be very great, the Congress in Rome (1938) added some signatories to those of the First Report (the latter being : C. J. VAN NIEUWENBURG, president, W. BÖTTGER, F. FEIGL, A. S. KOMAROWSKY and N. STRAFFORD); this group of co-workers consisting of R. DELABY, J.V. DUBSKY, J. GILLIS, F. L. HAHN, A. KLING, P. KLINGER, K. RAST, I. WADA, P. E. WENGER and H. H. WILLARD. Some months later H. E. CROSSLEY, London and Z. KARAOGLANOW, Sofia were also nominated.

H. H. WILLARD, A. KLING and F. L. HAHN resigned shortly afterwards. The work was shared out by the President of the Committee, who created a little " Working Committee " in order to facilitate the publication of the Second Report; it comprised C. J. VAN NIEUWENBURG, president, W. BÖTTGER, F. FEIGL and N. STRAFFORD.

As F. FEIGL could not promise to lend his assistance in those difficult days, he was replaced by P. E. WENGER.

In this way four working teams were formed :

Group 1 : W. BÖTTGER; co-workers: P. KLINGER, Z. KARAOGLANOW, K. RAST and I. WADA.

Group 2 : P. E. WENGER ; co-workers : J. V. DUBSKY, F. L. HAHN and A. S. KOMAROWSKY.

Group 3 : N. STRAFFORD; co-worker : H. E. CROSSLEY.

Group 4 : C. J. VAN NIEUWENBURG; co-workers : R. DELABY, J. GILLIS, A. KLING.

However, the war was soon to deprive us of the useful cooperation of many colleagues and it became impossible to communicate with others too. The colleagues meant were W. BÖTTGER, H. E. CROSSLEY, F. L. HAHN, Z. KARAOGLANOW, P. KLINGER, K. RAST, N. STRAFFORD and I. WADA. We fully understand their difficulties, whilst we regret to be separated from such efficient co-workers.

During a reunion in Paris (1940), which took place at the request of the Secretary General of the International Union of Chemistry, a new " Working Committee " was installed : C. J. VAN NIEUWENBURG, president, J. GILLIS and P. E. WENGER, members. The work was also shared out anew, whereby the following items were taken into account : two reports received from J. V. DUBSKY and A. S.

KOMAROWSKY and some laboratory studies in hand by members of the Committee and R. DELABY.

We also wish to acknowledge, that in his investigations C. J. VAN NIEUWENBURG was assisted by Miss M. J. SMIT; J. V. DUBSKY by Dr A. OKÁČ and P. WENGER by Dr R. DUCKERT. J. GILLIS received a grant from the " Fonds National de la Recherche scientifique " of Belgium and was assisted by Lic. A. CLAEYS, Lic. M. DE RIDDER, Dr J. HOSTE, Lic. J. PELSERS, and Lic. M. WIJGAERTS.

During the same reunion in Paris the contents of the 2nd Report were definitely agreed upon by the members of the Working Committee being in unison with the Bureau of the International Union of Chemistry, as represented by its secretary, J. GERARD.

At the end of 1942 the studies of the Committee had made sufficient progress to make its president consider publishing the 2nd Report; but with a view to the prevailing circumstances he had to wait another year so that all the problems connected with the publication could be solved.

The president then asked P. WENGER to undertake its editing, care was to in which be taken to obtain the greatest possible homogenity in the wording of the various writings submitted by the members of the Committee.

We are now happy to be in a position to offer the English edition of the " Deuxième Rapport," which appeared in 1945.

We sincerely hope that in future the " Committee on New Analytical Reactions and Reagents " will be able to continue its activities in better circumstances. It will continue to criticize reagents, which are proposed in great numbers, every year; it will study any suggestions made by colleagues, when inorganic analysis will have to contend with serious problems that are always new.

Finally, the editors hereby express their gratitude towards Misses M. L. BUSSET, D. RIETH and Y. RUSCONI, who assisted in the preparation of this report.

C. J. VAN NIEUWENBURG, Delft, *president.*
J. GILLIS, Ghent, *member.*
P. E. WENGER, Geneva, *member.*
EDITORIAL :
P. E. WENGER, Geneva, *editor.*
R. DUCKERT, Geneva, *associate editor.*

PREFACE TO THE ENGLISH EDITION

Owing to the international situation, we have not been able to edit the book in English simultaneously with the French Edition. However, the reader should know that this English version is not the literal translation of the French Edition. The text has been revised and the bibliography completed. The book contains several new data about the reactions, and moreover a number of micro-photographs of crystalls, made by Dr J. HOSTE in the Laboratory of Prof. J. GILLIS are added.

We wish to express our grateful thanks to Dr JANET MATTHEWS (Basingstoke) and to Dr N. STRAFFORD (Manchester), members of the International Committee on New Analytical Reactions and Reagents of the International Union of Chemistry, for their invaluable assistance in correcting the English translation and checking its final wording.

The Editors.

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TECHNICAL INTRODUCTION

The development of analysis by spot tests, and generally speaking, of the whole of the micro- and semi-microchemical technique of qualitative inorganic analysis, is a proof of the practical interest it awakes. However, it must be observed that the very large number of reagents, which are often studied incompletely or hastely described, does not allow of a ready use of these valuable techniques of modern chemistry. There is a plethora of reagents but critical studies are lacking. Through the present Second Report of the International Committee on New Analytical Reactions and Reagents we hope to fill this gap by providing the practical chemical analyst with the means that are adequate to the tasks with which he is faced.

This report has been devised and worded especially with a view to practical analysis and this purpose, which has been constantly pursued, was the fundamental criterion when we were selecting the reagents. Consequently this work does not, for example, constitute a critical document on spot test analysis.

The data from the literature are not the only sources to which we have had recourse. A great number of the indications are original and many of them unpublished, although some short studies appeared in various periodicals [1].

The reagents proposed by us are all recommended, as we consider them to be sufficiently sensitive and selective for normal analytical requirements. They were selected from those mentioned in the First Report of the International Committee on New Analytical

(1) J. GILLIS, *Mikrochemie*, **31** (1943) 58; **31** (1944) 178.

J. V. DUBSKÝ, *Chem. Obzor*, **15** (1940) 140; J. V. DUBSKÝ and A. LANGER, *Chem. Obzor*, **13** (1938) 49, 78, 99, 123, 144 and **15** (1940) 11; J.V. DUBSKÝ and V. SINDELÁŘ, *Chem. Obzor*, **15** (1940) 34, 67; J. V. DUBSKÝ and M. NOVÁKOVÁ, *Chem. Obzor*, **15** (1940) 136.

A. OKÁČ, *Chem. Obzor*, **14** (1939) 203 and **16** (1941) 10, 27, 55.

P. E. WENGER and R. DUCKERT (assistants : Misses M.-L. BUSSET, D. RIETH and Y. RUSCONI), *Helv. Chim. Acta*, **24** (1941) 657, 889, 1143, **25** (1942) 406, 599, 699, 1110, 1547, **26** (1943) 338, 416, 1465.

Reactions and Reagents and from recent literature, consulted up to the end of June 1943. Unfortunately, the present circumstances have deprived us of many periodicals in the English tongue (England, Dominions, U.S.A., Far East).

We wish to point out that it may be desirable, when dealing with very special tasks, to have recourse to other reagents than the ones we propose (for example in cases when a very high sensitivity is required, regardless of selectivity; when traces are to be investigated; when special selectivity is required in mixtures of elements which are rather rare). The reagents proposed by us form the average type, so to speak, for every-day analysis. We think that the practical data contained in the following pages will be adequate, so that it will not be necessary, generally speaking, to refer to bibliographical sources this being a matter that takes much time and very often cannot be done at all because of lack in specialised periodicals.

The Committee decided to maintain a maximum of five reagents per element, as it did not wish to overload this report; this system nevertheless allowed us to take reagents that can be used in various techniques generally employed; tests on spot plate or on paper, electrography, analysis in test-tubes and micro-crystallography.

But this selection of reagents was difficult, as a profound study of a great number of them was required. We append the essential characteristics that ought to be possessed by a given reagent, in our judgment, in order to make us recommend its use :

Sensitivity. As high as possible; generally within the limits of dilution 10^{-4} and 10^{-6} (1 : 10^4 and 1 : 10^6). It should be noted that a reagent of very high sensitivity (10^{-8} for exemple) can only be recommended if its properties of selectivity are outstanding, lest serious errors result from it.

Selectivity. In a certain number of cases it should be as high as can be realized for an element with regard to the whole of the chemical elements and, for the majority of other cases, with regard to the ions of an analytical group.

We would observe that particular chemical properties, which allow of previous separation of some elements, or even of a single ion, may leave scope for the use of reagents of lesser selectivity. In such

cases one can only be guided by critical judgement. These observations particularly apply to amphoteric elements, which can be converted to the anionic state whilst making investigations into elements of a metallic nature.

Possibility of obtaining the reagent. The majority of reagents that we have recommended in this report are to be found in the price-lists of firms selling chemical products. Some must be synthetically prepared, usually without great difficulty. In that case we have given a concise description of the method of preparation (with bibliographical references). We are confident that these few reagents will soon be available in the market.

As we have always taken into account that the end to be attained is a strictly practical one, some reagents have been left out because they offered no sufficient guarantee of sensitivity or selectivity, or because their preparation presented serious difficulties.

Stability. We recommend reagents whose stability has been tested, except in rare cases, when the reader is duly notified. For some elements we cannot offer any reagent and in other instances we must content ourselves with those of lesser quality and await the more interesting inventions of research workers.

For each reagent we have given the following indications :

1. The valency under which the element must be found is always quoted as well as the reference number the reagent bears in the First Report of the " Committee on Reagents." The anions of elements with markedly electropositive characteristics have been classed with the cations.

2. The chemical name given is either that in common use, or accords with the nomenclature for inorganic compounds adopted by the " Committee for the Reform of Inorganic Chemical Nomenclature, 1940." (The Report appeared in *J. Chem. Soc.* (1940) 1404 and in *J. Amer. Chem. Soc.* **63** (1941) 889).

For organic compounds, we have followed as closely as possible the " Definitive Report of the International Committee on Organic Chemical Nomenclature, 1930." (*J. Chem. Soc.* (1931) 1607; *J. Amer. Chem. Soc.* **55** (1933) 3905; see also CLARENCE SMITH, Modern Chemical Nomenclature, *J. Chem. Soc.* (1936) 1067).

3. We have also indicated the names commonly used by the authors, even if they are incocent, in order to facilitate search of the literature. With regard to this, we hope that unsuitable or wrong terms still used will be abandoned, in order to give greater clarity and precision.

4. The reagents have been formulated in accordance with rules adopted by the " Committee for the Reform of Inorganic Chemical Nomenclature, 1940," as far as inorganic substances are concerned.

5. The bibliography has been summed up in one table at the end of this volume, so that the text is not impeded by foot notes which would often have been very long. References are grouped according to elements in order to facilitate the reading of the table. We have always quoted extracts of the " Chemisches Zentralblatt," " American Chemical Abstracts," as well as of the " Zeitschrift für analytische Chemie " or the " Mikrochemie," when they might be elucidating. It is obvious, that we have not quoted all the bibliographical references, but only those that may assist investigators in the carrying out of their practical analytical investigations.

6. It seemed to us to be both instructive and useful to give a brief account of the mechanism of reactions. This will help to avoid errors in cases where very complex mixtures are analysed.

We regret that in many cases the study of analytical reactions is so little advanced and we hope that the gaps, which we previously indicated, will gradually be filled through our colleagues' researches. In this field are some tasks to be undertaken, which are of as much practical as theoretical interest.

7. The technique of each test is described as clearly as possible. We have always made sure that a person, who is not initiated in the difficulties of chemical analysis, should be able to deal with the operations according to the indications as transcribed by us.

8. For each element we have tried to indicate some reagents that can be used in the various modern techniques of qualitative chemical analysis, such as : drop plate tests or " on paper," semi-microchemical analysis in test-tubes, micro-crystallography. In the latter case it is advisable to consult the micro-photographs that are of great practical value and brought together at the end of this Report. The authors acknowledge their indebtedness to Dr J. HOSTE, assistant at the

University of Ghent, who undertook the preparation of these micro-photographs.

9. The sensitivity is generally indicated by the dilution limit.

It would seem useful to recapitulate some definitions; sensitivity, according to FEIGL [1], whose notation is very widely used, can be symbolised as follows :

$$X[S]^Y$$

in which X represents the minimum quantity of the element that can be revealed with certainty (in γ) and Y the volume of the solvent (expressed in ml or cm^3). The letter S defines the analytical techniques employed during the test (A : drop plate test, B : test on filter paper). The limit of perceptibility, minimum quantity revealed (expressed in γ), should quite strictly be :

$$X[S],$$

since the sensitivity only differs from it by the indication of the volume of the solvent (Y).

The dilution limit is defined as follows, again according to FEIGL :

$$1 : \frac{\text{volume of solvent} \cdot 10^6}{\text{limit of perceptibility (in } \gamma)}$$

or

$$1 : \frac{Y \cdot 10^6}{X}$$

Because the values found are generally small, we prefer to indicate them by using negative exponents so as to simplify the script.

For example :

limit of identification : $0{,}03\ [S]$

sensitivity : $0{,}03\ [S]^{0.03}$

dilution limit : $1 : \dfrac{0{,}03 \cdot 10^6}{0{,}03}$

or $1 : 1{,}000{,}000$ or 10^{-6}.

Other example :

sensitivity : $2\ [S]^{0.03}$

dilution limit : $1 : \dfrac{0{,}03 \cdot 10^6}{2}$

(1) F. FEIGL, *Mikrochemie*, 1 (1928) 8; F. FEIGL, *Laboratory Manual of Spot Tests*, New-York, 1943.

See also : J. GILLIS and B. V. J. CUVELIER, *Ann. chim. anal. chim. applic.* (3), 22 (1940) 164; J. GILLIS, *Bull. soc. chim. France*, (1946) 177.

or 1 : 15,000.

With negative exponents :

$$1 : 1.5 \cdot 10^4 = \frac{1}{1.5} \cdot 10^{-4} = 6.67 \cdot 10^{-5} = 10^{-4.17}$$

In the Second Report we have generally expressed the sensitivity by the dilution limit and in the text we have taken the liberty to abbreviate the script, for example : sensitivity $D = 10^{-6}$, when actually we should express this quite accurately as follows : sensitivity, dilution limit $= 10^{-6}$.

In order to make it possible to calculate the identification limit (which in itself is also very interesting), we adopted standard volumes for these tests, being :

under the microscope	0.01 ml
on the drop plate	0.03 ml
on filtre paper	0.03 ml
in micro test-tube	1 ml
in macro test-tube	5 ml
in Emich tube	0.1 ml

Generally speaking, these volumes are not indicated in the text.

It can be seen from the foregoing that the identification limit is given by the volume of solvent multiplied by 10^6 and multiplied by the dilution limit or concentration limit.

10. The selectivity of a reaction has generally been studied as a function of the elements of an analytical group under consideration and rarely as a function of all the elements. This critical study has taken a long time and has been difficult task, which explains why all the cases (to date, at least) could not be thoroughly studied.

In the text the name of an element or its symbol indicates the element at its usual valency in chemical analysis, for example : iron or Fe indicates iron as its two normal cations Fe^{+2} and Fe^{+3}, but does not include the anion FeO_4^{-2}, which is much less frequent. When it was necessary to state precisely to which ionic form one should have recourse, we have done so.

Obviously sensitivity only becomes of practical importance in cases when an ion has to be detected in a mixture. Accordingly we have given the greatest possible number of indications with regard to the

disturbing action of various ions of the same analytical group. It is essential to give the proportion of the disturbing element, which we have done by adopting the following principle : the quantity of the element looked for is taken as unity.

Example : identification of the cation Ag^{+1} by metol; the elements Cu, Pb, Cd, As..., in a proportion 1 : 3,000, do not reduce the sensitivity. This expression means that the relation between Ag and each of the disturbing elements is 1: 3,000; the element to be investigated is always taken as unity.

11. We have given details about reagents to be used, which broadly speaking cannot be found in the literature, which is in many cases a source of inaccuracy and error.

At the end of each analytical group or sub-group we have given a brief analytical procedure to be followed. It goes without saying that it is a necessary preliminary to separate into such groups by the well known methods.

This Second Report is not, properly speaking, a practical treatise on analysis; we should have gone beyond our task and it would not have been so quickly completed. Accordingly it only contains brief indications concerning an analysis to be followed. However, as its first object is to define the conditions of use of sensitive and selective reagents, we could not attain that without giving a short description of the manner in which they must be used.

At first sight it might seem strange that the classical reagents are not recommended in this work. But it must be agreed that a great number of those no longer conform to the modern definition of analytical reagent, especially as regards sensitivity and selectivity. They do not entirely disappear from the field of analysis, but they must be used judiciously.

In point of fact a considerable number of these reagents have been retained. In the case of organic reagents some possibilities were found that are very interesting indeed; moreover, they have been adopted in laboratories and consequently they are no novelties in actual fact.

THE EDITORS.

DISTRIBUTION OF WORK

Group C. J. VAN NIEUWENBURG :

Hg — Cu — Pb — Bi — Cd — As — Sb — Sn — Au — Ru —Rh — Pd — Os — Ir — Pt — Al — Ti — Ca — Sr — Ba — Mg — all anions.

Group J. GILLIS :

Se—Te—Ge—Mo—W- V- Nb—Ta—Li—Na—K—Rb—Cs—NH_4^{+1}

Group P. E. WENGER :

Ag — Fe — Cr — U — Ce — rare earths — Y — Zr — Hf(Ct) — Th — Gl(Be) — Tl — Sc — Ga — In — Zn — Mn — Re — Co — Ni.

A. S. KOMAROWSKY made a preliminary study of rare earths with Ce — Th — Ga — In.

J. V. DUBSKÝ and A. OKÁČ made a preliminary study of the elements U — Zr — Hf — Gl(Be).

At the beginning of the study on each element we have mentioned the name of the group-leader who is responsible for the work.

LIST OF ABBREVIATIONS

The system of abbreviations has been considerably simplified in order to make the reading of this work easy and quick, without any previous memorizing of symbols that are only rarely used.

D = dilution limit, indicating sensitivity.
NR = new reaction, not figuring in the First Report of the " Committee on Reagents."
AN = atomic number.
AW = atomic weight.
IW = ionic weight.
MW = molecular weight.

We have adopted the system of symbols contained in the Report of the " Committee for the Reform of Inorganic Chemical Nomenclature, 1940 " [published in *J. Chem. Soc.* (1940) 1404 and in *J. Amer. Chem. Soc.* **63** (1941) 889], which differs from the one used in the First Report of the " Committee on Reagents " of the " International Union of Chemistry."

The periodicals are indicated by abbreviations that are approved by the Union and given in the " List of Periodicals " as being the abbreviations used in the " American Chemical Abstracts."

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I. CATIONS

1. SILVER

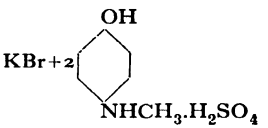
BY

P. E. WENGER

AN 47 **AW 107.880**

A. Ag^{+1}, 64.

POTASSIUM BROMIDE + METHYLAMINO-4-PHENOL SULPHATE *(metol)*



BIBLIOGRAPHY : 1-2.

MECHANISM OF REACTION.

Precipitation of the salt AgBr.

Photoreduction of this salt by a " developer," or in this case, metol in citrate medium; appearance of black stain of metallic silver.

A. J. VELCULESCU (1).

DETAILS OF TEST.

On filter paper.

Place a drop of the solution to be analysed on a filter paper and mark it by drawing a line in pencil round it. Let it dry and then immerse the paper in a solution of potassium bromide; leave it for two minutes. Wash it thoroughly with distilled water and " develop " the silver in the metol solution. In the presence of this cation a black stain, or a grey one appears for concentrations that are near the limit.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

The dilution limit is not reduced by ions of the following elements (in a proportion of 1 : 3000), viz. Cu, Pb, Cd, As, Sb, Pt, Al, Fe, Cr, U, Zn, Mn, Co, Ni, alkaline earths, Mg and alkalis. It is reduced to 10^{-5} (1 : 10^5) by Hg^{+2}, Bi^{+3}, V^{+3}, Ce^{+3}, molybdenum (Mo^{+6}) and tungsten (W^{+6}) ions in a proportion of 1 : 300. The Hg^{+1}, Sn^{+2}, Au^{+3}, Pd^{+2} ions and the ions of Se and Te interfere giving brown to brownblack precipitates.

REAGENTS.

1. Potassium bromide 0,02 N.

2. Developer : dissolve 10 g metol and 50 g citric acid in 500 ml water. Before use add 2 ml solution of silver nitrate 0.1 N for 50 ml of developer.

B Ag^{+1}, 104.

DIAMMONIUM TRISULPHATOCERIATE (IV) + HYDROCHLORIC ACID OR	$(NH_4)_2[Ce(SO_4)_3]$ + HCl or
DIAMMONIUM HEXANITRATOCERIATE (IV) + HYDROCHLORIC ACID	$(NH_4)_2[Ce(NO_3)_6]$ + HCl

BIBLIOGRAPHY : 3-4.

MECHANISM OF REACTION.

Catalysis, by AgCl, of oxidation-reduction :

$$Ce^{+4} + Cl^{-1} \rightarrow Ce^{+3} + Cl^{0}$$

or decolourisation of the solution of yellow Ce^{+4} cation by formation of colourless Ce^{+3}.

F. FEIGL and E. FRÄNKEL (3).

DETAILS OF TEST.

On a spot plate.

Place on the plate two drops of the reagent solution and add a drop of the solution to be analysed, slightly acidified (nitric acid). In the presence of silver, the yellow solution of cerium (IV) is decolourised. It is essential to have a blank test parallel with it, for the reduction of cerium (IV) is obtained even without silver, but less quickly.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^{6}).

The ions of the following elements (in a proportion of 3000 : 1) do not reduce the sensitivity : Cu, Pb, Bi, Cd, As, Sb, Sn, Te, U, Th, Tl, Zn, Co, Ni, Ca, Sr, Ba. It is reduced to 10^{-5} (1 : 10^{5}) by the ions of Hg, Au, Pt, Mo, W, Al, Fe (Fe^{+3}), Cr and Ce in a proportion of 1 : 300.

In the presence of selenium (in a proportion of 1 : 100) the sensibility

is $10^{-4.48}$ ($1 : 3 \cdot 10^4$). Reducing agents must be absent, as they bring about immediate decolourisation of the cerium solution ; this is especially the case with the Fe^{+2}, Sn^{+2} (etc.) cations. Manganese always interferes, as it gives a brown precipitate [hydrated oxide of manganese (IV)].

REAGENTS.

1. Solution of 10^{-}% of cerium (IV) sulphate in hydrochloric acid 10 N.

Or alternatively :

1*a*. Solution of 0.25 % of cerium (IV) nitrate in 1 % nitric acid.

2. Hydrochloric acid 10 N.

C Ag^{+1}, 103.

MANGANOUS (II) SULPHATE + POTASSIUM PERMANGANATE + HYDROCHLORIC ACID — $MnSO_4 + KMnO_4 + HCl$

BIBLIOGRAPHY : 5-6.

MECHANISM OF REACTION.

Catalysis, by AgCl, of oxydation-reduction :

$$Mn^{+4} + 2\ Cl^{-1} \rightarrow Mn^{+2} + 2\ Cl^0.$$

Disappearance of brown colour due to cation Mn^{+4}, by reduction to cation Mn^{+2}.

F. FEIGL and E. FRÄNKEL (5).

DETAILS OF TEST.

On a spot plate.

Place on the plate two drops of the reagent solution and one drop of the solution to be analysed, as little acid as possible (hydrolysis acidity of nitrate solution). The solution, which is brown due to the presence of manganous oxide (IV), is decolourised, if there is any silver present. For tests that are near the limit, it is advisable to carry out a blank test in parallel.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 5 \cdot 10^4$).

The ions of the following elements (in a proportion of 100: 1) do not reduce the sensitivity : Hg, Cu, Pb, As, Sb, Ce (Ce^{+3}). The

latter is reduced to 10^{-4} (1 : 10^4) by the ions of Bi, Cd, Sn, Au, Pt, Se, Mo, W, Fe, Al, U and Th in the same proportion (100 : 1). The presence of reducing agents which also cause the decolourisation must be avoided; they are, in particular, the Hg^{+1}, Cu^{+1}, As^{+3}, Sb^{+3}, Sn^{+2}, V^{+3}, Fe^{+2} and TeO_3^{-2} ions.

Rhodium, palladium and iridium interfere also.

REAGENTS.

1*a*. Solution of manganous sulphate (II) 0.1 %, in water.

b. Potassium permanganate 0,1 N.

c. Hydrochloric acid 10 N.

Take a drop of each solution to prepare the reagent; the mixture cannot be kept.

D. Ag^{+1}, 2.

RUBIDIUM CHLORIDE (PHOTO 1) RbCl

BIBLIOGRAPHY : 7.

MECHANISM OF REACTION.

Precipitation of colourless crystals according to the formula :

2 RbCl . AgCl.

J. VERMANDE (7).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed (which is slightly acidified with nitric acid), and introduce some rubidium chloride crystals. Gently evaporate the above over a micro-flame; colourless needle-shaped crystals are gradually produced.

SENSITIVITY AND SELECTIVITY. D = 10^{-5} (1 : 10^5).

The majority of cations also give crystalline precipitates. However, the sensitivity is not reduced by the ions of the following elements : As, Au, Se and Co (in a proportion of 1000 : 1), but (in a proportion of 100 : 1) it is brought back to 10^{-4} (1 : 10^4) by the ions of : Hg, Cu, Cd, Os, Ir, Al, Fe, Cr, Ce (Ce^{+3}), Zr, Th, Zn, Mn, Ni, Ca, Sr and

Ba. In the same proportion the ions V^{+3}, Ce^{+4} and MoO_4^{-2} reduce the sensitivity even further ($10^{-3.52}$ or $1 : 3.3 \cdot 10^3$).

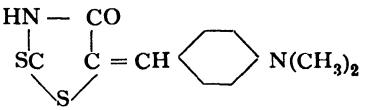
The ions of Pb, Sb, Sn, Rh, Pd, Te and Gl give exactly the same crystals and prevent the detection of silver and the same is true for the ions of Bi, Pt and Tl, whose crystals are however different.

REAGENT.

1. Solid rubidium chloride.

E Ag^{+1}, 57.

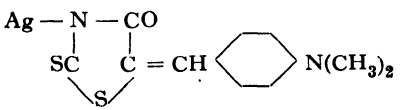
4-(*p*-DIMETHYLAMINOPHENYLMETHYLENE) -2-THIONE-5-THIAZOLIDONE, 5-(4'-DIMETHYLAMINO)BENZALRHODANINE
(p-dimethylaminobenzylidenerhodanine)



BIBLIOGRAPHY : 8-21.

MECHANISM OF REACTION.

Formation of a purple-coloured salt according to the formula :



F. FEIGL (11).

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the reagent solution and then a drop of the solution to be analysed, which is slightly acidified with nitric acid. The ruby-red colour of the reagent turns into purple-red in the presence of silver. For concentrations near the limit it is essential to carry out a control test.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ $(1 : 5 \cdot 10^5)$.

In a proportion of 1 : 1000 the sensitivity is not diminished by ions of the following elements : Cd, Sb, Sn, Mo, W, Fe, Cr, U, Ce, Zr, Th, Tl, Zn, Mn, Co, Ni, alkaline earths and alkalies; it is reduced to $10^{-4.70}$ $(1 : 5 \cdot 10^4)$ by the same proportion of arsenic, vanadium or tellurous anion (TeO_3^{-2}). The elements Hg, Cu, Pb, Bi, Au, Rh, Pd, Os and Pt give the same reaction and consequently interfere.

REAGENT.

1. Solution of *p*-dimethylaminobenzylidenerhodanine, 0.03 %, in alcohol or in acetone.

2. MERCURY

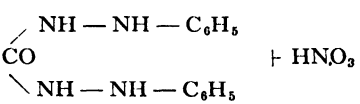
BY

C. J. VAN NIEUWENBURG

AN 80 **AW 200.61**

A. Hg^{+1}, Hg^{+2}, 30.

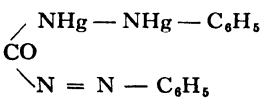
***sym*-DIPHENYLCARBAZIDE + NITRIC ACID**



BIBLIOGRAPHY : 22-29.

MECHANISM OF REACTION.

Formation of the blue compound of the formula :



which is actually a mercury salt of diphenylcarbazone.

B. ODDO (23).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the solution to be examined, which is about neutral, then a drop of nitric acid and a drop of the reagent. In the presence of mercury a blue or purplish-blue colour is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

Good reaction; the reaction is doubtful at the limit $10^{-5,40}$ ($1 : 2.5 \cdot 10^5$).

The sensitivity is not reduced by ions of the elements Ag, Cu, Pb, Bi, Cd, As, Sb, Sn, Pt, Se, Te, W and Tl in the proportion of 100 : 1. Gold interferes, giving a blackish precipitate and vanadium a blue or purplish-blue precipitate. The anions MoO_4^{-2} and CrO_4^{-2} interfere by giving a purple colouration. However, the interference due to the MoO_4^{-2} anion can be avoided by adding a drop of a 5 % oxalic acid solution, which changes it into a non-active complex. By reducing the CrO_4^{-2} anion with sulphur dioxide its interference is prevented.

In neutral medium (i.e. without adding nitric acid) the cations of copper, iron, chromium and cobalt also give colours that interfere with the reaction of mercury; but at the limit of sensitivity of mercury they do not interfere any longer (the sensitivity of their reactions is less); it is therefore recommended to have the reaction performed in neutral medium if traces of mercury are present.

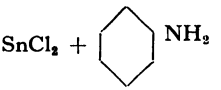
If it is a question of identifying mercury in a mixture of sulphides the latter can be attacked with brominewater; the excess of bromine is eliminated with the aid of phenol and dilute sulphuric acid, then a drop of the reagent and a drop of potassium hydroxide solution are added. A red colour is produced (colour of the reagent in alkaline medium). However owing to the acidity of the original solution, the formation of blue threads can be observed, which are due to the reaction of the mercury.

REAGENTS.

1. Nitric acid 0.2 N.
2. Solution of diphenylcarbazide, 1 %, in 96 % alcohol.
3. 5 % solution of oxalic acid, in water.

B. Hg^{+1}, Hg^{+2}, 55.

TIN (II) CHLORIDE, (STANNOUS CHLORIDE) + ANILINE



BIBLIOGRAPHY : 30-32.

MECHANISM OF REACTION.

Reduction of mercury according to the following equation :

$$Sn^{+2} + Hg^{+2} \rightarrow Sn^{+4} + Hg^{0}$$

Aniline gives to the medium a p_H, which makes it possible to avoid the identical reaction of the Sb^{+3} cation.

N. A. TANANAEFF (30).

DETAILS OF TEST.

On filter paper.

Place on a paper filter a drop of the solution to be analysed, then a drop of the stannous chloride solution and a drop of aniline. A brown or black stain of metallic mercury is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3,30}$ $(1 : 2 \cdot 10^3)$.

In a proportion of 100 : 1 the sensitivity is not reduced by ions of the elements Ag, Cu, Pb, Bi, Cd, As, Sb, Sn, Se, Te, W and V. Copper gives a brown stain; if copper and mercury both occur in the mixture then the brown colour is produced at the edge of the black mercury stain. Iron gives an orange-coloured stain; only a large quantity interferes; platinum gives a yellow-orange stain and palladium a brown stain; there is interference only if the ions of these two elements are in a proportion greater than 10 : 1. Gold gives a purplish brown stain, molybdenum a stain which is of a deep bluish green; their ions always interfere.

The reaction is fairly selective but not very sensitive.

REAGENTS.

1. Stannous chloride in a 5 % solution in hydrochloric acid 10 N.
2. Pure aniline.

C. Hg^{+1}, 21.

SODIUM NITRITE + SILVER NITRATE $NaNO_2 + AgNO_3$

BIBLIOGRAPHY : 33.

MECHANISM OF REACTION.

Reduction of mercury to metallic state according to the equation :

$$2\ Hg^{+1} + 2\ NO_2^{-1} \rightarrow Hg^0 + Hg^{+2} + 2\ NO_2^{-1}$$
$$2\ HgNO_3 + 2\ NaNO_2 \rightarrow Hg + Hg(NO_2)_2 + 2\ NaNO_3$$

at a p_H near 7.

The reaction is made sensitised by the cation Ag^{+1}.

N. A. TANANAEFF (33).
C. J. VAN NIEUWENBURG.

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of a solution saturated with sodium nitrite, then a drop of a silver nitrate solution. A white precipitate of silver nitrite is formed. Then add a drop of the neutral solution to be analysed. A black stain of reduced mercury is formed. Avoid strong acidity which will redissolve the mercury which was formed. Mercuric (II) salts do not react.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ ($1 : 10^4$).

The sensitivity is not reduced by ions of the elements Cu, Bi, Cd, Sb, Sn, Pt, Se, Te, Mo, W and V in a proportion of 100 : 1. Lead and arsenic, in the same proportion, reduce it to $10^{-3.40}$ ($1 : 2{,}5 \cdot 10^3$); but in a proportion of 10 : 1 they do not change it. Gold gives a purplish blue stain; it interferes in a proportion of 100 : 1 and in a proportion of 10 : 1 it reduces the concentration limit to 10^{-3} ($1 : 10^3$).

Coloured ions, which would make the mercury stain less distinct, can be eliminated by washing the stain with water by means of a small capillary tube.

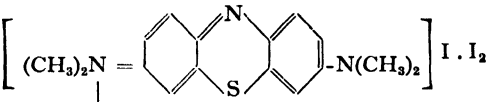
If the mercury solution is too strongly acid, it is advisible to add a drop of diluted ammonia after the reaction. If silver nitrate is not added, the reaction is less sensitive, $10^{-3.40}$ ($1 : 2{,}5 \cdot 10^3$).

REAGENTS.

1. Solution of silver nitrate, 10 %, in water.
2. Saturated solution of sodium nitrite in water.

D. Hg^{+1}, Hg^{+2}, NR.

2 : 7-BIS-(DIMETHYLAMINO) PHENOTHIAZONIUM DI-IODO-IODIDE
(iodine derivative of methylene blue)



BIBLIOGRAPHY : 34-35.

MECHANISM OF REACTION.

Fixation of iodine of the organic complex by a cation (mercury) and regeneration of soluble blue.

$$HgI_2 . (I_2 . HI . Bl)_2 + 2\,HgNO_3 \rightarrow HgI_2 + 2\,HgI + I_2 + 2\,HNO_3 . Bl.$$

G. BOUILLOUX (35).

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the aqueous suspension of the reagent then a drop of the solution to be analysed (slightly acid); a blue colour is produced. If the mercury is in the monovalent state, a brown ring of iodine that is set free appears at the same time. Strongly acid solutions (and also rather concentrated ammonia) give an analogous reaction, even in the absence of mercury. Accordingly it is necessary to reduce the acidity of the solution to be examined by means of a solution of sodium carbonate, 0.2 N, or sodium acetate, 5 %, in water.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ $(1 : 10^4)$.

Good reaction; the reaction is doubtful at the limit $10^{-4.30}$ $(1 : 2 \cdot 10^4)$.

The sensitivity is not reduced by ions of the elements Pb, Bi, Cd, Sb, Sn, Pt, Se, Te, Mo, W and V in a proportion of 100 : 1. Copper in the same proportion, reduces it to 10^{-3} $(1 : 10^3)$, but in a proportion

of 10 : 1 it does not change the limit of dilution. Silver and arsenic give an analogous reaction. Gold gives a deep purple stain in the presence of mercury (I); but if mercury is in a bivalent state, gold does not interfere. Palladium gives a brownish stain, which does not interfere in the proportion 10 : 1 (at the limit of dilution). Iron gives a yellow stain and does not interfere, except when it is present in large proportions. Reducing agents react in the same way as mercury and must be absent. It should be borne in mind that the reagent turns more or less blue after about a quarter of an hour in the absence of mercury.

REAGENTS.

1. Suspension of iodised methylene blue in a very dilute solution of potassium iodide in 0,01 N sulphuric acid.

2. 0.2 N solution of sodium carbonate in water or 5 % solution of sodium acetate in water.

PREPARATION OF REAGENT.

Add an excess of solution of iodine 0.1 N in potassium iodide to a solution of methylene blue (0.1 %). Stir frequently and filter after 24 hours. Wash with a very dilute solution of potassium iodide in sulphuric acid 0.01 N.

3. COPPER

BY

C. J. VAN NIEUWENBURG

AN 29 **AW 63.57**

A. Cu^{+2}, 10.

ZINC SULPHATE + DIAMMONIUM TETRATHIOCYANATO-MERCURATE (II) *(ammonium mercurithiocyanate)* $ZnSO_4 + (NH_4)_2[Hg(CNS)_4]$

BIBLIOGRAPHY : 36-41.

MECHANISM OF REACTION.

Formation of mixed crystals (dark purple), of the composition :

$Zn[Hg(CNS)_4] . Cu[Hg(CNS)_4]$.

F. FEIGL, G. HIRSCH and I. TAMCHYNA (37)

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the zinc sulphate solution and a drop of the very dilute solution to be analysed (copper in a bivalent state). Add a drop of sulphuric acid 2 N and a drop of the reagent solution. A precipitate is formed having the formula :

$$Zn[Hg(CNS)_4]$$

which is white in a pure state, but coloured purple by the cation Cu^{+2}.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

Good reaction; doubtful at the limit $10^{-5.70}$ ($1 : 5 \cdot 10^5$).

The sensitivity is not reduced by ions of the elements Ag, Pb, Bi, Cd, As, Sb, Au, Pt, Se, Te, Mo, V, W and Tl in the proportion of 100 : 1.

Cobalt gives an analogous reaction (blue colouration), which makes the detection of copper impossible. Nickel gives a pale green colouration and only interferes in strong concentrations. In a 1 % copper solution, nickel (in equal quantity) does not bring about any disturbance. The Fe^{+3} cation interferes, giving a dark brown colouration; when reduced to a bivalent state (previously adding an oxalic acid crystal) it does not disturb the reaction any longer. In this case it is recommended that sulphuric acid be not added. Gold gives a pink-orange colouration which scarcely interferes.

REAGENTS.

1. Solution of zinc sulphate, 10 %, in water.

2. Diammonium tetrathiocyanatomercurate (II) : dissolve 30 g of mercury (II) chloride and 33 g of ammonium thiocyanate in 100 ml water.

3. Sulphuric acid 2 N.

B. Cu^{+2}, 84.

IRON (III) THIOCYANATE, (FERRIC THIOCYANATE) + SODIUM THIOSULPHATE $Fe(CNS)_3 + Na_2S_2O_3$

BIBLIOGRAPHY : 42-46.

MECHANISM OF REACTION.

Immediate formation of a compound of trivalent iron with the thiosulphuric anion :

$$Fe^{+3} + 2\ S_2O_3^{-2} \rightleftarrows \left[Fe(S_2O_3)_2\right]^{-1}.$$

Catalytic acceleration, by the Cu^{+2} cation, of the following reaction :

$$\left[Fe(S_2O_3)_2\right]^{-1} + Fe^{+3} \rightleftarrows 2\ Fe^{+2} + S_4O_6^{-2}.$$

The CNS^{-1} anion acts as redox indicator with the Fe^{+3} cation.

F. FEIGL (46).

DETAILS OF TEST.

On a spot plate.

The copper (II) salts accelerate the reduction (decolourisation) of ferric thiocyanate (III) by alkaline thiosulphate. The detection of copper is effected in parallel with a blank test.

In two adjacent sections of the spot plate place a drop of the solution to be examined and a blank, i.e. pure water, free from copper. In these two sections add first a drop of ferric thiocyanate, then a drop of sodium thiosulphate (drops of equal size). Compare the rate of decolourisation.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

Good reaction; at the limit of 10^{-7} (1 : 10^7) the reaction is doubtful.

The sensitivity is not reduced by the ions of Ag, Hg (Hg^{+1}, Hg^{+2}), Pb, Bi, Cd, As, Sb, Sn, Au, Pt, Te, Mo, V and Tl in a proportion of 100 : 1. Tungsten and, to a lesser extent, selenium cause a catalytic acceleration that is similar to that of copper. A yellow colouration is produced at the same time. Arsenic and zinc delay the decolourisation, without preventing the detection of copper, even in a dilution of

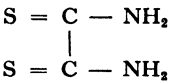
10^{-6} (1 : 10^{6}) and in the presence of these metals in a proportion of 100 : 1.

REAGENTS.

1. Iron (III) thiocyanate : dissolve 1.5 g of iron (III) chloride and 2g of potassium thiocyanate in 100 ml of water.
2. Solution of sodium thiosulphate, 1 %, in water.

C. Cu^{+2}, 30.

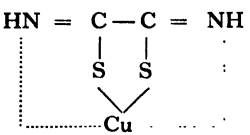
1 : 2-ETHANEDITHIAMIDE, DITHIOOXAMIDE *(rubeanic acid)*



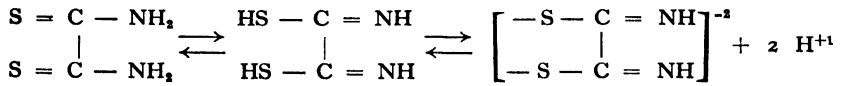
BIBLIOGRAPHY : 47-53.

MECHANISM OF REACTION.

Formation of green internal complex, having the following structure :



the three forms of rubeanic acid being given, in equilibrium :



F. FEIGL and H. J. KAPULITZAS (49) and (50)

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the solution to be analysed (copper in a bivalent state) which is nearly neutral and beside it a drop of the reagent. Expose the paper to ammonia vapours. A very dark green colour is produced in the contact zone of the two drops.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

Good reaction; a solution diluted to 10^{-6} (1 : 10^6) gives still a very weak reaction which can be revealed beside a blank test.

The sensitivity is not reduced by the ions of the following elements : Pb, Bi, Cd, As, Sb, Sn, Au, Pt, Se, Te, Mo, W, V and Tl in a proportion of 100 : 1. Nickel gives a dark purple stain, cobalt a dark brown stain. However, it is possible to detect copper in the presence of cobalt and nickel, by waiting a few moments before adding the reagent. As the diffusion of copper is less rapid than that of cobalt and nickel, the colouration of the copper will be noticeable in the centre of the stain, alongside the colouration due to cobalt and nickel. Nevertheless the reaction is scarcely to be recommended in the presence of these two cations.

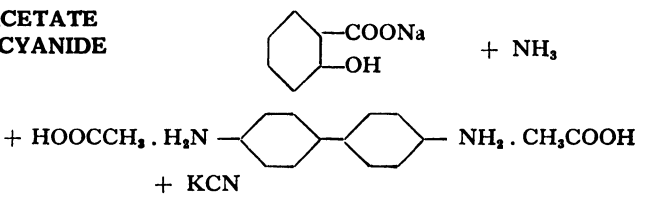
The cation Hg^{+1} interferes, giving a black stain with ammonia. The cations Ag^{+1} and Hg^{+2} give brown stains and interfere with the reaction of copper, when they are present in large proportions.

REAGENT.

1. Solution of rubeanic acid, 0.5 %, in 96 % alcohol. The solution must preferably be prepared at the moment it will be used.

D. Cu^{+2}, NR.

SODIUM 2-HYDROXYBENZOATE, SODIUM SALICYLATE
+ AMMONIA
+ BENZIDINE ACETATE
+ POTASSIUM CYANIDE



BIBLIOGRAPHY : 54.

MECHANISM OF REACTION.

The mechanism of this reaction and the reaction products are not known yet.

DETAILS OF TEST.

In a micro test tube.

Put 1 ml of the solution to be analysed in the test tube (neutral or slightly acid); add 4 drops of a sodium salicylate solution, 4 drops of ammonia, 1 drop of a benzidine acetate solution and a drop of a potassium cyanide solution. In the presence of copper a red colour is produced. When the concentration of copper exceeds the value of 10^{-4} ($1 : 10^4$), the colour is somewhat blue or purple blue (the colour of the amine complex predominating).

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

Good reaction. The reaction is doubtful at the limit $10^{-5.70}$ ($1 : 5 \cdot 10^5$).

The sensitivity is not reduced by the ions of the following elements: Ag, Hg (Hg^{+2}), Pb, Bi, Cd, As, Sb, Sn, Au, Pt, Se, Te, Mo, W, V and Tl in a proportion of 100 : 1. The reaction is disturbed by mercury (I) (black precipitate), by the cation (UO_2^{+2}) (orange precipitate), by iron (III) (brownish red precipitate), by manganese (brown), cobalt (brown), and cerium (III) (white precipitate which becomes brown in the presence of copper). In the presence of cations which form compounds with the hydrocyanic anion, e.g. the cations Ag^{+1}, Cd^{+2}, Au^{+3}, Zn^{+2} and Ni^{+2}, it is advisable to add a little more of the potassium cyanide solution.

REAGENTS.

1. Solution of sodium salicylate, 3 %, in water.
2. Concentrated ammonia 7.5 N.
3. Benzidine in 0.1 % solution in acetic acid (20 %).
4. Solution of potassium cyanide, 1 %, in water.

4. LEAD

BY

C. J. VAN NIEUWENBURG

AN 82 AW 207.21

A. Pb^{+2}, NR.

THIOCARBAMIDE (THIOUREA) NITRIC ACID (PHOTO 2)

$+ HNO_3$

BIBLIOGRAPHY : 55-57.

MECHANISM OF REACTION.

Formation of colourless needles, according to the formula :

$$2\,Pb(NO_3)_2 \cdot 11\,CS(NH_2)_2.$$

C. MAHR and H. OHLE (55).

DETAILS OF TEST.

Under the microscope.

Evaporate a drop of the solution to be examined on a slide till it is dry; add a little drop of nitric acid to the residue and then some thiourea crystals. A crystallization of small colourless needles will be produced, whose refractive index is so high that they seem to be black.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

Good reaction; it is doubtful at the limit $10^{-4,40}$ (1 : $2.5 \cdot 10^4$).

The sensitivity is not reduced by the ions of the following elements : Hg(Hg^{+1}, Hg^{+2}), Bi, Cd, As, Au, Pt, Pd, Te, and V in a proportion of 100 : 1. The ions of antimony in a proportion of 10 : 1 do not change the sensitivity, but in a proportion of 100 : 1 they reduce the limit to 10^{-3} (1 : 10^3). Silver gives longer and thinner needless; this cation interferes in a proportion of 100 : 1, but in a proportion of 10 : 1 the lead can still be distinguished in a concentration of 10^{-3} (1 : 10^3). Mercury (I) gives an amorphous precipitate which does not interfere. Mercury (II) gives needles which are soluble in an

excess of reagent. Selenium gives a crystallization which is very different from the one caused by lead; in a proportion of 100 : 1 the limit of solution for lead is $10^{-3.70}$ ($1 : 5 \cdot 10^3$). The anions MoO_4^{-2} and WO_4^{-2} interfere, because they eliminate the lead from the solution as a precipitate which no longer gives the reaction. Thallium gives a reaction which is analogous to that of lead.

Copper produces crystals analogous to those of lead. In practice they can be distinguished, however: the copper crystals are larger than the lead crystals, they grow more quickly and they have oblique terminal planes (only visible when magnified 250 times).

Even so it is hardly possible to distinguish between copper and lead in the presence of very small quantities of copper. Therefore our conclusion must be that copper interferes.

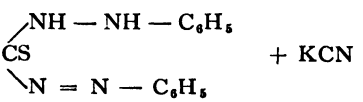
Lead sulphate gives the reaction excellently.

REAGENTS.

1. Nitric acid 2 N.
2. Solid thiourea.

B. Pb^{+2}, 41.

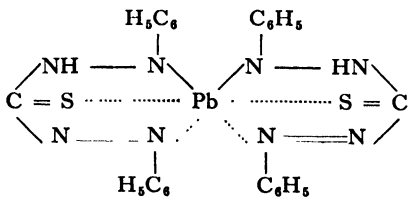
DIPHENYLTHIOCARBAZONE *(dithizone)* **+ POTASSIUM CYANIDE**



BIBLIOGRAPHY : 58-64.

MECHANISM OF REACTION.

A red coloured internal complex is formed :



The potassium cyanide prevents reaction with a large number of cations.

F. FEIGL (64).

DETAILS OF TEST.

In a micro test tube.

Put 1 ml of the neutral or slightly alkaline solution to be analysed in a micro test tube. Add some potassium cyanide crystals and then 2 drops of the freshly prepared reagent solution. Shake for half a minute. In the presence of lead, the green colour of the reagent changes into red.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ ($1 : 10^{6}$).

Good reaction; the reaction is doubtful at the limit $10^{-6.30}$ ($1 : 2 \cdot 10^{6}$).

The sensitivity is not reduced by the ions of the following elements : Ag, Hg, Cu, Cd, As, Au, Pt, Se, Te, Mo, W and V in a proportion of 100 : 1. Potassium cyanide serves to eliminate the analogous reaction of a large number of the above-mentioned cations. It is advisable to carry out a blank test, because potassium cyanide often contains some traces of lead.

In the presence of potassium cyanide the reaction is always disturbed by bismuth which gives an orange colour, by thallium which gives a red colour like lead, by tin (II) which gives a purplish red colour (but which does not interfere in a proportion of 10 : 1 and after oxidation into tin (IV)).

Contrary to the indications in the literature (C. J. VAN NIEUWENBURG), zinc gives a red colour, even with a fairly big excess of potassium cyanide. However, in the presence of potassium cyanide zinc does not react with dithizone in strongly alkaline medium (addition of excess of potassium hydroxide); but the selectivity of the reaction of lead is then considerably reduced.

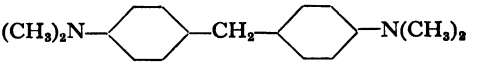
Excellent reaction, but often too sensitive and not selective.

REAGENTS

1. Solution of diphenylthiocarbazone, 0.05 %, in carbon tetrachloride (unstable solution).
2. Solid potassium cyanide.

C. Pb^{+2}, 39.

BIS-(*p*-DIMETHYLAMINOPHENYL) METHANE,
(*p*-TETRAMETHYLDIAMINO-DIPHENYLMETHANE)
+ HYDROGEN PEROXIDE
+ POTASSIUM HYDROXIDE

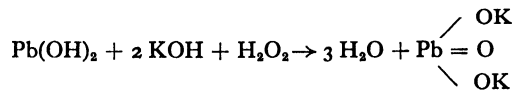


$+ H_2O_2 + KOH$

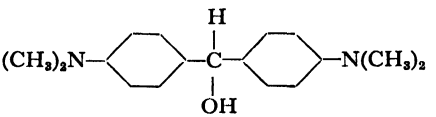
BIBLIOGRAPHY : 65-68.

MECHANISM OF REACTION.

Lead is first oxidized to the tetravalent state according to the equation :



The tetravalent lead in its turn oxidizes the base, yielding the corresponding hydrol, which is soluble in acetic acid medium, giving a blue derivative of the formula :



A. TRILLAT (65).

DETAILS OF TEST.

In a centrifuge tube.

Put in a centrifuge tube 1 ml of the solution to be analysed and add 1 ml potassium hydroxide, also 0.5 to 1 ml hydrogen peroxide. Wait 3 to 5 minutes (15 to 20 minutes if the solution is very diluted). Separate the precipitated plumbate from the solution by centrifuging and wash once with cold water. Then add 2 ml of the amine solution. Shake the contents of the tube and then separate again the precipitate from the solution by centrifugin. In the presence of lead the solution becomes blue.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The sensitivity is not reduced by the ions of the following elements : Ag, Hg, Cd, As, Sb, Sn, Au, Pt, Se, Te, Mo, W and V in a proportion of 100 : 1. The ions of Bi, Ce, Tl and Mn give an analogous reaction (oxidation of the hydroxides by hydrogen peroxide), although the colour of the solution is more or less different from that produced by lead. Copper in a large proportion (e.g. 100 : 1) interferes, giving a green colour; in a proportion of 10 : 1 it reduces the sensitivity to 10^{-3} (1 : 10^3). Iron interferes always.

REAGENTS.

1. Potassium hydroxide 2 N.
2. Solution of hydrogen peroxide, 3 %, in water.
3. Solution of tetramethyldiaminodiphenylmethane, 0.5-1 %, in a mixture of 96 % alcohol (5 p.) and glacial acetic acid (1 p.).

5. BISMUTH

BY

C. J. VAN NIEUWENBURG

AN 83 **AW 209.00**

A. Bi^{+3}, 1.

TIN (II) CHLORIDE, STANNOUSCHLORIDE + POTASSIUM HYDROXIDE $SnCl_2$ + KOH

BIBLIOGRAPHY : 69-77.

MECHANISM OF REACTION.

Reduction of bismuth to the metallic state by potassium stannite according to the equation :

$$2\ Bi(OH)_3 + 3\ K_2SnO_2 \rightarrow 2\ Bi + 3\ K_2SnO_3 + 3\ H_2O.$$

L. VANINO and F. TREUBERT (69).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the slightly acid solution to be anal-

ysed; add 3 drops of potassium hydroxide and one microdrop of stannous chloride (II) solution. A black precipitate of metallic bismuth is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.30}$ ($1 : 2 \cdot 10^4$).

The sensitivity is not reduced by ions of the following elements : Cu, Pb, Cd, As, Sb, Pt, Se, Mo, W and V in a proportion of 100 : 1. As solutions of the Cu^{+2} cation are reduced by alkaline stannite in a few minutes, it is advisable to add one drop of a 5 % potassium cyanide solution in the presence of copper; the complex thus formed is not reduced. Platinum interferes in high concentrations; in a diluted solution it gives a yellow colour in spite of which the detection of bismuth is possible, if necessary by comparison with a blank test. The ions of Ag, Hg (Hg^{+2}), Au and Te give an analogous reaction; the Hg^{+1} cation interferes because it gives a black precipitate with potassium hydroxide. The Pb^{+2} cation gives an analogous reaction, but only after a fairly long time (15 minutes) and in the absence of bismuth (cf. reaction B). The ions of iron (brown precipitate), cobalt (blue precipitate) and nickel (green precipitate) do not interfere, except in large proportions.

REAGENTS.

1. Potassium hydroxide 2 N.
2. Solution of stannous chloride, 5 %, in hydrochloric acid 2.5 N.

B. Bi^{+3}, 46.

TIN (II) CHLORIDE, (STANNOUS CHLORIDE) + POTASSIUM HYDROXIDE + LEAD ACETATE $SnCl_2 + KOH + Pb(CH_3CO_2)_2$

BIBLIOGRAPHY : 78-82.

MECHANISM OF REACTION.

Reduction of lead to the metallic state by potassium stannite :

$$Pb(OH)_2 + K_2SnO_2 \rightarrow Pb + K_2SnO_3 + H_2O$$

which is activated by the simultaneous reduction of the traces of bismuth according to the equation under A.

F. FEIGL (82).

DETAILS OF TEST.

On a spot plate.

Whilst the reduction of lead solutions by alkaline stannites is only achieved after a considerable time (15 minutes, cf. reaction A), this reaction becomes nearly instantaneous in the presence of traces of bismuth, even if the latter element does not itself cause reaction A.

Put the following on the spot plate : one drop of a lead acetate solution, one drop of the solution to be analysed (slightly acid), 3 drops of potassium hydroxide solution and a small drop of stannous chloride solution. The result is a black precipitate of metallic lead, which is formed instantaneously or after a few minutes, according to the quantity of bismuth.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ (1 : 5 · 10^5) after 6 minutes.

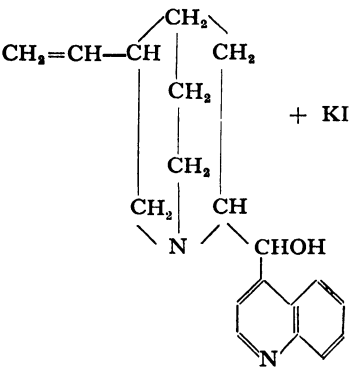
The sensitivity is not reduced by the ions of the following elements : Cu, Cd, As, Sb, Se, Mo, W, V and Tl in a proportion of 100 : 1. In the presence of copper it is advisable to add some potassium cyanide (cf. reaction A). The ions of Ag, Hg (Hg^{+2}) and Au give an analogous reaction; the Hg^{+1} cation interferes, giving a black precipitate with potassium hydroxide. Platinum causes an orange colouration with a blackish precipitate (which interferes). The reaction of tellurium depends on the valency of the element : in the hexavalent state (TeO_4^{-2}) it gives a black precipitate after a few minutes; in the tetravalent state (TeO_3^{-2}) the reduction is instantaneous (even in acid medium) and it precedes the reaction caused by the traces of bismuth. Under all circumstances tellurium prevents the detection of bismuth.

REAGENTS.

1. Potassium hydroxide 2 N.
2. Solution of stannous chloride, 5 %, in hydrochloric acid 3 N.
3. Solution of lead acetate (1 %) in water.

C. Bi^{+3}, 22.

CINCHONINE+POTASSIUM IODIDE



+ KI

BIBLIOGRAPHY : 83-90.

MECHANISM OF REACTION.

Precipitation of orange complex, having the formula :

BiI_3 ..... Cinch. HI

F. FEIGL (87).

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the slightly acid solution to be examined and add a drop of the freshly prepared reagent. An orange coloured stain is the result.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.30}$ ($1 : 2 \cdot 10^4$).

Good reaction; the reaction is doubtful at the limit $10^{-4.70}$ ($1 : 5 \cdot 10^4$).

The ions of the following elements give a yellow stain (colouration or precipitate) : Ag, $Hg(Hg^{+2})$, Pb, Sb, V and Tl; nevertheless, in a proportion of 100 : 1 they do not interfere in dilute solutions as they do at the concentration limit. The orange coloured stain can actually be very well observed, beside the other stains. The sensitivity is not reduced by the ions of Ag, $Hg(Hg^{+2})$, Cu, Pb, Cd, As, Sb, Sn, Pt, Te, Mo, W, V and Tl in a proportion of 100 : 1 and by $Hg(Hg^{+1})$ and Se, in a proportion of 10 : 1. Copper gives a brown colour (iodine), which does not interfere because it appears more slowly than that caused by bismuth. Mercury (I), gold and selenium only disturb the reaction in a proportion of 100 : 1. Platinum does

not interfere; it gives first of all a pink colour which becomes rather purple after a few minutes; at the limit of dilution the colouration due to bismuth is clearly visible before that of platinum in a proportion of 100 : 1.

REAGENT.

1. Solve 1 g of cinchonine in 100 ml of hot water, adding some drops of concentrated nitric acid. After cooling add 2 g of potassium iodide. The solution does not keep long.

D. Bi^{+3}, 18.

POTASSIUM THIOCYANATE KCNS

BIBLIOGRAPHY : 91.

MECHANISM OF REACTION.

Formation of the yellow coloured salt $Bi(CNS)_3$.

DETAILS OF TEST.

On a spot plate.

Add a few potassium thiocyanate crystals to a drop of the slightly acid solution to be analysed. A yellow colour is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ $(1 : 5 \cdot 10^4)$.

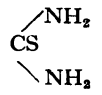
The sensitivity is not reduced by the ions of the following elements : Ag, $Hg(Hg^{+2})$, Pb, Cd, As, Sb, Sn, Se, Te, W and Tl in a proportion of 100 : 1. The Hg^{+1} cation gives a black precipitate, which interferes in a proportion of 100 : 1, where as it reduces the sensitivity to 10^{-4} $(1 : 10^4)$ in a proportion of 10 : 1. Platinum, molybdenum and the UO_2^{+2} cation give analogous reactions. Copper, gold, iron (Fe^{+3}) interfere, giving colour or precipitates (copper : brownish green; gold : orange; iron : dark red). Osmium, vanadium, and the CrO_4^{-2} anion interfere because of their own colours. The Cr^{+3} cation gives a blue colour, the Co^{+2} cation gives a purple colour and the Ni^{+2} cation gives a green colour. They only interfere when they are present in large proportions or along with very little bismuth.

REAGENT.

1. Solid potassium thiocyanate.

E. Bi^{+3}, 51.

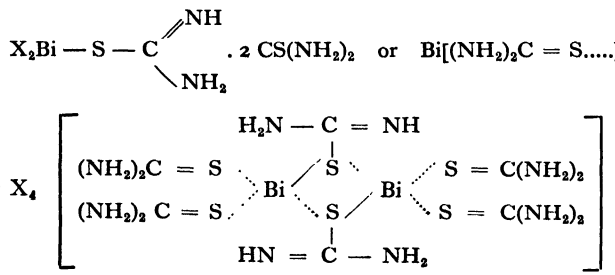
THIOCARBAMIDE (THIOUREA)



BIBLIOGRAPHY : 92-95.

MECHANISM OF REACTION.

Formation of a yellow complex of one of the following types :



J. V. DUBSKY, A. OKAC and B. OKAC (93).

DETAILS OF TEST.

On a spot plate.

Add a thiourea crystal to a drop of the slightly acid solution to be analysed. A yellow colour is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.48}$ ($1 : 3 \cdot 10^4$).

The sensitivity is not reduced by the ions of the following elements : Ag, Hg(Hg^{+2}), Cu, Pb, Cd, As, Sn, Au, Te, Mo and W in a proportion of 100 : 1.

The Hg^{+1} cation gives a black precipitate which interferes in a proportion of 100 : 1; it does not change the dilution limit, being $10^{-4.48}$ ($1 : 3 \cdot 10^4$), in a proportion of 10 : 1.

The Fe^{+3} cation interferes, when used in excess, by giving a pink colour (due to impurities of the reagent?). Antimony gives an

analogous reaction. Selenium gives a red precipitate. Because of their yellow colour, osmium, platinum, vanadium and the CrO_4^{-2} anion interfere. Gold does not interfere, even in a proportion of 100 : 1, because its solution is colourless.

REAGENT.

1. Solid thiourea.

6. CADMIUM

BY

C. J. VAN NIEUWENBURG

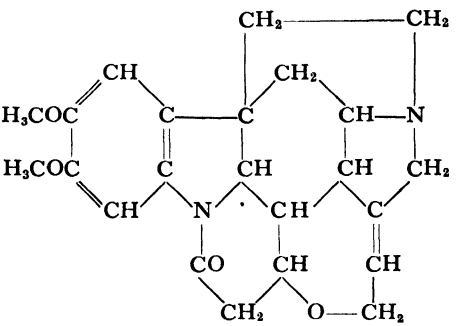
AN 48 **AW 112.41**

A. Cd^{+2}, 12.

BRUCINE ACETATE + SODIUM BROMIDE

(PHOTO 3)

$C_{23}H_{26}O_4N_2 . CH_3CO_2H + NaBr$



BIBLIOGRAPHY : 96-100.

MECHANISM OF REACTION.

Formation of colourless crystals, probably according to one of the following two formulae :

$$\left[Cd \begin{matrix} Br_2 \\ (CH_3CO_2H)_2 \end{matrix} \right] 2B \quad \text{or} \quad Br_2(CdB_6)NaBr \qquad (B = \text{Brucine})$$

P. E. WENGER and R. DUCKERT.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the neutral solution to be analysed and next a drop of the reagent. Some colourless, monoclinic prisms are formed, often in the form of rosettes. If necessary, heat until crystallization sets in at the edge of the drop.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

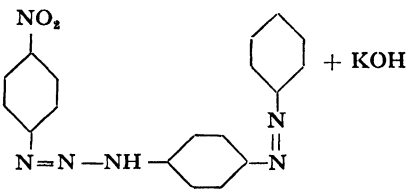
The sensitivity is not reduced by the ions of the following elements: Ag, Cu, Pb, As, Sb, Sn, Se, Te, Tl, and Zn in a proportion of 100: 1. However, a precipitate is formed with the ions of Ag^{+1}, Pb^{+2} and Tl^{+1}. The ions of Hg^{+1}, Hg^{+2} and Bi^{+3} give an analogous reaction. The ions of tungsten and vanadium interfere because they give abundant precipitates, whereas the ions of gold, platinum and molybdenum only interfere when they are in large proportions. Platinum gives birefractive needles, often in clusters or in rosettes, but bigger than the cadmium ones, so much so that the detection of the latter is possible in the presence of platinum (the two elements being in equal proportions).

REAGENT.

1. Dissolve 6.5 g of brucine + 10 g of sodium bromide in 50 ml acetic acid, 4 N and 150 ml water.

B. Cd^{+2}, NR.

p-NITROPHENYLDIAZOAMINO-BENZENE p-AZOBENZENE (*„cadion"*) + **POTASSIUM HYDROXIDE**



BIBLIOGRAPHY : 101-105.

MECHANISM OF REACTION.

Adsorption of the colouring matter on the hydroxide $Cd(OH)_2$, giving the latter an orange-red colour.

F. P. DWYER (101).

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the neutral or slightly acid solution to be analysed, which is acid with acetic acid; add a drop of the reagent solution and finally a drop of the potassium hydroxide solution. In the presence of cadmium a pink stain can be observed, whereas it is purple in the absence of that element.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

Good reaction; the reaction is doubtful at the limit $10^{-5.48}$ (1 : $3 \cdot 10^5$).

The sensitivity is not reduced by the ions of the following elements : Pb, Bi, As, Sb, Sn, Au, Pt, Se, Te, Mo, W, V, Tl and Zn in a proportion of 100 : 1. The ions of copper, chromium, cobalt and nickel give a bluish colour; those of magnesium give a blue colour and those of iron a yellow colour. All these colours, which make the identification of cadmium more or less difficult, can be avoided by adding one drop of a 10 % sodium potassium tartrate solution before the reagent is added. The Ag^{+1}, Hg^{+1} and Hg^{+2} ions give brownish orange-coloured precipitates which interfere.

If a drop of a potassium cyanide solution (10 % in water) is added immediately before the potassium hydroxide, then cadmium does not react, and that is how the magnesium can be revealed beside the cadmium.

REAGENTS.

1. Solution of " cadion", 0.02 %, in ethyl alcohol, 96 %, the latter being 0.02 N in potassium hydroxide.
2. Potassium hydroxide 2 N.

PREPARATION OF REAGENT.

a) Preparation of *p*-nitrodiazoaminobenzene.

E. NOELTING and F. BINDER (104).

Dissolve one part of *p*-nitraniline and one part of aniline in the minimum quantity of hydrochloric acid. Cool strongly and add one part of sodium nitrite (the temperature must not exceed 5°). Add a concentrated solution of sodium acetate, which causes the precipitation of the compound. Filter without heating, recrystallize from benzene. Yellow needles. M.P. 148°.

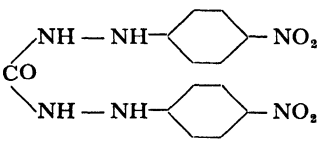
b) Preparation of *p*-nitrophenyldiazoaminobenzene *p*-azobenzene.

B. FISCHER and H. WIMMER (105).

Dissolve the nitrodiazoaminobenzene in the minimum quantity of glacial acetic acid. Cool and keep at 14° for 20 minutes. Pour it into a large quantity of water and leave it at 0° for 45 minutes. Filter and wash it. Dissolve the precipitate in hot ammonia containing a little alcohol; add water and cool to cause precipitation. Yellow needles. M.P. 151°.

C. Cd^{+2}, 45.

***sym*-BIS-(*p*-NITROPHENYL) CARBAZIDE**
***sym*-DI-*p*-NITRODIPHENYLCARBAZIDE**
+ POTASSIUM CYANIDE
+ SODIUM HYDROXIDE
+ FORMALDEHYDE

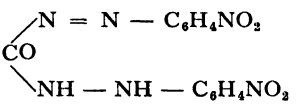


+ KCN + NaOH + HCHO

BIBLIOGRAPHY : 106-109.

MECHANISM OF REACTION.

It is probable that a salt of the corresponding carbazone is formed :



particularly the formaldehyde makes the reaction more sensitive.

P. KRUMHOLZ and F. HÖNEL (107).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the neutral or slightly acid solution to be analysed, add in succession : a drop of sodium hydroxide solution, a drop of potassium cyanide solution, a drop of reagent (carbazide) and finally 3 to 4 drops of formaldehyde.

Before the formaldehyde is added, the colour is brown; with the formaldehyde it is purple, without a precipitate and at the end, in the presence of formaldehyde and cadmium, a green colour appears followed by a blue precipitate.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The sensitivity is not reduced by the ions of the following elements : Ag, Hg(Hg^{+2}), Cu, Pb, Bi, Sb, Sn, Au, Se, Mo, W, V and Tl in a proportion of 100 : 1. The Hg^{+1} ion and those of arsenic do not cause any disturbance when they are in a proportion of 10 : 1. The ions of cobalt cause a brown precipitate, those of platinum a yellow one and interfere with the detection of cadmium, and so does a large proportion of tellurium and iron ions.

REAGENTS.

1. Sodium hydroxide 5 N.
2. Solution of potassium cyanide, 5 %, in water.
3. Solution of sym-dinitrodiphenylcarbazide, 0.1 %, in ethyl alcohol, 96 % (the solution does not keep).
4. Solution of formaldehyde, 38-40 %, in water.

D. Cd^{+2}, 67.

SODIUM OXALATE $Na_2C_2O_4$

BIBLIOGRAPHY : 110-113.

MECHANISM OF REACTION.

Reduction by sodium oxalate of cadmium salts to elementary cadmium, thereby forming a metallic mirror, generally surrounded by a halo of brown oxide. Finally transformation of the metal into its yellow sulphide (CdS), by fusion with sulphur.

DETAILS OF TEST.

In a tube of combustion glass.

Evaporate on a slide a drop of the solution to be analysed; the residue is mixed with some crystals of sodium oxalate, placed in a small glass combustion tube, and heat. A mirror of metallic cadmium with brown edges is formed. After cooling add some granules of sulphur to redness and heat again. Gradually the metallic mirror

is transformed, at a high temperature, into orange-coloured sulphide which becomes yellow after cooling. Be careful not to mistake the yellow of the cadmium sulphide for the yellow of the sulphur which distils.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The salts of mercury, arsenic and zinc give an identical reaction, although the mirror is not brown-edged. No other element interferes. Excellent reaction, not very sensitive, but selective in most cases.

REAGENTS.

1. Solid sodium oxalate.
2. Elementary sulphur.

7. ARSENIC

BY

C. J. VAN NIEUWENBURG

AN 33 **AW 74.91**

A. As^{+3} and As^{+5}, 23.

ZINC $Zn + HCl + HgCl_2$
+ HYDROCHLORIC ACID
+ MERCURY (II) CHLORIDE, MERCURIC CHLORIDE

BIBLIOGRAPHY : 114-119.

MECHANISM OF REACTION.

Reduction of arsenic, in all its forms, to arsine (AsH_3); then reaction of the mercury salts with this gas, giving the following series of compounds :

$$AsH_2(HgCl), \quad AsH(HgCl)_2, \quad As(HgCl)_3, \quad As_2Hg_3.$$

ROSE (114).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube : 1 ml of the solution to be analysed, a granule of zinc and 1 ml hydrochloric acid. In the top part of the test tube is a cotton wad, soaked in a copper (I) chloride solution to retain the hydrogen sulphide and antimoniuretted hydrogen. On the test tube is placed a paper filter, steeped in a drop of mercury (II) chloride solution. In the presence of arsenic, a yellow or brown stain is produced on the filter paper in a few minutes.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 5 \cdot 10^4$).

In a 10^{-4} concentration ($1 : 10^4$) the reaction is still very clear.

The sensitivity is not decreased by the ions of the following elements: Ag, Cu, Pb, Bi, Cd, Sb, Sn, Au, Pt, Se, Mo, W, V and Tl in a proportion of 100 : 1. In the presence of silver an excess of hydrochloric acid is required. The Hg^{+1} and Hg^{+2} cations interfere, if in large proportions (10 : 1 and 100 : 1).

Mercury, in the same amounts as arsenic, does not affect the sensitivity. Tellurium in a proportion of 100 : 1 interferes and in a proportion of 10 : 1 it reduces the dilution limit to 10^{-3} ($1 : 10^3$).

REAGENTS.

1. Granulated metallic zinc.
2. Hydrochloric acid 5 N.
3. Copper (I) chloride solution, 15 %, in hydrochloric acid 10 N.
4. Solution of mercury (II) chloride, 3 %, in water.

B. As^{+3}, 25

ALUMINIUM $Al + KOH + HgCl_2$
+ POTASSIUM HYDROXIDE
+ MERCURY (II) CHLORIDE, MERCURIC CHLORIDE

BIBLIOGRAPHY : 120.

MECHANISM OF REACTION.

The reaction is identical with the preceding one, but only applies

to the cation As^{+3}. Antimony derivatives are not reduced, whereas they are by the zinc and hydrochloric acid method.

DAUVE (120).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube : 1 ml of the solution to be examined, some aluminium cuttings and 1 ml of a potassium hydroxide solution. In the top part of the test tube is a cotton wad, soaked in a lead acetate solution to retain the hydrogen sulphide. On the test tube is placed a paper filter, steeped in a drop of mercury (II) chloride solution. In the presence of arsenic, a yellow or brown stain is produced after a few minutes.

Antimony is not reduced under these circumstances, neither is arsenic (V). Therefore arsenic (V) must in certain cases be previously reduced to a trivalent state by means of sulphur dioxide (hot, for some minutes in weakly acid medium).

Some ions slow down the release of arseniuretted hydrogen, viz. those of the following elements : Hg, Pt, Te, Nb, Ti, Ga and Zn. In their presence it is advisable to heat slightly.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ $(1 : 10^4)$.

The sensitivity is not reduced by the ions of the following elements : Hg, Pb, Cd, Sb, Sn, Se, Mo, V and Tl in a proportion of 100 : 1. The ions of bismuth and tungsten in the same proportion reduce it to $10^{-3.48}$ $(1 : 3 \cdot 10^3)$. For the ions of Ag, Cu, Au, Pt and Te in a proportion of 100 : 1 the limit of dilution is 10^{-3} $(1 : 10^3)$. Lastly, the ions of Ag, Cu, Bi, Au, Pt, Te and W, if in a proportion equal to the one for arsenic, do not affect the sensitivity.

REAGENTS.

1. Aluminium cuttings.
2. Potassium hydroxide 2 N.
3. Saturated solution of lead acetate in water.
4. Solution of mercury (II) chloride, 3 %, in water.

C. As^{+5}, NR.

IRON (II) MOLYBDATE, (FERROUS MOLYBDATE) $FeMoO_4$

BIBLIOGRAPHY : 121.

MECHANISM OF REACTION.

Reduction by the Fe^{+2} cation of the molybdic anion in a heteropolyacid state (arsenomolybdic acid) to lower oxides (" molybdenum blue"). The simple molybdic anion, MoO_4^{-2}, cannot be reduced.

J. H. VAN DER MEULEN (121).

DETAILS OF TEST.

In a macro test tube.

Place in a macro test tube : 5 ml of the reagent solution, 5 to 10 drops of a sodium fluoride solution and one drop of the solution to be analysed. After a few minutes a dark blue colour is produced in the presence of arsenic. As often happens, the solution is slightly blue in colour, even in the absence of arsenic, and therefore it is advisable to carry out a blank test.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The sensitivity is not reduced by the ions of the following elements : Hg, Cu, Pb, Cd, Sb and Sn in a proportion of 100 : 1. In the same proportion the Ag^{+1} cation reduces it to 10^{-4} (1 : 10^4).

Gold gives a dark blue and tungsten a greenish blue colour.

The ions of Bi, Gl, Tl and Sc give a pale blue colour; those of palladium, platinum and vanadium produce yellow and brown colour which interfere. The ions of selenium and tellurium reduce the sensitivity : selenium in a proportion of 100 : 1 brings it back to $10^{-3.70}$ (1 : $5 \cdot 10^3$), tellurium in a proportion of 10 : 1 decreases it to 10^{-3} (1 : 10^3).

Addition of fluoride develops the blue colouration and prevents the SiO_3^{-2} ion from giving an analogous reaction. The PO_4^{-3} anion gives the same reaction.

REAGENT.

1. Dissolve 0.484 g sodium molybdate ($Na_2MoO_4 . 2 H_2O$) in 90 ml water, add 4 ml of a solution of 2.78 g ferrous sulphate ($FeSO_4 . 7 H_2O$) in 100 ml sulphuric acid N. The solution is at first brownish red. When it is discoloured, the solution is diluted to 100 ml with distilled water.

2. Saturated solution of sodium fluoride in water.

8. ANTIMONY

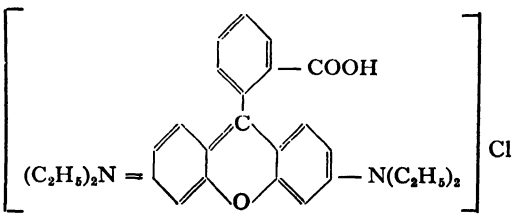
BY

C. J. VAN NIEUWENBURG

AN 51 AW 121.76

A. Sb^{+3}, 20.

3 : 6-BIS-DIETHYLAMINO-9-(2'-CARBOXYPHENYL)-XANTHONIUM CHLORIDE, *rhodamine B, tetraethylrhodamine*



BIBLIOGRAPHY : 122-128.

DETAILS OF TEST.

The constitution of the precipitate is not exactly known yet, but it is probably an oxidation product of rhodamine B.

F. FEIGL (125).

DETAILS OF TEST.

On a spot plate.

Place a drop of the solution to be examined on the plate. Add hydrochloric acid until its concentration is finally about 15 %.

Oxidize the antimony to the pentavalent state with a little potassium nitrite. Then remove the excess of nitrous acid by means of a red hot platinum wire, which is repeatedly immersed in the solution. Add a micro drop of the solution thus obtained to a drop of the reagent. The colour of the latter changes from red to purple blue.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The sensitivity is not reduced by the ions of the following elements : Cu, Pb, Bi, Cd, As, Sn, Pt, Se, Te and Tl, in a proportion of 100 : 1. The ions of Hg, Au, Mo, W and V give an analogous reaction. The Fe^{+3} cation, in large proportions, interferes because of its yellow colour.

REAGENTS.

1. Solid potassium nitrite.
2. Solution of rhodamine B, 0.05 %, in a solution of 15 % potassium chloride in hydrochloric acid 2 N.

B. Sb^{+3}, 29.

HEPTAHYDROGEN HEXADIMOLYBDATOPHOSPHORIC ACID, DODECAMOLYBDOPHOSPHORIC ACID DIHYDRATE, PHOSPHOMOLYBDIC ACID $H_7[P(Mo_2O_7)_6]$

BIBLIOGRAPHY : 129-133.

MECHANISM OF REACTION.

Simple molybdic acid does not react with antimony (Sb^{+3}); but in the complex phosphomolybdic state, it is reduced on heating to the blue oxide of molybdenum, with a general formula : Mo_2O_5.

F. FEIGL (131).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube : 1 ml of the solution to be analysed, (antimony in a trivalent state) and 0.5 to 1 ml of the reagent. Heat a little. The reagent is reduced to a blue compound which can be extracted by means of amyl alcohol.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5) (clear).

At $10^{-5.70}$ (1 : $5 \cdot 10^5$) the reaction is weak. This limit is achieved with a fresh reagent. After a week it is reduced to 10^{-3} (1 : 10^3).

The sensitivity is not reduced by the ions of the following elements : Ag, Hg, Pb, Bi, Cd, As, Sn (Sn^{+4}), Pd and Pt, in a proportion of 100 : 1. The ions of Au, Se, Te, Mo, W and Tl, in a proportion of 100 : 1, reduce the sensitivity to about 10^{-4} (1 : 10^4). Copper in high concentrations interferes, as well as vanadium, which gives a yellow precipitate. Strong reducing agents, especially the Sn^{+2} and Fe^{+2} cations, give the same reaction.

REAGENTS.

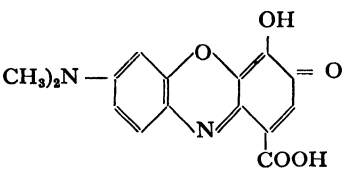
1. Solution of phosphomolybdic acid (5 %) in water. The solution will not keep.
2. Amyl alcohol.

PREPARATION OF REAGENT.

Solve ammonium phosphomolybdate in aqua regia; evaporate until dry; dissolve again and recrystallize twice in water.

C. Sb^{+3}, Sb^{+5}, NR.

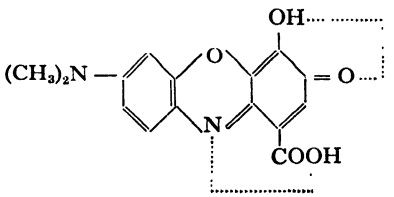
1-HYDROXY-2-OXY-4-CARBOXY-7-DIMETHYLAMINO-OXAZINE
(gallocyanine)



BIBLIOGRAPHY : 134-136.

MECHANISM OF REACTION.

The constitution of the antimony-gallocyanine compound is not yet known; the following diagram shows the two possibilities between which a choice will most likely be made :



J. V. DUBSKY (135).

DETAILS OF TEST.

On a drop plate.

Add 1 or 2 drops of the reagent to a few drops of the solution to be analysed, containing the minimum quantity of acid that is required to keep the antimony in solution. The wine-red colour of the reagent changes to blue. In a very concentrated solution a blue precipitate is produced. The same reaction is given by antimony in both states of oxidation.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The sensitivity is not reduced by the ions of the following elements : Ag, Hg, Cu, Pb, Bi, Cd, As, Sn, Pt, Se, Te and Tl, in a proportion of 100 : 1. The Hg^{+1} cation causes the formation of mercury, which adsorbs a little of the reagent, without interfering with the reaction. The ions of the following elements give the same reaction : Mo, W, Fe, Zr, Th, Sc and Ga. To observe the change of colour, one must have some experience.

REAGENT.

1. Solution of gallocyanine, 0.05 %, in hydrochloric acid N.

9. TIN

BY

C. J. VAN NIEUWENBURG

AN 50 **AW 118.70**

A. Sn^{+2}, NR.

ZINC + HYDROCHLORIC ACID Zn + HCl

BIBLIOGRAPHY : 137-141.

MECHANISM OF REACTION.

According to E. SCHRÖER and A. BALANDIN (138) the equation of the reaction that causes fluorescence is as follows :

$$2\ SnCl_3 \rightarrow SnCl_2 + SnCl_4.$$

See also F. L. HAHN (140).

DETAILS OF TEST.

In a porcelain crucible.

Place 5 drops of the solution to be examined in a porcelain crucible, then about 5 ml concentrated hydrochloric acid and a small piece of zinc. Dip a micro test tube filled with cold water in the solution and then put it in the reducing zone of the flame from a Bunsen burner. In the presence of tin, a blue luminescence is produced on the test tube.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.70}$ $(1 : 5 \cdot 10^3)$.

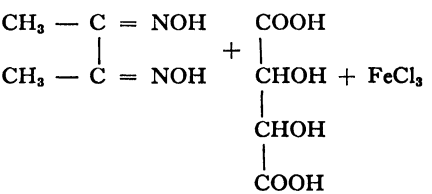
Niobium gives an analogous reaction; gold gives a green luminescence which does not interfere badly with the reaction of tin. The limit of dilution is not reduced by the ions of the following elements : Ag, Hg(Hg^{+1}), Pb, Bi, Cd, Sb, Au, Pt, Se, Te and Tl, in a proportion of 100 : 1. The sensitivity remains the same in the presence of the Hg^{+2} cation and also in the presence of ions of the following elements : Cu, As, Mo, W and V in a proportion of 10 : 1. In a proportion of 100 : 1 they reduce the dilution limit to $10^{-3.30}$ $(1 : 2 \cdot 10^3)$. The reaction is selective, but not very sensitive.

REAGENTS.

1. Granules of zinc.
2. Hydrochloric acid 10 N.

B. Sn^{+2}, Sn^{+4}, 16.

2 : 3-BUTANE DIOXIME, DIMETHYLGLYOXIME + TARTARIC ACID + IRON (III) CHLORIDE (FERRIC CHLORIDE)



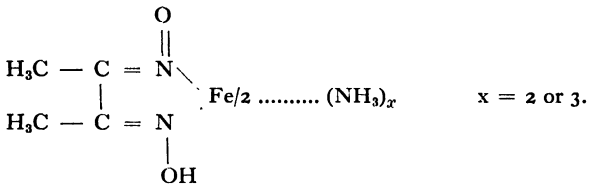
BIBLIOGRAPHY : 142-144.

MECHANISM OF REACTION.

Reduction of the Fe^{+3} cation to the state of a bivalent cation :

$$2\ Fe^{+3} + Sn^{+2} \rightarrow 2\ Fe^{+2} + Sn^{+4}$$

permitting the latter to react with dimethylglyoxime and ammonia, giving the following compound :



F. FEIGL (142-143).

DETAILS OF TEST.

In a micro test tube.

If tin is in the tetravalent state, it is reduced to the bivalent state with some aluminium filings and hydrochloric acid. Filter the aluminium and transfer the solution to a micro test tube. Add about 0.5 ml of a iron (III) chloride solution. If necessary, the solution is acidified (hydrochloric acid 2 N). Add also 0.5 to 1 ml of a tartaric acid solution, 5 drops of a dimethylglyoxime solution and about 1 ml ammonia. A red colour is produced due to the formation of the compound of iron (II) with dimethylglyoxime.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

The sensitivity is not reduced by the ions of the following elements : Hg, Pb, Cd, As, Sb and Tl, in a proportion of 100 : 1. Bismuth in the same proportion reduces the dilution limit to 10^{-4} (1 : 10^4). The ions of vanadium, the UO_2^{+2} cation, the ions of titanium, cobalt and nickel give an analogous reaction. The salts of iron (II) and reducing agents which affect iron (III) chloride must be absent. The cations of chromium, manganese and scandium interfere with the reaction. The ions of gold, palladium, platinum, selenium and tellurium interfere also, as they form colloidal solutions and very fine suspensions. The copper cation, the molybdic anions and

tungsten anions give a blue colour, which makes identification difficult. Gold can be removed by treating the hot solution with aluminium in an acid solution (hydrochloric acid 2 N) for 5 minutes; the metallic gold and the excess of aluminium can be separated by filtration before the test.

REAGENTS.

1. Metallic aluminium filings.
2. Hydrochloric acid 2 N.
3. Solution of iron (III) chloride (ferric chloride) 0.1 N.
4. Solution of tartaric acid, 5 %, in water.
5. Solution of dimethylglyoxime, 1 %, in ethyl alcohol.
6. Ammonia 4 N.

C. Sn^{+2}, 29.

CACOTHELINE $C_{21}H_{21}(OH)_2(NO_2)N_2O_3 . HNO_3$

BIBLIOGRAPHY : 145-152.

MECHANISM OF REACTION.

Redox system in which cacotheline takes the part of redox indicator. The purple colouration corresponds with the reduced form of cacotheline.

F. FEIGL (146).

DETAILS OF TEST.

In a micro test tube.

The acid solution (hydrochloric acid 2 N) must be previously reduced with some aluminium filings, so that the tin is in a bivalent state. Filter and heat a little afterwards with a few drops of the reagent. A purplish colour is produced.

SENSITIVITY AND SELECTIVITY : $D = 10^{-4}$ (1 : 10^4).

At a dilution of 10^{-5} (1 : 10^5) the reaction is doubtful. As the reaction is not specific for the Sn^{+2} cation, because it is due to the reduction of cacotheline, it is obvious that strong reducing agents must be absent, sulphuretted hydrogen for one. However, because

the salts of iron (II) do not reduce the reagent, it is possible to use iron in order to change tin (IV) to the bivalent state, without it being necessary to filter the solution. In the presence of phosphorus and hydrofluoric anions which increase the reducing potentiality of the Fe^{+2} cation through the formation of compounds, the salts of iron (II) interfere the test. The dilution limit is not changed by the cations of silver, lead and cadmium in a proportion of 100 : 1. In the same degree of concentration this limit is reduced to $10^{-3.30}$ ($1 : 2 \cdot 10^3$) by copper, arsenic and thallium. The ions of these metals have no appreciable influence in a 10 : 1 proportion. The ions of the following metals give an analogous reaction, viz. V, Nb, Ta, U and Ti. Those of Hg, Bi, Au, Pd, Pt, Se, Te, Mo, W, Co, Ni and a large proportion of zinc and manganese interfere either by their reducing action or their colour. Gold can be removed by treating the hot acid solution (hydrochloric acid 2 N) with aluminium for five minutes and by separating metallic gold and aluminium by filtration.

The reaction is not selective, but fairly sensitive and it is recommended for a normal analysis in which tin will only be accompanied by arsenic, antimony and more or less rare elements of this group.

REAGENTS.

1. Aluminium filings.
2. Hydrochloric acid 2 N.
3. Solution of cacotheline, 0.25 %, in water.

10. GOLD

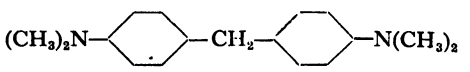
BY

C. J. VAN NIEUWENBURG

AN 79 **AW 197.2**

A. Au^{+3}, 16.

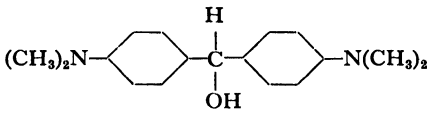
BIS-(*p*-DIMETHYLAMINOPHENYL)METHANE, *p*-TETRAMETHYLDIAMINO-DIPHENYLMETHANE



BIBLIOGRAPHY : 153-154.

MECHANISM OF REACTION.

Oxidation of the amine by the Au^{+3} cation with formation of the corresponding carbinol, which is blue :



A. TRILLAT (154).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube : 1 ml of the solution to be analysed, which must be very slightly acid (hydrochloric acid), and add a drop of the reagent. A blue colour is produced and, in the diluted solutions, only after a few minutes. Since the reaction is interfered with by concentrated acids, it is advisable to neutralise the latter by sodium hydroxide.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ ($1 : 10^6$).

The sensitivity is not changed by the ions of the following elements : Ag, Cu, Pb, Bi, Cd, As, Sb, Sn, Pt, Se, Te, Mo, W and Tl, in a proportion of 100 : 1. Vanadium in a 10 : 1 proportion reduces it to about 10^{-5} ($1 : 10^5$). In a 100 : 1 proportion this element interferes (yellow colouration).

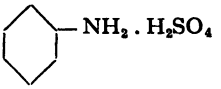
The plumbates [Pb (IV)] give an analogous reaction as well as a large number of other strong oxidizing agents. The Cu^{+2} and Cr^{+3} cations, in large proportions, interfere because of their colour. In a concentration lower than 10^{-3} ($1 : 10^3$) they no longer interfere. In doubtful cases it is advisable to compare the colour obtained with that of a blank test.

The reaction is not selective, but very sensitive.

REAGENTS.

1. Solution, 0.5 %, of *p*-tetramethyldiaminodiphenylmethane in ethyl alcohol, 5 % acetic acid.
2. Solid sodium hydroxide.

B. Au^{+3}, 55.



ANILINE SULPHATE

BIBLIOGRAPHY : 155.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube : 1 ml of the solution to be analysed, which is slightly acid (hydrochloric acid) and has been previously heated to boiling point, and 0.5 to 1 ml of reagent.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

The colour obtained depends on the quantity of gold that is present. With 10^{-3} to 10^{-4} concentrations ($1 : 10^3$ to $1 : 10^4$) a dark blue colour is produced first, after a few minutes heating, which soon changes to green. Immediately after that, a green flocculent precipitate is formed. After sedimentation the solution is lilac-coloured. In a $10^{-4.70}$ solution ($1 : 5 \cdot 10^4$) a precipitate is no longer formed; the solution shows a colour varying from greenish blue to purple. In a 10^{-5} ($1 : 10^5$) solution a vague bluish colour can still be observed.

The vanadium and chromium anions and the Fe^{+3} cation give an analogous reaction. The nitrous anion produces an orange colour which interferes with the reaction. In the presence of strongly coloured ions, it is advisable to make a blank test.

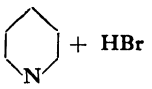
The sensitivity is not reduced by the ions of the following elements : Ag, Cu, Pb, Bi, Cd, Se, Te, Mo, W and Tl, in a proportion of 100 : 1, nor by arsenic, antimony, tin and platinum in a 10 : 1 proportion. The latter elements, when in a 100 : 1 proportion, reduce the dilution limit to 10^{-4} ($1 : 10^4$).

REAGENT.

1. Saturated solution of aniline in sulphuric acid, N to 0.5 N

C. Au^{+3}, 5.

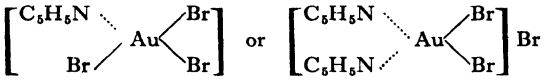
PYRIDINE
+ HYDROBROMIC ACID (PHOTO 4)



BIBLIOGRAPHY : 156-159.

MECHANISM OF REACTION.

In all probability one of the following two compounds is formed :



Ch. St. GIBSON and W. M. COLLES (159),
P. E. WENGER and R. DUCKERT.

DETAILS OF TEST.

Under the microscope.

Place on a slide : 2 drops of the solution to be analysed (slightly acid : HCl) and 1 drop of the reagent. A brownish red precipitate is produced consisting of crystals in the shape of little sticks, which are often crossed or fixed together at an angle of 60°.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.48}$ to $10^{-4.70}$ ($1 : 3 \cdot 10^4$ to $1 : 5 \cdot 10^4$).

The sensitivity is not decreased by the ions of the following elements : Hg(Hg^{+2}), Cu, Bi, Cd, Sn, Pt, Se, Te, Mo and V, in a proportion of 100 : 1. Platinum gives yellow crystals of a different shape and does not interfere. Silver, mercury (I), lead and thallium interfere, as well as a large quantity (100 : 1) of arsenic, antimony or tungsten. These elements, in a 10 : 1 proportion, reduce the limit of dilution to $10^{-4.47}$ ($1 : 3 \cdot 10^4$).

REAGENT.

1. 1 part of pyridine + 8 parts of hydrobromic acid 5 N.

11. RUTHENIUM

BY

C. J. VAN NIEUWENBURG

AN 44 AW 101.7

A. Ru^{+3}, 11.

THIOCARBAMIDE (THIOUREA)

BIBLIOGRAPHY : 160-163.

MECHANISM OF REACTION.

Not yet known, although it has been studied for other elements of this group, for instance osmium.

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube : one drop of concentrated hydrochloric acid, one drop of the acid solution to be analysed (hydrochloric acid) and some thiourea crystals. After moderate heating, the solution takes a blue colour.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

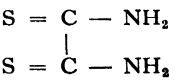
The osmium ions give a red colour. Those of the other elements of the platinum group do not interfere.

REAGENTS.

1. Hydrochloric acid 10 N.
2. Solid thiourea.

B. Ru^{+3}, 13.

1 : 2-ETHANEDITHIAMIDE, DITHIOXAMIDE *(rubeanic acid)*



BIBLIOGRAPHY : 164-165.

MECHANISM OF REACTION.

It is not yet possible to define the product that is formed in the course of the reaction.

DETAILS OF TEST.

In a micro crucible.

Place in a micro crucible a drop of the solution to be analysed (ruthenium in a trivalent state), a drop of diluted hydrochloric acid and a drop of the reagent solution. After heating it over a micro burner, a blue colour is observed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ $(1 : 10^5)$.

The ions of gold, palladium and platinum give a dark precipitate, which is removed by centrifuging. The ions of the other elements of the platinum group do not interfere. The ions of copper, cobalt and nickel interfere.

REAGENTS.

1. Hydrochloric acid 2 N.
2. Solution of rubeanic acid, 2 %, in glacial acetic acid.

12. RHODIUM

BY

C. J. VAN NIEUWENBURG

AN 45 **AW 102.91**

A. Rh^{+3}, 14.

TIN (II) CHLORIDE (STANNOUSCHLORIDE) $SnCl_2$

BIBLIOGRAPHY : 166-169.

MECHANISME OF REACTION.

Reduction of rhodium salts to colloidal metallic rhodium.

V. N. IVANOV (166).

DETAILS OF TEST.

In a micro test tube.

Add to the solution to be analysed an equal volume of the reagent solution. After heating, a brown colour is produced, which changes to red when cooled down.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

Gold and palladium give dark precipitates, which unfortunately cannot easily be avoided. Platinum gives an analogous colour; ruthenium, osmium and iridium also give a reaction.

At the moment we have no selective and sensitive rhodium reaction.

REAGENT.

1. Solution of stannous chloride, 40 %, in hydrochloric acid 8 N.

13. PALLADIUM

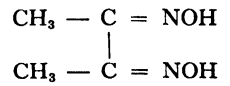
BY

C. J. VAN NIEUWENBURG

AN 46 **AW 106.7**

A. Pd^{+2}, 21.

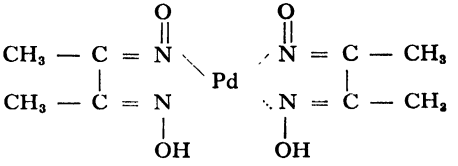
2 : 3-BUTANE DIOXIME, DIMETHYLGLYOXIME (PHOTO 5)



BIBLIOGRAPHY : 170-175.

MECHANISM OF REACTION.

A complex is formed with two oxime molecules, which probably has a structure analogous to that of the nickel complex.



M. WUNDER and V. THÜRINGER (171).

DETAILS OF TEST.

Under the microscope.

Place on a slide a crystal of the reagent in a drop of the slightly acid solution to be analysed. After some minutes, a precipitate is formed of long, yellow very characteristic needles.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

Excellent reaction. The ions of other metals of the platinum group do not interfere. Gold and nickel give a similar reaction.

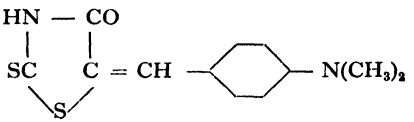
REAGENT.

1. Solid dimethylglyoxime.

B. Pd^{+2}, 22.

4-(*p*-DIMETHYLAMINOPHENYLMETHYLENE) 2-THIONE-5-THIAZOLIDONE, 5-(4'-DIMETHYLAMINO)BENZALRHODANINE

(p-dimethylaminobenzylidenerhodanine)



BIBLIOGRAPHY : 176-180.

MECHANISM OF REACTION.

Precipitation, probably, of a reaction product of palladium chloride and the organic molecule.

E. RAJMANN (176).

DETAILS OF TEST.

On filter paper.

Place a drop of the solution to be analysed on a filter paper that is soaked in the reagent. Buffer with sodium acetate. A purple stain is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

Gold interferes; platinum gives a similar stain, but only after a few minutes. Iridium gives a light blue colour, which does not interfere. The Hg^{+2} and Ag^{+1} cations give a red colour.

REAGENT.

1. Reagent paper : soak a filter paper with a saturated solution of *p*-dimethylaminobenzylidenerhodanine in ethyl alcohol. Leave it to dry in air.

C. Pd^{+2}, 3.

MERCURY (I) CHLORIDE (MERCUROUS CHLORIDE) Hg_2Cl_2

BIBLIOGRAPHY : 181.

MECHANISM OF REACTION.

Reduction of palladium ions to the state of metallic palladium :

$$PdCl_2 + Hg_2Cl_2 \rightarrow Pd + 2\ HgCl_2$$

G. G. PIERSON (181).

DETAILS OF TEST.

In a micro test tube.

Shake the slightly acid solution to be analysed with solid mercurous chloride. The latter turns grey. Not to be heated.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

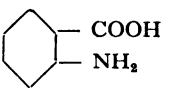
Gold gives a similar reaction. The other metals of the platinum group do not interfere.

REAGENT.

1. Solid mercurous chloride.

D. Pd^{+2}, NR.

o-AMINOBENZOIC ACID
(anthranilic acid)



BIBLIOGRAPHY : 182.

MECHANISM OF REACTION.

The structure of the compound formed is not yet known.

DETAILS OF TEST.

In a micro test tube.

Add a drop of the reagent solution to the slightly acid solution to be analysed (buffer with sodium acetate, if necessary). After some minutes a light yellow precipitate is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

Gold interferes giving a similar precipitate; the other metals of the platinum group do not interfere.

REAGENT.

1. Solution of anthranilic acid, 5 %, in water.

14. OSMIUM

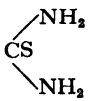
BY

C. J. VAN NIEUWENBURG

AN 76 AW 190.2

A. Os^{+4}, Os^{+8}, 23.

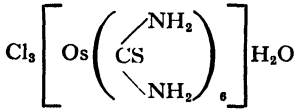
THIOCARBAMIDE (THIOUREA)



BIBLIOGRAPHY : 183-184.

MECHANISM OF REACTION.

A red compound is formed of the following formula :



L. TSCHUGAEFF (183).

DETAILS OF TEST.

In a micro test tube.

Place some reagent crystals in the hydrochlorous solution, 5 %, to be analysed. After heating, a red colour is produced. The reaction is selective.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

Osmium (IV) gives the same reaction. Ruthenium gives a blue colour which does not interfere. The ions of the other metals of the platinum group do not interfere.

REAGENT.

1. Solid thiourea.

B. Os^{+8}, 18.

POTASSIUM THIOCYANATE KCNS

BIBLIOGRAPHY : 185.

MECHANISM OF REACTION.

Has not been studied.

DETAILS OF TEST.

In a micro test tube.

Place a few potassium or ammonium thiocyanate crystals in the slightly acid (nitric acid) solution to be analysed. Extract with ether or with amyl alcohol. These solvents turn blue.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

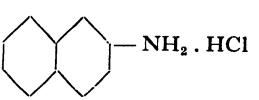
Osmium (IV) does not give this reaction. The other metals of the platinum group do not interfere.

REAGENTS.

1. Solid potassium thiocyanate or ammonium thiocyanate.
2. Ether or amyl alcohol.

C. Os^{+4}, Os^{+6}, 28.

β-NAPHTHYLAMINEHYDROCHLORIDE



BIBLIOGRAPHY : 186.

MECHANISM OF REACTION.

The formula of the compound created has not been worked out yet.

DETAILS OF TEST.

In a micro test tube.

Add the solid reagent to the slightly acid solution to be analysed.

Heat if necessary. A dark blue colour is produced (and a black precipitate in the event of a large percentage of cations).

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

Gold, iridium and platinum in large proportions will interfere. Osmium (VIII) only gives the reaction after a few minutes.

REAGENT.

1. β-Naphthylamine hydrochloride, solid or in a saturated aqueous solution.

15. IRIDIUM

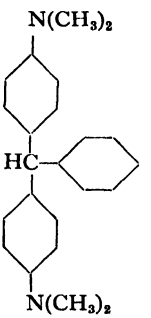
BY

C. J. VAN NIEUWENBURG

AN 77 **AW 193.1**

A. Ir^{+4}, 15.

BIS-(*p*-DIMETHYLAMINO-PHENYL)-PHENYLMETHANE
(leucobase of malachite green)



BIBLIOGRAPHY : 187.

MECHANISM OF REACTION.

The leucobase is oxidized by the $[IrCl_6]^{-2}$ anion and supplies the colouring agent, according to the following schedule :

$$2\,H_2[IrCl]_6 + [(CH_3)_2N - C_6H_4]_2 = CH - C_6H_5 + H_2O \rightleftarrows$$

$$2\,H_3[IrCl]_6 + [(CH_3)_2N - C_6H_4]_2 = COH - C_6H_5.$$

P. E. WENGER and R. DUCKERT.

DETAILS OF TEST.

In a micro test tube.

Add some drops of the reagent to the solution to be analysed. A green colour is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

An excess of ruthenium interferes; gold gives the same reaction. Oxidizing agents should not be present as they react in the same manner.

REAGENT.

1. Solution of the leucobase of malachite green, 1 %, in acetic acid 2 N.

B. Ir^{+4}, NR.

SULPHURIC ACID + NITRIC ACID (or SILVER NITRATE, or AMMONIUM NITRATE)

H_2SO_4 + HNO_3 or $AgNO_3$ or NH_4NO_3

BIBLIOGRAPHY : 188-190.

MECHANISM OF REACTION.

It seems probable that the blue colour can be attributed to the formation of a hydrated iridium oxide $IrO_2 . n H_2O$, which is rendered soluble by strong acids.

P. E. WENGER and R. DUCKERT, LECOQ DE BOISBAUDRAN (188) and L. WÖHLER and L. WITZMANN (189).

DETAILS OF TEST.

In a micro test tube or in a micro crucible.

Heat a drop of the solution to be analysed with an excess of concentrated sulphuric acid (2 to 3 drops) to eliminate the hydrochloric acid. Add either a drop of concentrated nitric acid, or some silver nitrate crystals, or some ammonium nitrate. On reheating, a blue colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.90}$ (1 : $8 \cdot 10^3$).

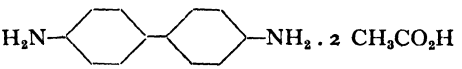
An excess of ruthenium, rhodium or palladium interferes. We prefer the use of silver nitrate or ammonium nitrate to that of nitric acid.

REAGENTS.

1. Sulphuric acid 7.5 N.
2. Nitric acid ($d = 1.52$), or
3. Solid silver nitrate or solid ammonium nitrate.

C. Ir^{+4}, 7.

BENZIDINE ACETATE

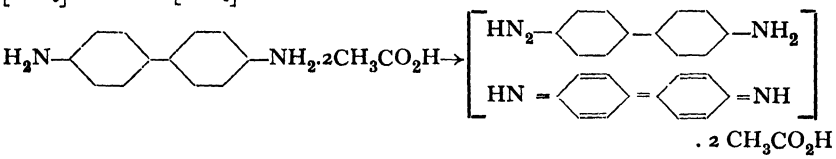


BIBLIOGRAPHY : 191.

MECHANISM OF REACTION.

It is probably an oxidation-reduction reaction :

$[IrCl_6]^{-2} \longrightarrow [IrCl_6]^{-3}$ and



P. E. WENGER AND R. DUCKERT.

DETAILS OF TEST.

On filter paper.

Place on a filter paper : a drop of the solution to be analysed and a drop of the reagent. A blue stain is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.70}$ $(1 : 5 \cdot 10^3)$.

Gold, ruthenium and osmium (Os^{+8}) give a similar reaction.

REAGENT.

1. Saturated solution of benzidine in glacial acetic acid.

16. PLATINUM

BY

C. J. VAN NIEUWENBURG

AN 78 AW 195.23

A. Pt^{+4}, 3.

POTASSIUM CHLORIDE (PHOTO 6) KCl

BIBLIOGRAPHY : 192-193.

MECHANISM OF REACTION.

Precipitation of dipotassium hexachloroplatinate (IV) :

$$K_2[PtCl_6]$$

DETAILS OF TEST.

Under the microscope.

Place on a slide some potassium chloride crystals in a drop of the acid (HCl) solution to be analysed. Heat if necessary until crystallization begins and some yellow octahedra of potassium hexachloroplatinate (IV) are formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

Osmium gives a similar reaction, iridium gives red octahedra. However, the platinum reaction is good as a preliminary test.

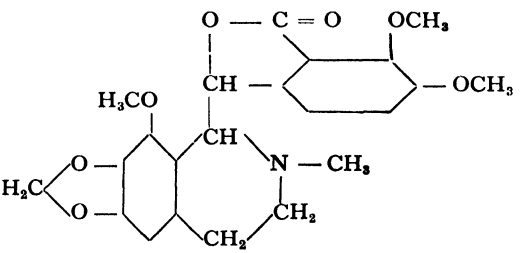
REAGENT.

1. Solid potassium chloride.

B. Pt^{+4}, NR. 1.

NARCOTINE + TIN (II) CHLORIDE, STANNOUS CHLORIDE + IRON (II) SULPHATE, FERROUS SULPHATE

$C_{22}H_{23}NO_7$ or



+ $SnCl_2$ + $FeSO_4$

BIBLIOGRAPHY : 194.

MECHANISM OF REACTION.

Is not yet known.

DETAILS OF TESTS.

On filter paper.

Place on a filter paper a drop of the solution to be analysed and a drop of the reagent. A yellow colour is produced. Excellent reaction.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

A large proportion of gold and also of palladium will interfere.

REAGENT.

1. Mixture of the following three solutions, in equal volumes :

a. Solution of narcotine, 1 %, in sulphuric acid 10 N.

b. Solution (suspension) of stannous chloride, 10 %, in water.

c. Solution of ferrous sulphate, 10 %, in water.

C. Pt^{+4}, 7.

SODIUM IODIDE + AMMONIUM HYDROXIDE (PHOTO 7) $NaI + NH_4OH$

BIBLIOGRAPHY : 195.

MECHANISM OF REACTION.

A complex of the following type is formed :

$$Me_2[PtX_6] \cdot nH_2O$$

Here X may represent the Cl^{-1} and I^{-1} anions and Me the Na^{+1} and NH_4^{+1} cations. It is doubtful whether the constitution of the complex is as simple as stated above.

P. E. WENGER and R. DUCKERT.

DETAILS OF TESTS.

Under the microscope.

Add ammonia to the solution to be analysed until it reacts slightly alkaline, then sodium iodide crystals. Dark red needles are formed, generally united in bundles.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

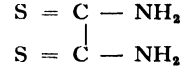
A large proportion of ruthenium and of palladium will interfere. Excellent reaction.

REAGENTS.

1. Solid sodium iodide.
2. Ammonia, 1 %.

D. Pt^{+4}, 14.

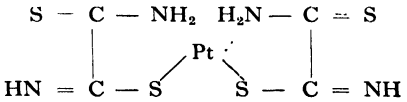
1 : 2-ETHANEDITHIAMIDE, DITHIOXAMIDE *(rubeanic acid)*



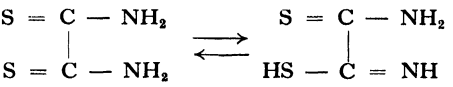
BIBLIOGRAPHY : 196-197.

MECHANISM OF REACTION.

The precipitate is formed by a complex of the following formula :



resulting from a hemi-acid form of the dithioxamide



H. WÖLBLING and B. STEIGER (196), F. FEIGL (197).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the acid (HCl) solution to be analysed and a drop of the reagent. A purplish red precipitate is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

Palladium and a large proportion of gold or of ruthenium will interfere.

REAGENT.

1. Solution of rubeanic acid, 0.02 %, in glacial acetic acid.

17. SELENIUM

BY

J. GILLIS

AN 34 **AW 78.96**

A. Se^{+4}, Se^{+6}, 13.

SULPHUR DIOXIDE *(gaseous)* **or** SO_2 or $Na_2S_2O_5$
SODIUM METABISULPHITE *(solid)*

BIBLIOGRAPHY : 198-200.

MECHANISM OF REACTION.

Reduction of the SeO_3^{-2} and SeO_4^{-2} anions to the state of red elementary selenium according to the following equations :

$$SeO_3^{-2} + 2\ SO_3^{-2} + 2\ H^{+1} \longrightarrow Se + 2\ SO_4^{-2} + H_2O$$
$$SeO_4^{-2} + 3\ SO_3^{-2} + 2\ H^{+1} \longrightarrow Se + 3\ SO_4^{-2} + H_2O$$

P. E. WENGER and R. DUCKERT.

DETAILS OF TEST.

In a micro test tube.

a. With gaseous sulphur dioxide.

Add 1 ml concentrated sulphuric acid 35 N to 1 ml of the solution to be analysed; saturate it by a current of sulphur dioxide, heat it to boiling point for 1 minute and then leave it to cool down.

b. With sodium hydrogen sulphite.

Bring in the test tube successively 1 ml of the solution to be analysed, some crystals of sodium hydrogen sulphite and 1 ml of concentrated sulphuric acid. Heat to boiling point for 1 minute and leave it to cool down.

The red colour which is due to elementary selenium, appears more or less quickly according to the concentration of selenium and the temperature.

SENSITIVITY AND SELECTIVITY. *a.* $D = 10^{-5.18}$ ($1 : 1.5 \cdot 10^5$) for the selenious anion and 10^{-5} ($1 : 10^5$) for the selenic anion; *b.* $D = 10^{-5.3}$ ($1 : 2 \cdot 10^5$) for the selenious anion and $10^{-4.7}$ ($1 : 5 \cdot 10^4$) for the selenic anion.

The following ions do not interfere in the same conditions : As^{+3}, Sn^{+4}, Ge^{+4}, TeO_3^{-2}, and TeO_4^{-2}. The Sn^{+2} cation interferes.

a. The Sb^{+3} cation increases the sensitivity from $10^{-5.18}$ to $10^{-5.60}$ ($1 : 1.5 \cdot 10^5$ to $1 : 4 \cdot 10^5$), whereas molybdenum (VI) decreases the sensitivity and reduces it from $10^{-5.18}$ to $10^{-4.30}$ ($1 : 1.5 \cdot 10^5$ to $1 : 2 \cdot 10^4$).

b. The Sb^{+3} cation and molybdenum (VI) in a proportion of 100 : 1 Se do not interfere.

REAGENTS.

1. Sulphuric acid 35 N.

2*a*. Gaseous sulphur dioxide (sodium hydrogen sulphite + sulphuric acid 35 N) or

2*b*. Solid sodium metabisulphite.

B. Se^{+4}, 18.

HYDRIODIC ACID HI

BIBLIOGRAPHY : 201-206.

MECHANISM OF REACTION.

Reduction of the selenious anion to the state of red elementary selenium, according to the equation :

$$SeO_3^{-2} + 4\,I^{-1} + 6\,H^{+1} \rightarrow Se + 2\,I_2 + 3\,H_2O$$

J. MEYER and W. VON GARN (202).

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of a concentrated solution of hydriodic acid (or of a solution of potassium iodide and concentrated hydrochloric acid) and a drop of the acid (HCl) solution to be analysed. A brownish black stain is produced : if this stain disappears when a drop of a sodium thiosulphate solution is added, no selenium is present; if on the contrary the stain remains, then selenium is present.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.40}$ ($1 : 2.5 \cdot 10^4$).

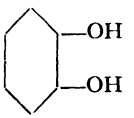
An excess of tellurium (IV) reduces the sensitivity to $10^{-4.066}$ ($1 : 1.25 \cdot 10^4$). All oxidizing agents must be previously eliminated. The As^{+3} and Ge^{+4} cations, in a 100 : 1 proportion, prevent the reaction. The Sb^{+3} and Sn^{+4} ions do not interfere. Molybdenum (VI) interferes, because it gives a similar reaction to that of selenium.

REAGENTS.

1. Hydriodic acid, 46 % (d = 1.50).
2. Solution of potassium iodide, 100 %, in water.
3. Hydrochloric acid 10 N.
4. Solution of sodium thiosulphate, 5 %, in water.

C. Se^{+4}, 37.

1 : 2-DIHYDROXYBENZENE, PYROCATECHOL



BIBLIOGRAPHY : 207.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

On a spot plate.

Place the following in succession on the plate : some crystals of pyrocatechol, a drop of sulphuric acid 35 N and a drop of the solution to be analysed.

In the event of high selenium concentrations a blue colour appears immediately; for low concentrations the colour is green and it appears only after the bottom of the drop plate has been rubbed with a glass rod.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.30}$ ($1 : 2 \cdot 10^4$).

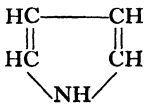
The TeO_3^{-2} anion gives, under the same conditions, a yellow colour, which does not interfere with the identification of selenium. The As^{+3}, Sb^{+3}, Sn^{+4}, Ge^{+4} ions and molybdenum (Mo^{+6}) do not interfere, whereas the Sn^{+2} ion disturbs the test.

REAGENTS.

1. Solid pyrocatechol.
2. Sulphuric acid 35 N.

D. Se^{+4}, 39.

PYRROLE
+ IRON (III) CHLORIDE, FERRIC CHLORIDE
+ PHOSPHORIC ACID



+ $FeCl_3$
+ H_3PO_4

BIBLIOGRAPHY : 208-209.

MECHANISM OF REACTION.

The structure of the colouring agent, called pyrrole blue, which is formed is not known.

DETAILS OF TEST.

On a spot plate.

Add to the solution to be examined a drop of a ferric chloride solution, 7 drops of phosphoric acid and 2 drops of an alcoholic solution of pyrrole. The bluish green colour, which appears after everything has been well mixed, indicates the presence of selenium(IV).

For low selenium concentrations a blank test is used.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.18}$ ($1 : 1.5 \cdot 10^5$).

The telluric anion does not influence the reaction, contrary to the tellurous anion and the silicomolybdic anion, which interfere. A 100 : 1 proportion of the As^{+3}, Sb^{+3}, Ge^{+4} and MoO_4^{-2} ions does not influence the reaction. The Sn^{+4} ion reduces the sensitivity, which is decreased from $10^{-5.18}$ ($1 : 1.5 \cdot 10^5$) to 10^{-5} ($1 : 10^5$).

REAGENTS.

1. Solution of ferric chloride, 5 %, in water.
2. Syrupy phosphoric acid ($d = 1.75$).
3. Solution of pyrrole, 1 %, in ethyl alcohol, 96 %, (without aldehyde).

E. Se^{+4}, NR.

AMMONIUM THIOCYANATE + HYDROCHLORIC ACID $NH_4CNS + HCl$

BIBLIOGRAPHY : 210.

MECHANISM OF REACTION.

The selenious anion is reduced by the thiocyanic anion to the state of red elementary selenium, according to the equations :

$$HCNS + 2\,H_2O + H^+ \longrightarrow NH_4^+ + CO_2 + H_2S$$
$$2\,H_2SeO_3 + HCNS \longrightarrow 2\,Se + CO_2 + SO_4^{-2} + H^+ + NH_4^+$$
$$H_2SeO_3 + 2\,H_2S \longrightarrow 2\,S + Se + 3\,H_2O$$

W. T. HALL (210).

DETAILS OF TEST.

In a macro test tube.

Boil for 30 seconds a mixture of 0.5 ml of the solution to be analysed, 2 ml of an ammonium thiocyanate solution, 5 ml hydrochloric acid and 2.5 ml water. The red colour, which is due to elementary selenium, indicates the presence of this element (compare with a blank test).

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

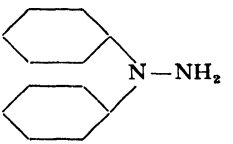
Tellurium (Te^{+4} and Te^{+6}) in a 750 : 1 proportion reduces the sensitivity to $10^{-4.60}$ ($1 : 4 \cdot 10^4$). The As^{+3}, Sb^{+3}, Sn^{+2} and Fe^{+2} cations and molybdenum (Mo^{+6}) interfere also. The Sn^{+4} and Ge^{+4} cations reduce the sensitivity to $10^{-4.60}$ ($1 : 4 \cdot 10^4$).

REAGENTS.

1. Saturated solution of ammonium thiocyanate in water.
2. Hydrochloric acid N.

F. Se^{+4}, NR 2.

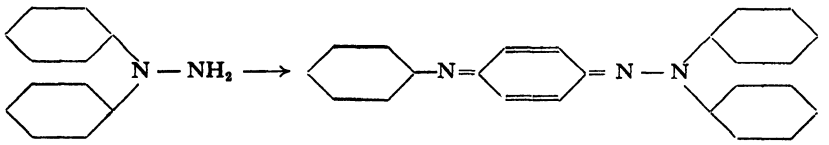
as-DIPHENYLHYDRAZINE



BIBLIOGRAPHY : 211-212.

MECHANISM OF REACTION.

The selenious anion oxidises diphenylhydrazine to a purple colouring agent, quinoneanil-diphenylhydrazone :



F. FEIGL and V. DEMANT (211).

DETAILS OF TEST.

On a spot plate.

Place on the plate 4 drops of the *as*-diphenylhydrazine solution, a drop of hydrochloric acid and a drop of the solution to be analysed. In the presence of selenium a colour is immediately produced, which is red and later on turns to purple. In the presence of small quantities of selenious anions the reaction only takes place after a certain length of time and it is advisable to make a blank test.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

All oxidizing agents interfere and must be previously eliminated. Tellurium (Te^{+4}) do not prevent the reaction. Arsenic (As^{+3}), germanium (Ge^{+4}) and molybdenum (Mo^{+6}) do not interfere in a 100:1 proportion. The Sb^{+3} and Sn^{+4} cations reduce the sensitivity.

REAGENTS.

1. Freshly prepared solution of *as*-diphenylhydrazine (1 g in 99 ml glacial acetic acid).
2. Hydrochloric acid 2 N.

18. TELLURIUM

BY

J. GILLIS

AN 52 **AW 127.61**

A. Te^{+6}, 4.

AMMONIUM POLYSULPHIDE + SODIUM SULPHITE $(NH_4)_2S_n + Na_2SO_3$

BIBLIOGRAPHY : 213.

MECHANISM OF REACTION.

First of all a tetrasulphotellurate is formed from Na_2TeS_4 which is reduced to the state of elementary tellurium (black) by alkaline sulphite, according to the equation :

$$Na_2TeS_4 + 3\,Na_2SO_3 \longrightarrow Te + 3\,Na_2S_2O_3 + Na_2S$$

A. BRUKL and W. MAXYMOWICZ (213).

DETAILS OF TEST.

In a micro test tube.

Render a drop of the solution to be analysed slightly alkaline with ammonia (1 drop) in a micro test tube; carefully increase the temperature to that of a boiling water-bath; then add drop by drop some ammonium polysulphide until the precipitate, which was formed originally, is dissolved again. Then add 5 to 6 drops of a saturated solution of sodium sulphite and heat in a boiling water-bath for 15 minutes; the yellow solution is first discoloured and then the tellurium precipitates hot in the shape of big black floccules, which are easily filtered.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.875}$ ($1 : 7.5 \cdot 10^4$).

The SeO_3^{-2}, SeO_4^{-2} and GeO_3^{-2} anions do not interfere. Arsenic (As^{+3}), antimony (Sb^{+3}), tin (Sn^{+2} and Sn^{+4}) and molybdenum (Mo^{+6}) interfere.

REAGENTS.

1. Ammonia 3 N.
2. Aqueous solution of yellow ammonium polysulphide (ammonia 7 N saturated with a prolonged current of sulphuretted hydrogen).
3. Saturated solution of sodium sulphite in water.

B. Te^{+4}, Te^{+6}, 5.

HYPOPHOSPHOROUS ACID H_3PO_2

BIBLIOGRAPHY : 214-215.

MECHANISM OF REACTION.

Reduction of the tellurous and telluric anions by the hypophosphorous anion, according to the equations :

$$TeO_3^{-2} + H_2PO_2^{-1} \longrightarrow Te + PO_4^{-3} + H_2O$$
$$2\ TeO_4^{-2} + 3\ H_2PO_2^{-1} \longrightarrow 2\ Te + 3\ PO_4^{-3} + 2\ H^{+1} + 2\ H_2O$$

F. FEIGL (215).

DETAILS OF TEST.

In a micro crucible.

Evaporate in a micro crucible until nearly dry : a drop of the slightly acid solution to be analysed and a drop of the hypophosphorous acid solution. Tellurium gives a black precipitate from strong concentrations and a grey one from weak concentrations. A blank test is advisable.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.48}$ ($1 : 3 \cdot 10^5$).

The SeO_3^{-2} and SeO_4^{-2} anions interfere, because they give a red precipitate by reduction to elementary selenium. Arsenic (As^{+3}) also interferes. Germanium (Ge^{+4}) and molybdenum (Mo^{+6}) do not interfere in a 100 : 1 proportion. Antimony (Sb^{+3}) and tin (Sn^{+4}) in the same proportion (100 : 1) reduce the sensitivity to $10^{-5.48}$-$10^{-5.30}$ ($1 : 3 \cdot 10^5$ to $1 : 2 \cdot 10^5$).

REAGENT.

1. Hypophosphorous acid (15 ml sulphuric acid 35 N + 20 ml water + 10 g sodium hypophosphite).

C. Te^{+4}, 13.

TIN (II) CHLORIDE, STANNOUS CHLORIDE + SODIUM HYDROXIDE $SnCl_2 + NaOH$

BIBLIOGRAPHY : 216-220.

MECHANISM OF REACTION.

Reduction of tellurous anion to the state of elementary tellurium :

$$TeO_3^{-2} + 2\,SnO_2^{-2} + 2\,H^{+1} \longrightarrow Te + 2\,SnO_3^{-2} + H_2O$$

F. FEIGL (220).

DETAILS OF TEST.

On a spot plate.

Place on the plate successively a drop of a sodium hydroxide solution, a drop of a stannous chloride solution and a drop of the alkaline solution to be analysed. In the presence of tellurium a black precip-

itate is obtained. For low concentrations, however, a grey colour appears only after one or two minutes. A blank test is advisable.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.60}$ (1 : $4 \cdot 10^4$).

The SeO_3^{-2} and SeO_4^{-2} anions do not influence the reaction in any way; but the ions of the following elements interfere, viz. Ag, Cu, Bi, As(As^{+3}), Sb(Sb^{+3}), Sn(Sn^{+4}) and Mo(Mo^{+6}).

REAGENTS.

1. Sodium hydroxide 6 N.
2. Stannous chloride : 0.5 g stannous chloride dissolved in 0.5 ml hydrochloric acid 10 N; dilute with water to 10 ml.

D. Te^{+6}, 28.

COPPER (II) SULPHATE, CUPRIC SULPHATE $CuSO_4 . 5\ H_2O$
+ SODIUM HYDROXIDE + NaOH
+ POTASSIUM PEROXYDISULPHATE + $K_2S_2O_8$
(potassium persulphate)

BIBLIOGRAPHY : 221-223.

MECHANISM OF REACTION.

By peroxydation of copper a complex of tellurous acid and copper (III) is formed, which is brown to yellow-brown.

The compound thus obtained has one of the two formulae that follow :

$2\ K_2O . Cu_2O_3 . 3\ TeO_3 . x$ aq. or $2\ K_2O . CuO . 2\ Cu_2O_3 . 3\ TeO_3 . x$ aq.

B. BRAUNER and B. KUZMA (221).

DETAILS OF TEST.

In a test tube.

Add to a drop of the alkaline solution to be analysed (tellurium in the state of K_2TeO_4), a drop of a cupric sulphate solution, a drop of sodium hydroxide and finally some sodium (or potassium) persulphate crystals. Heat to boiling point; a yellow colour indicates the presence of tellurium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.48}$ ($1 : 3 \cdot 10^4$).

An excess of selenium (Se^{+4}), viz. 1000 : 1, reduces the sensitivity to $10^{-4.18}$ ($1 : 1.5 \cdot 10^4$). The following ions interfere as well : As^{+3}, Sn^{+2}, Ge^{+4}, MoO_4^{-2} and IO_4^{-1}.

REAGENTS.

1. Solution of cupric sulphate, 1 : 50.000, in water.
2. Sodium hydroxide 2 N.
3. Solid potassium persulphate.

E. Te^{+6}, 35.

MANGANESE (II) SULPHATE, MANGANOUS SULPHATE + COPPER (II) CATION, CUPRIC CATION + SODIUM HYPOBROMITE $MnSO_4 + Cu^{+2} + NaOBr$

BIBLIOGRAPHY : 222-223.

MECHANISM OF REACTION.

The Mn^{+2} cation is oxidized to dioxide MnO_2 by the hypobromous anion. The Cu^{+2} cation accelerates the reaction

$$NaOBr \rightarrow NaBr + O$$

and allows the Mn^{+2} cation to be oxidized, not to manganous dioxide (MnO_2), but to the permanganic anion (MnO_4^{-1}). That is therefore the reaction of the blank test. But in the presence of TeO_4^{-2} anions copper (Cu^{+2}) is involved in another process : it probably changes to the Cu^{+3} state (see reaction D) and can no longer function as accelerator; consequently no more permanganate is formed in the presence of the TeO_4^{-2} anion, but a little yellowish dioxide MnO_2.

F. FEIGL and R. UZEL (222).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube a drop of the solution to be analysed (tellurium in the K_2TeO_4 state), a drop of the solution of copper and manganous sulphate and a drop of sodium hypobromite; a blank

test is made at the same time. The two test tubes are heated to boiling point; in the presence of tellurium the solution is colourless or slightly yellow; the check test is coloured purple.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.30}$ ($1 : 2 \cdot 10^5$).

Selenium (the SeO_4^{-2} anion) in a 1.500 : 1 proportion reduces the sensitivity to $10^{-4.18}$ ($1 : 1.5 \cdot 10^4$). Germanium (Ge^{+4}) reduces the sensitivity to $10^{-4.30}$ ($1 : 2 \cdot 10^4$). The ions of the following elements interfere : arsenic (As^{+3}), antimony (Sb^{+3}), tin (Sn^{+4}) and molybdenum (Mo^{+6}).

REAGENTS.

1. Solution of manganous sulphate ($MnSO_4 \cdot 7\ H_2O$), 0.05 %, in water to which is added a drop of a cupric sulphate solution, 4 %, ($CuSO_4 \cdot 5\ H_2O$).

2. Aqueous solution of sodium hypobromite : freshly prepared solution of 0.1 ml bromine per 5 ml sodium hydroxide, 2 N.

19. GERMANIUM

BY

J. GILLIS

AN 32 **AW 72.60**

A. Ge^{+4}, 7.

AMMONIUM MOLYBDATE $(NH_4)_2MoO_4$

BIBLIOGRAPHY : 224.

MECHANISM OF REACTION.

A heteropolyacid of an intensely yellow colour is formed :

$$H_8[Ge(Mo_2O_7)_6] \cdot 28\ H_2O$$

octahydrogen hexadimolybdatogermanic acid.

I. P. ALIMARIN and B. N. IWANOW-EMIN (224).

DETAILS OF TEST.

On a spot plate.

Place on the plate, a drop of the solution to be analysed, a drop of the ammonium molybdate solution and some drops of nitric acid to acidify. After 5 minutes a yellow colour appears, which indicates the presence of germanium. For low concentrations comparison with a blank test is necessary.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.30}$ $(1 : 2 \cdot 10^5)$.

The anions of arsenic, phosphorus and silicium must be eliminated, because they form similar complex acids. The ions of antimony (Sb^{+3}), tin (Sn^{+2} and Sn^{+4}), selenium (Se^{+4}), tellurium (Te^{+4} and Te^{+6}) and molybdenum (Mo^{+6}) do not interfere.

REAGENTS.

1. Solution of ammonium molybdate, 5 %, in water.
2. Nitric acid 14 N.

B. Ge^{+4}, 21.

AMMONIUM MOLYBDATE + BENZIDINE ACETATE $(NH_4)_2MoO_4$ + H_2N—⟨⟩—⟨⟩—$NH_2.CH_3CO_2H$

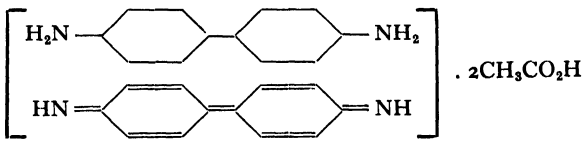
BIBLIOGRAPHY : 225-226.

MECHANISM OF REACTION.

First of all is formed the octahydrogen hexadimolybdatogermanic heteroacid

$$H_8[Ge(Mo_2O_7)_6]$$

whose very high oxidation potential (in respect of germanic acid) permits the oxidation of benzidine to benzidine-blue.



The molybdenum is at the same time reduced to molybdenum-blue Mo_2O_5.

A.S. KOMAROWSKY and N.S. POLUEKTOFF (225).

DETAILS OF TEST.

On a spot plate.

Place on the plate, a drop of the solution to be analysed, a drop of ammonium molybdate, a drop of the benzidine solution and some drops of a saturated sodium acetate solution in order to obtain the favourable *p*H. A blue colour appears in the presence of germanium, due to the reduced molybdenum and molybdenum-blue.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.60}$ ($1 : 4 \cdot 10^5$).

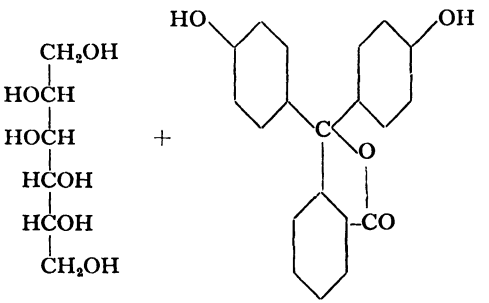
Reducing agents as well as arsenic, phosphorus and silicon interfere. Antimony (Sb^{+3}) reduces the sensitivity to $10^{-4.30}$ ($1 : 2 \cdot 10^4$). The TeO_3^{-2} and TeO_4^{-2} anions reduce the sensitivity to $10^{-4.70}$ ($1 : 5 \cdot 10^4$). Molybdenum (Mo^{+6}) does not interfere.

REAGENTS.

1. Dissolve 1 g ammonium molybdate in 10 ml water, then add 10 ml of concentrated nitric acid 14 N.
2. Solution of benzidine, 0.1 %, in glacial acetic acid.
3. Saturated solution of sodium acetate in water.

C. Ge^{+4}, 23.

d-MANNITOL + PHENOLPHTHALEIN



BIBLIOGRAPHY : 227-229.

MECHANISM OF REACTION.

The formation of mannitogermanic acid, which is a strong acid, reduces the *p*H of the solution, which results in a definite change from red to colourless of the indicator, phenolphthalein :

$H_2[Ge_2O_5(m)n]$ m = mannitol; n = minimum : 2.

N. S. POLUEKTOFF (228) and A. TCHAKIRIAN (227).

DETAILS OF TEST.

On a spot plate.

Mix carefully : a drop of the slightly acid solution to be analysed, a drop of phenolphthalein and some drops of sodium hydroxide, till a red colour appears. If mannitol is added hereafter, the red colour will disappear or fade in the presence of germanium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.875}$ ($1 : 7.5 \cdot 10^4$).

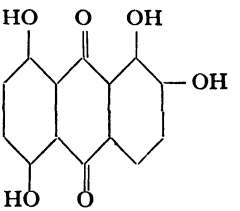
In the absence of boric anions the reaction is specific for germanium. The following ions do not interfere : arsenic (As^{+3}), antimony (Sb^{+3}), tin, tellurium (TeO_3^{-2} and TeO_4^{-2} anions). Molybdenum (Mo^{+6}) reduces the sensitivity to $10^{-4.70}$ ($1 : 5 \cdot 10^4$).

REAGENTS.

1. Solution of phenolphthalein, 1 %, in ethyl alcohol.
2. Sodium hydroxide 0.01 N.
3. Solid mannitol.

D. Ge^{+4}, 25.

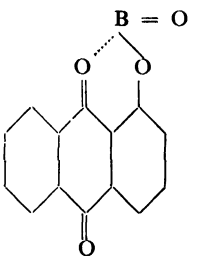
1 : 2 : 5 : 8-TETRAHYDROXY-ANTHRAQUINONE
(quinalizarin, alizarin bordeaux)



BIBLIOGRAPHY : 230-231.

MECHANISM OF REACTION.

The reaction is analogous to that of boron [see F. FEIGL and P. KRUMHOLZ (230)], with which an internal complex is formed, according to the following formula



in the case of alizarin. No formula has been given for germanium. N. S. POLUEKTOFF (231).

DETAILS OF TEST.

In a micro crucible.

Evaporate until dryness in a micro crucible, a drop of the acid or alkaline solution to be analysed which is free from Cl^{-1} and Br^{-1} ions. After cooling, add 2 or 3 drops of a quinalizarin solution. It is sometimes necessary to heat gently for some seconds. The change in colour from purplish red to light blue indicates the presence of germanium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

In the absence of boric anions the reaction is absolutely specific for germanium.

REAGENT.

1. Solution of quinalizarin, 0.01 %, in sulphuric acid 35 N.

E. Ge^{+4}, NR.

AMMONIUM MOLYBDATE + SODIUM STANNITE $(NH_4)_2MoO_4 + Na_2SnO_2$

BIBLIOGRAPHY : 232.

MECHANISM OF REACTION.

The reaction indicating the reduction of molybdenum (Mo^{+6}) to blue oxide (Mo_2O_5) is caused by the formation of octahydrogen hexadimolybdatogermanic heteroacid

$$H_8[Ge(Mo_2O_7)_6]$$

whose oxidation potential is greater than that of simple molybdic acid, which is not reducible.

DETAILS OF TEST.

On a spot plate.

The Ge^{+4} reaction mentioned under A can be changed as follows : take a drop of the solution to be analysed, a drop of the ammonium

molybdate solution (without addition of nitric acid) and some drops of an alkaline stannite solution : the molybdenum compound is reduced and causes the appearance of a blue colour.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

Apart from the anions of As, P and Si the reducing agents, such as the Sn^{+2}, As^{+3}, SeO_3^{-2} and Fe^{+2} ions, interfere as well. The ions of antimony (Sb^{+3}), tin (Sn^{+4}) and molybdenum (Mo^{+6}) do not interfere.

REAGENTS.

1. Solution of ammonium molybdate, 5 %, in water.
2. Solution of stannous chloride, 5 %, in sodium hydroxide 5 N.

20. MOLYBDENUM

BY

J. GILLIS

AN 42 **AW 95.95**

A. Mo^{+6}, 1.

THALLIUM (I) NITRATE, THALLOUS NITRATE (PHOTO 8) $TlNO_3$

BIBLIOGRAPHY : 233-234.

MECHANISM OF REACTION.

Crystals of thallous molybdate Tl_2MoO_4 are formed, which are colourless or slightly yellow.

BEHRENS-KLEY (233).

DETAILS OF TEST.

Under the microscope.

Place on a slide, a crystal of thallous nitrate in the alkaline solution to be analysed (sodium or potassium hydroxide; molybdenum in the state of the MoO_4^{-2} anion). Formation of thin hexagonal characteristic crystals (colourless or slightly yellow), hexagonal skeletons, stars and rosettes. The crystals are best formed in 0.1 % solutions of molybdic anhydride with a slight excess of sodium hydroxide.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.48}$ ($1 : 3 \cdot 10^5$).

Tungsten gives a similar reaction and must be previously removed. The SeO_3^{-2}, TeO_3^{2-} and TeO_4^{-2} anions reduce the sensitivity to 10^{-5} ($1 : 10^5$). Germanium (Ge^{+4}) interferes, because it also gives crystals. Arsenic (As^{+3}), antimony (Sb^{+3}) and tin (Sn^{+2} and Sn^{+4}) also interfere.

REAGENTS.

1. Solid thallous nitrate.
2. Sodium hydroxide N.

B. Mo^{+6}, 22.

POTASSIUM THIOCYANATE + TIN (II) CHLORIDE, STANNOUS CHLORIDE

KCNS + $SnCl_2$

BIBLIOGRAPHY : 235-239.

MECHANISM OF REACTION.

The MoO_4^{-2} anion is reduced by stannous chloride to the molybdic cation Mo^{+3}, which forms a tripotassic hexathiocyanatomolybdate (III), which is red :

$$K_3[Mo(CNS)_6]$$

F. C. KRAUSKOPF and C. E. SWARZ (237).

DETAILS OF TEST.

On filter paper.

Place on a filter paper, a drop of the solution to be analysed and then a drop of the alkaline thiocyanate solution. In the presence of iron a red stain is formed, which disappears when stannous chloride or a sodium thiosulphtae solution is added. If molybdenum is present, however, the red colour appears and remains after the reducing agent has been added.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ ($1 : 5 \cdot 10^5$).

The WO_4^{-2} anion, in a 1000 : 1 proportion, reduces the sensitivity to $10^{-4.30}$ ($1 : 2 \cdot 10^4$). The SeO_3^{-2}, TeO_3^{-2} and TeO_4^{-2} anions are

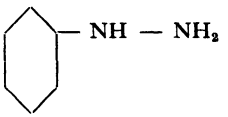
reduced as well and therefore interfere. Tin (Sn^{+4}) and germanium (Ge^{+4}) reduce the sensitivity to $10^{-4.30}$ ($1 : 2 \cdot 10^4$), arsenic (As^{+3}) and antimony (Sb^{+3}) reduce it to $10^{-5.30}$ ($1 : 2 \cdot 10^5$). The PO_4^{-3} anion and the organic acids also interfere.

REAGENTS.

1. Potassium thiocyanate solution, 10 %, in water.
2. Stannous chloride solution, 5 %, in hydrochloric acid 3 N.

C. Mo^{+6}, 30.

PHENYLHYDRAZINE



BIBLIOGRAPHY : 240-243.

MECHANISM OF REACTION.

Phenylhydrazine is oxidized by ammonium molybdate to a diazonium salt; the latter combines with the excess of phenylhydrazine in the presence of molybdate and gives a colour as red as blood.

L. SPIEGEL and TH. A. MAASS (240).

DETAILS OF TEST.

On a spot plate or on filter paper.

Place a drop of the solution to be analysed and a drop of the reagent on a spot plate or on filter paper. In the presence of molybdenum a red colour is produced. A blank test is necessary.

SENSITIVITY AND SELECTIVITY : on the spot plate : $D = 10^{-5.60}$ ($1 : 4 \cdot 10^5$), on filter paper : $D = 10^{-5.78}$ ($1 : 6 \cdot 10^5$).

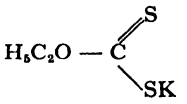
Selenium (Se^{+4}), tellurium (Te^{+4}, Te^{+6}), antimony (Sb^{+3}) and tin (Sn^{+4}) interfere. Germanium (Ge^{+4}) reduces the sensitivity to $10^{-5.48}$ ($1 : 3 \cdot 10^5$). The WO_4^{-2}, VO_4^{-3}, IO_3^{-1}, $C_2O_4^{-2}$ and SO_4^{-2} anions interfere.

REAGENT.

1. Phenylhydrazine solution, 33 %, in glacial acetic acid.

D. Mo^{+6}, 32.

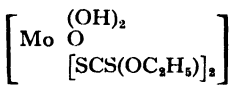
POTASSIUM ETHYLXANTHATE, POTASSIUM XANTHOGENATE



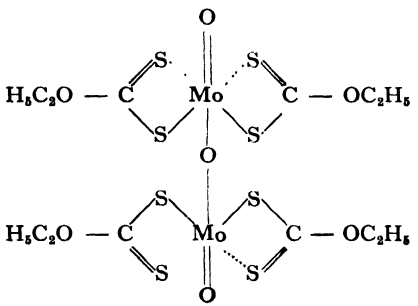
BIBLIOGRAPHY : 244-251.

MECHANISM OF REACTION.

The compound formed is a complex of hexavalent molybdenum according to F. EPHRAÏM (248),



wheras R. MONTEQUI (249) gives a formula in which molybdenum is pentavalent and hexaco-ordinated,



DETAILS OF TEST.

On a spot plate.

Dissolve on the plate some potassium xanthogenate crystals in a drop of the neutral or slightly acid solution to be analysed; then add 2 drops of hydrochloric acid. According to the concentration of the molybdic anion a colour is produced varying from pink to purple.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6.18}$ ($1 : 1.5 \cdot 10^6$).

Tungsten does not interfere as long as its concentration is no higher than 1 %. The ions of the following elements interfere : Cu, Te, Fe, U, Co and Ni. The SeO_3^{-2} anion reduces the sensitivity to $10^{-5.60}$ ($1 : 4 \cdot 10^5$). Arsenic (As^{+3}) and germanium (Ge^{+4}) reduce

the sensitivity to $10^{-5.30}$ ($1 : 2 \cdot 10^5$). Antimony (Sb^{+3}) and tin (Sn^{+4}) decrease it to $10^{-4.30}$ ($1 : 2 \cdot 10^4$).

REAGENTS.

1. Solid potassium xanthogenate.
2. Hydrochloric acid 2 N.

E. Mo^{+6}, 34.

ETHYL ACETATE + SODIUM THIOSULPHATE $CH_3CO_2C_2H_5 + Na_2S_2O_3$

BIBLIOGRAPHY : 252.

MECHANISM OF REACTION.

The mechanism of the reaction is not known.

DETAILS OF TEST.

In a macro test tube.

Place in a test tube, 1 ml of an acid (hydrochloric acid) solution to be analysed; the molybdenum must be in the Mo^{+6} form. Add 0.5 ml ethyl acetate and 3 or 4 ml of a sodium thiosulphate solution. Stir vigorously. In the presence of molybdenum the acetic ester layer assumes a brownish red colour. A blank test is necessary.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ ($1 : 10^6$).

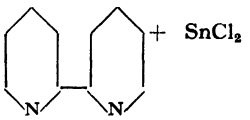
In acid medium potassium tungstate forms a white precipitate which does not interfere with the identification of molybdenum. Selenium (SeO_3^{-2} anion) and tellurium (TeO_3^{-2} and TeO_4^{-2} anions), when in a 100 : 1 proportion, reduce the sensitivity to $10^{-5.30}$ ($1 : 2 \cdot 10^5$). The As^{+3}, Sb^{+3}, and Sn^{+4} cations decrease it to 10^{-5} ($1 : 10^5$) and germanium brings the sensitivity back to $10^{-4.30}$ ($1 : 2 \cdot 10^4$).

REAGENTS.

1. Ethyl acetate.
2. Sodium thiosulphate solution, 25 %, in water.

F. Mo^{+6}, 37.

2 : 2'-DIPYRIDYL, α:α'-DIPYRIDYL
+ TIN (II) CHLORIDE, STANNOUS CHLORIDE



BIBLIOGRAPHY : 253.

MECHANISM OF REACTION.

The reaction is due to a lower oxide of molybdenum, obtained by reduction with stannous chloride.

A. S. KOMAROWSKI and N. S. POLUEKTOW (253).

No other information can be found in the literature as regards the valency of the molybdenum and the formula of the complex formed.

DETAILS OF TEST.

On a spot plate.

Place on the plate, a drop of the solution to be analysed and add 2 drops of an alcoholic solution of α:α'-dipyridyl. An intensely red colour which appears after a drop of the stannous chloride solution has been added indicates the presence of molybdenum.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

Tungsten does not interfere, if the precaution is taken to add a drop of tartaric acid before the reaction, so that a complex tungsten salt is formed. The Fe^{+2} and Fe^{+3} cations interfere, as well as tin (Sn^{+4}) and the anions SeO_3^{-2}, TeO_3^{-2} and TeO_4^{-2}. Antimony (Sb^{+3}) reduces the sensitivity to 1 : 10^5 (to be examined at once, because soon afterwards a yellow colour and precipitate appear, which make it impossible to detect the red colour due to molybdenum). Arsenic (As^{+3}) and germanium (Ge^{+4}) do not interfere.

REAGENTS.

1. Solution of α:α'-dipyridyl, 3 %, in alcohol 96 %.
2. Solution of stannous chloride, 50 %, in hydrochloric acid 10 N.
3. Solution of tartaric acid, 10 %, in water.

21. TUNGSTEN

BY

J. GILLIS

AN 74 AW 183.92

A. W^{+6}, 1.

THALLIUM (I) NITRATE, THALLOUS NITRATE $TlNO_3$

(PHOTO 9)

BIBLIOGRAPHY : 254-255.

MECHANISM OF REACTION.

Thallous tungstate crystals Tl_2WO_4 are formed.

BEHRENS-KLEY (254).

DETAILS OF TEST.

Under the microscope.

Place on the slide, a drop of the tepid and slightly alkaline solution to be analysed (the tungsten must be present as tungstate Na_2WO_4), then add a crystal of thallous nitrate. The thallous tungstate is formed in hexagonal crystals, which have a very strong resemblance to thallous molybdate crystals. For this reason it is essential first to remove the molybdenum.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.48}$ $(1 : 3 \cdot 10^5)$.

Molybdenum (anion : MoO_4^{-2}) gives an analogous reaction. Niobium and tantalum do not interfere.

REAGENT.

1. Solid thallous nitrate.

B. W^{+6}, 18.

TIN (II) CHLORIDE, STANNOUS CHLORIDE $SnCl_2$

BIBLIOGRAPHY : 256-259.

α. — *In the absence of molybdenum*

MECHANISM OF REACTION.

Reduction of hexavalent tungsten to the blue oxide W_2O_5 (analogous to that of molybdenum), by means of stannous chloride.

F. FEIGL (257).

DETAILS OF TEST.

On a spot plate.

Mix on the plate 1 or 2 drops of the solution to be analysed and 3 to 5 drops of the stannous chloride solution. A precipitate or a blue colour appears immediately, which indicates the presence of tungsten.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

Niobium and tantalum do not interfere.

REAGENT.

1. Solution of stannous chloride, 25 %, in hydrochloric acid 10 N.

β. — *In the presence of molybdenum*

MECHANISM OF REACTION.

As in the preceding test the blue oxide of tungsten, W_2O_5, is formed; in order to avoid the analogous reaction of molybdenum the latter is converted to the red thiocyanic complex $[Mo(CNS)_6]^{-3}$, of which the red colour disappears in concentrated hydrochloric medium and only the blue oxide W_2O_5 persists.

F. FEIGL (257).

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of hydrochloric acid; add in its centre a drop of the solution to be analysed. Tungsten gives a yellow stain. If a drop of potassium thiocyanate and a drop of stannous chloride is added, the yellow stain becomes blue, because the blue oxide of tungsten is formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

Under similar conditions molybdenum gives a red stain, which disappears when concentrated hydrochloric acid is added and therefore does not interfere with the determination of tungsten. Niobium and tantalum do not interfere.

REAGENTS.

1. Hydrochloric acid 10 N.
2. Solution of stannous chloride, 25 %, in hydrochloric acid 10 N.
3. Solution of potassium thiocyanate, 10 %, in water.

22. VANADIUM

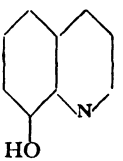
BY

J. GILLIS

AN 23 **AW 50.95**

A. V^{+5}, 6.

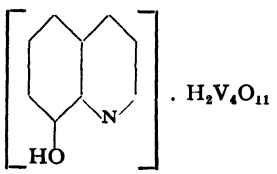
8-HYDROXYQUINOLINE



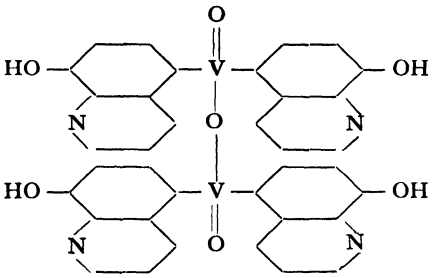
BIBLIOGRAPHY : 260-261.

MECHANISM OF REACTION.

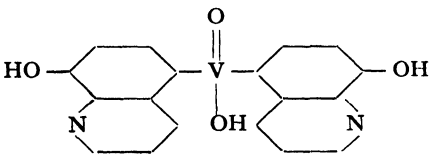
8-Hydroxyquinoline reacts upon alkaline vanadates and yields a salt of tetravanadic acid, of yellow colour :



The reaction develops on heating and finally gives, after cooling down a bluish black compound which is soluble as Bordeaux red in chloroform. It is the following anhydride :



of the acid :



F. FEIGL (261).

DETAILS OF TEST.

In a micro test tube.

Place in the test tube 1 drop of the solution to be analysed (the vanadium is in the alkaline metavanadate state), then 2 drops of acetic acid, 1 drop of the reagent and 1 drop of chloroform; put a stopper on the test tube and shake. In the presence of vanadium the chloroform is coloured as claret red or purplish brown. For low vanadium concentrations a blank test is made.

SENSITIVITY AND SELECTIVITY. $D = 10^{5.845}$ $(1 : 7 \cdot 10^5)$.

Molybdenum, tungsten and titanium also form complexes with 8-hydroxyquinoline. Their ions are eliminated by treating the solution with a sodium hydroxide solution (Ti), then acidifying with acetic acid and precipitating the molybdenum and tungsten with barium acetate. Iron is also removed by means of sodium hydroxide.

REAGENTS.

1. Acetic acid 2 N.
2. 8-Hydroxyquinoline solution, 2.5 %, in acetic acid 6 %.
3. Chloroform.
4. Sodium hydroxide N.
5. Solution of barium acetate, 10 %, in water.

B. V^{+5}, 26.

HYDROGEN PEROXIDE H_2O_2

BIBLIOGRAPHY : 262-265.

MECHANISM OF REACTION.

The pink or red colour is due to the appearance of a peroxysalt of vanadium $\left(V\langle{}^{O}_{O}\rangle\right)_2(SO_4)_3$; an excess of hydrogen peroxide (which is to be avoided) gives the yellow orthoperoxyvanadic acid, according to the equation :

$$(VO_2)_2(SO_4)_3 + 6\ H_2O \underset{H_2O_2}{\overset{H_2SO_4}{\rightleftharpoons}} 2\ (VO_2)\ (OH)_3 + 3\ H_2SO_4$$

J. MEYER and A. PAWLETTA (263).

DETAILS OF TEST.

On a spot plate.

Mix thoroughly on the plate a drop of the solution to be analysed (alkaline metavanadate) and a drop of sulphuric acid. After a few minutes a drop of hydrogen peroxide is added. According to the concentration of vanadium a red or pink colour appears. For low concentrations a blank test is advisable.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.30}$ $(1 : 2 \cdot 10^5)$.

An excess of reagent must be avoided at all costs, for the red colour disappears in that case to make room for a yellow product. This

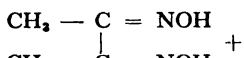
reaction can only be effected in the absence of the following anions : MoO_4^{-2}, CrO_4^{-2}, Cl^{-1}, Br^{-1}, and I^{-1}; all metallic ions interfere as well.

REAGENTS.

1. Sulphuric acid 3 N.
2. Solution of hydrogen peroxide, 1 %, in water.

C. V^{+5}, 32.

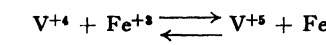
2 : 3-BUTANE DIOXIME, DIMETHYLGLYOXIME + IRON (III) CHLORIDE, FERRIC CHLORIDE + AMMONIUM HYDROXIDE



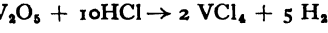
BIBLIOGRAPHY : 266-267.

MECHANISM OF REACTION.

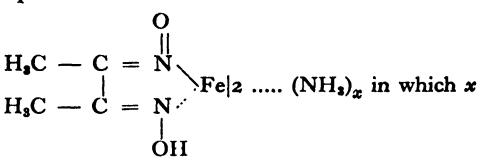
When the following reaction is carried out :



in acid medium, then the equilibrium is shifted to the right :



Bivalent iron which is thus formed can be identified in an ammoniacal medium by means of dimethylglyoxime, which gives the red soluble complex :



F. EPHRAÏM (266) and F. FEIGL (267).

DETAILS OF TEST.

In a micro crucible.

Place in the crucible 1 drop of the solution to be analysed (alkaline metavanadate) and 2 drops of hydrochloric acid; heat and evaporate to half the volume so as to reduce the vanadium. After cooling,

add 1 drop of ferric chloride, 3 drops of dimethylglyoxime solution and ammonia until alkaline. The following reaction takes place :

$$V^{+4} + Fe^{+3} \longrightarrow V^{+5} + Fe^{+2}$$

Bivalent iron forms with dimethylglyoxime in alkaline medium a complex of a cherry red colour. It is possible that in the case of low vanadium concentrations the brown ferric hydroxide precipitate hides the pink colour, which is due to the vanadium; then a strip of filter paper must be used; the ferric hydroxide is absorbed at the bottom of the paper, whilst the red complex is diffused with water.

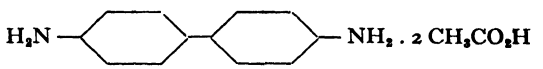
SENSITIVITY AND SELECTIVITY. $D = 10^{-5.18}$ ($1 : 1.5 \cdot 10^5$).

Tungsten in a 60 : 1 proportion reduces the sensitivity to $10^{-4.30}$ ($1 : 2 \cdot 10^4$). The MoO_4^{-2} anion in a 350 : 1 proportion reduces the sensitivity to $10^{-4.78}$ ($1 : 6 \cdot 10^4$). All oxidising agents interfere and must be removed.

REAGENTS.

1. Hydrochloric acid 11 N.
2. Solution of ferric chloride, 1 %, in water.
3. Solution of dimethylglyoxime, 1 %, in alcohol.
4. Ammonia 6 N.

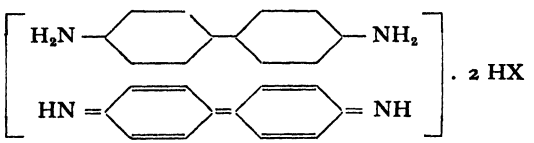
D. V^{+5}, 33.

BENZIDINE ACETATE 

BIBLIOGRAPHY : 268-269.

MECHANISM OF REACTION.

The benzidine is oxidized by the vanadic anion into a blue meriquinoid compound :



F. EPHRAÏM (268) and F. FEIGL (269).

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the solution to be analysed and a drop of a saturated solution of benzidine in acetic acid. With high concentrations of vanadium a green colour appears, with low concentrations the colour is blue.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.30}$ $(1 : 2 \cdot 10^5)$.

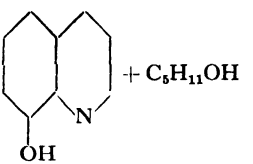
Hexavalent chromium interferes, as it forms a brownish black precipitate that masks the reaction. Molybdenum, in the form of sodium molybdate, only interferes if its concentration is 100 times that of vanadium. An excess of tungsten (2,000: 1) reduces the sensitivity to 10^{-5} $(1 : 10^5)$. If the concentration of tungsten is 20,000 times that of vanadium, the latter can no longer be identified.

REAGENT.

1. Saturated solution of benzidine in acetic acid 10 %.

E. V^{+5}, 35.

8-HYDROXYQUINOLINE + ISOAMYL ALCOHOL



BIBLIOGRAPHY : 270-273.

MECHANISM OF REACTION.

See reaction A. The use of isoamyl alcohol as a solvent in the extraction notably increases the sensitivity of the test.

J. M. BACH (273).

DETAILS OF TEST.

In a micro test tube.

Place in the test tube 1 ml of he solution to be analysed (alkaline metavanadate), one drop of acetic acid, 6 drops of the reagent and 6 to 7 drops of isoamyl alcohol; close the test tube, for example, with

a rubber stopper, and shake it vigorously. In the presence of vanadium, the alcohol layer will become claret red. A blank test is necessary for low concentrations.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6.70}$ $(1 : 5 \cdot 10^6)$.

The MoO_4^{-2} and WO_4^{-2} anions will interfere when their concentration is 2,000 times that of vanadium; the CrO_4^{-2} anion interferes when its concentration is 200 times that of vanadium. The Fe^{+3} cation interferes.

REAGENTS.

1. Acetic acid 2 N.
2. Solution of 8-hydroxyquinoline, 2.5 %, in acetic acid 6 %.
3. Isoamyl alcohol.

23. NIOBIUM (COLUMBIUM)

BY

J. GILLIS

AN 41 AW 92.91

A. Nb^{+5}, Cb^{+5}, 1.

SODIUM HYDROXIDE + SODIUM ACETATE (PHOTO 10) $NaOH + CH_3CO_2Na$

BIBLIOGRAPHY : 274-275.

MECHANISM OF REACTION.

Sodium niobate crystals are formed : $NaNbO_3$.

H. BEHRENS (274).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed (alkaline niobate), a drop of sodium hydroxide and a drop of a saturated solution

of sodium acetate. The sodium niobate crystals occur in two forms, needles and tetragonal prisms.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.40}$ ($1 : 2.5 \cdot 10^3$).

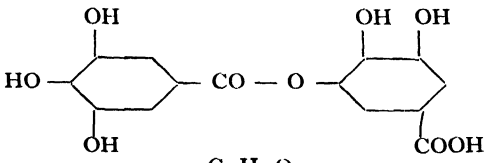
Sodium tantalate crystals are identical; tungsten (W^{+6}) and iron do not interfere.

REAGENTS.

1. Sodium hydroxide 2 N.
2. Saturated solution of sodium acetate in water.

B. Nb^{+5}, Cb^{+5}, 12.

m-DIGALLIC ACID



$C_{14}H_{10}O_9$

BIBLIOGRAPHY : 176-182.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

In a micro test tube.

Place in the test tube and heat to boiling point, 1 ml of the solution to be analysed (alkaline niobate) and add 0.1 g solid ammonium chloride and 0.2 g solid ammonium acetate. Then add some solid digallic acid and an orange coloured precipitate is formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 8 \cdot 10^4$).

Tungsten (W^{+6}) and titanium (Ti^{+4}) do not interfere with the reaction. Tantalum forms a yellow precipitate with digallic acid. Iron does not interfere when the medium is slightly acid.

REAGENTS.

1. Solid ammonium chloride.
2. Solid ammonium acetate.
3. Solid *m*-digallic acid.

C. Nb^{+5}, Cb^{+5}, 18.

POTASSIUM THIOCYANATE + ZINC + HYDROCHLORIC ACID KCNS + Zn + HCl

BIBLIOGRAPHY : 282-284.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube, some potassium thiocyanate crystals, 1 ml of the solution to be analysed (alkaline niobate), a little zinc (powder) and 5 drops of concentrated hydrochloric acid. For high concentrations of niobium it is dark yellow. A blank test is advisable.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.30}$ $(1 : 2 \cdot 10^4)$.

Tantalum (Ta^{+5}), in the form of an oxide, does not interfere. Titanium (Ti^{+4}) and tungsten (W^{+6}) also do not interfere.

REAGENTS.

1. Solid potassium thiocyanate.
2. Zinc (powder).
3. Hydrochloric acid 11 N.

D. Nb^{+5}, Cb^{+5}, 19.

ZINC Zn

BIBLIOGRAPHY : 285-291.

MECHANISM OF REACTION.

Reduction to lower oxides.

W. B. GILES (291).

DETAILS OF TEST.

In a micro test tube.

Place in the test tube, 1 ml of the solution to be analysed (alkaline niobate) and 1 ml phosphoric acid. This solution is again concentrated by evaporation until the precipitate that is formed is redissolved and the liquid becomes viscous. Then add 2 volumes of water and boil with 1 g zinc. The solution becomes black, brown or yellow, according to the quantity of niobium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.18}$ $(1 : 1.5 \cdot 10^3)$.

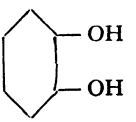
Tantalum does not interfere; the ions of the following elements interfere at maximum valency : Mo, W, V and Ti.

REAGENTS.

1. Phosphoric acid ($d = 1.70$).
2. Zinc (powder).

E. Nb^{+5}, Cb^{+5}, NR. 1.

1 : 2-DIHYDROXYBENZENE, PYROCATECHOL



BIBLIOGRAPHY : 292.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

In a micro test tube.

Heat in the test tube, 1 ml of the solution to be analysed (alkaline niobate) with about 0.25 g sodium acetate, then add pyrocatechol till a yellow colour appears. A blank test is necessary.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

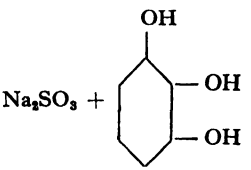
Tungsten (W^{+6}) does not interfere; titanium and iron (Fe^{+3}) ions interfere.

REAGENTS.

1. Solid sodium acetate.
2. Solid pyrocatechol.

F. Nb^{+5}, Cb^{+5}, NR. 2.

SODIUM SULPHITE + 1 : 2 : 3-TRIHYDROXYBENZENE, PYROGALLOL



BIBLIOGRAPHY : 293-296.

MECHANISM OF REACTION.

Has not been investigated.

DETAILS OF TEST.

In a micro test tube.

Place in the test tube, 1 ml of the slightly alkaline solution to be analysed (alkaline niobate) and 1 ml of the reagent. For low concentrations of niobium the solution is dark yellow, whereas the blank test is bright yellow.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

Tantalum does not interfere in alkaline medium. Titanium (Ti^{+4}) reacts in the same way and must therefore be previously removed.

REAGENT.

1. Solution of pyrogallol, 7 %, in a saturated aqueous solution of sodium sulphite.

24. TANTALUM

BY

J. GILLIS

AN 73 AW 180.88

A. Ta^{+5}, 1.

POTASSIUM FLUORIDE (PHOTO 11) KF

BIBLIOGRAPHY : 297-304.

MECHANISM OF REACTION.

The dipotassic heptafluotantalate (V) crystallises :

$$K_2[TaF_7]$$

H. BEHRENS (297).

DETAILS OF TEST.

Under the microscope.

Place on a cellophane slide, a drop of the solution to be analysed (alkaline tantalate) and a drop of a saturated solution of potassium fluoride. After some ten minutes, long and fine prisms of dipotassic heptafluotantalate (V) crystallize out.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.95}$ $(1 : 9 \cdot 10^3)$.

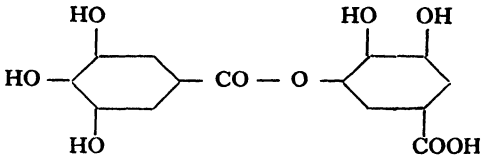
To test for tantalum in the presence of niobium, one should proceed as follows : precipitate the sodium salts by means of sodium hydroxide, wash them quickly with water, dissolve them in diluted hydrochloric acid and precipitate the tantalum in the form of dipotassic heptafluotantalate (V). However, the separation is difficult; the TiO_3^{-2} anion is often precipitated.

REAGENTS.

1. Sodium hydroxide N.
2. Hydrochloric acid N.
3. Saturated solution of potassium fluoride in water.

B. Ta^{+5}, 10.

m-DIGALLIC ACID



BIBLIOGRAPHY : 305-310.

MECHANISM OF REACTION.

Has not yet been investigated.

DETAILS OF TEST.

In a micro test tube.

Place in the test tube, 1 ml of the solution to be analysed (alkaline tantalate), 0.1 g ammonium chloride and 0.2 g ammonium acetate; after heating add digallic acid until a yellow precipitate is formed A blank test is necessary.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.40}$ ($1 : 2.5 \cdot 10^4$).

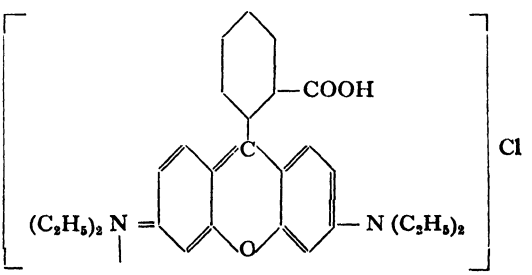
The niobium anion gives an orange coloured precipitate. Tungsten and titanium anions interfere. The Fe^{+3} cation does not interfere.

REAGENTS.

1. Solid ammonium chloride.
2. Solid ammonium acetate.
3. Solid *m*-digallic acid.

C. Ta^{+5}, NR. 1.

3 : 6 - BIS - DIETHYLAMINO -9- (2'CARBOXYPHENYL)-XANTHONIUM CHLORIDE
(rhodamine B, tetraethyl rhodamine)



BIBLIO GRAPHY : 311.

MECHANISM OF REACTION.

Has not been investigated.

DETAILS OF TEST.

In a micro test tube.

Place in the test tube, 1 ml of the solution to be analysed (tantalum in the form of TaF_5 or $K_2[TaF_7]$ and 0.05 g rhodamine B. Compare the contents of the test tube with a blank test, in incident light. Rhodamine B gives with tantalum a purple colour and a flocculent precipitate.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.60}$ $(1 : 4 \cdot 10^4)$.

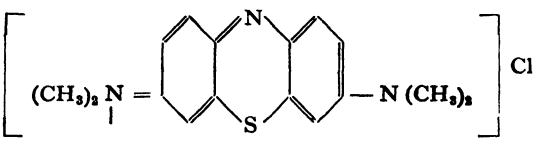
Niobium and titanium do not interfere; in a 300 : 1 proportion 2 γ tantalum can be detected. The ions of the elements Hg, Sb, Au, Mo (Mo^{+6}), W (W^{+6}), and Fe interfere because they form coloured precipitates themselves.

REAGENT.

1. Solid rhodamine B.

D. Ta^{+5}, NR. 2.

2 : 7-BIS-(DIMETHYLAMINO)PHENOTHIAZONIUM CHLORIDE
(methylene blue)



BIBLIOGRAPHY : 311.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

In a micro test tube.

Place in the test tube, 1 ml of the solution to be analysed (tantalum in the state of TaF_5 or $K_2[TaF_7]$) and 1 ml of a saturated solution of methylene blue. A fine blue precipitate is formed. Compare with a blank test.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ ($1 : 10^4$).

Niobium and titanium (Ti^{+4}) do not interfere. The ions of the following elements only interfere if present in high concentrations, viz. Sb, Sn, Mo, W, V and Al.

REAGENT.

1. Saturated solution of methylene blue in water.

QUALITATIVE SEPARATION OF ELEMENTS OF THE HYDROGEN SULPHIDE GROUP

In some cases it is an advantage to separate out the insoluble chlorides especially AgCl; but in the analysis of traces such a separation can no longer be achieved.

On the other hand it is usually preferable to make a precipitation with hydrogen sulphide and even a separation with ammonium polysulphide, according to the well-known, classical process.

Elements : Ag, Hg, Cu, Pb, Bi and Cd

a. DETECTION OF SILVER.

This test can be made by means of diammonium trisulphatocerate (IV) (reaction B, p. 4), without interferance from cations of the same group (Hg, Pb, Tl in particular and many others). Any reducing agent must be removed, however. Reaction A, p. 3, with metol, cannot be carried out in the presence of mercury, but it can be carried out in the presence of lead; this is also the case for reaction C, p. 5, with manganous sulphate and potassium permanganate. Rubidium chloride (reaction D, p. 6) does not allow of the detection of silver under the microscope in the presence of lead.

b. DETECTION OF MERCURY.

Small quantities of mercury (Hg^{+1} and Hg^{+2}) can be detected in the presence of an excess of copper, lead, bismuth and cadmium by means of reactions A and B, p. 8 and 10. However, in the presence of copper reaction B is preferable although it is not very sensitive. Copper also disturbs reaction D, p. 12; it is theoretically possible to separate copper by treating the sulphides with hot nitric acid ($d = 1.2$), but in practice mercuric sulphide often retains considerable quantities of copper sulphide; it is therefore advisable to make sure that copper is completely removed (dissolve in hydrochloric acid and hydrogen peroxide in order to effect the reaction of diammonium tetrathiocyanatomercurate (II) + zinc cation [Cu, A]).

In the presence of large quantities of silver and lead, the monovalent cation can be detected by means of the reactions A, B or C, p. 8-11.

When separating the mercuric sulphides (Hg^{+2}), copper sulphides, lead, bismuth and cadmium sulphides from the sulphides of arsenic, antimony, tin etc. with the aid of potassium hydroxide 2 N, the mercury is dissolved in considerable quantities in the presence of arsenic and analogous substances.

Therefore it is often necessary to examine for mercury in the presence of these elements or vice versa. The reactions A and B, p. 8 and 10, for mercury can be carried out in the presence of arsenic, antimony and tin. On the other hand it is preferable to effect a separation in order to detect these three elements when mercury is present. To that end the solution, which is alkaline because of the presence of potassium hydroxide 2 N, and contains mercury as well as arsenic, antimony and tin, is gently heated with an equal volume of concentrated hydrochloric acid 10 N. Antimony and tin are dissolved and can be detected through their reactions A, B, or C, p. 8-11; the residue formed by the sulphides of mercury (II) and arsenic (III) is treated with ammonia; arsenous sulphide is dissolved, whereas mercuric sulphide remains insoluble.

c. DETECTION OF COPPER.

In the presence of a large quantity of the following ions : mercury (Hg^{+1}), lead, bismuth and cadmium the reactions A, B, or D, p. 13, 15 or 17, can be used, which are not disturbed by a 100 : 1 proportion of these cations, even at the limit of concentration. Only mercury (Hg^{+2}) interferes with reaction C, p. 16.

d. DETECTION OF LEAD.

For the detection of lead in the presence of mercury (Hg^{+2}), bismuth and cadmium it is always preferable to effect a previous separation in order to avoid the complications caused by copper and bismuth. For that purpose the solution of the nitrates is heated with a drop of sulphuric acid until fumes of sulphur trioxide appear, the residue treated with a mixture of equal quantities of water and alcohol and filtered on a micro filter. After washing with the same mixture of water and alcohol the precipitate is dissolved in nitric acid 2 N. Lead can then be detected by means of thiourea (reaction A, p. 19).

Traces of lead can also be separated electrolytically in the presence of all other metals, except manganese, by deposition on the anode in the form of PbO_2.

e. DETECTION OF BISMUTH.

In the presence of large quantities of cations of mercury (Hg^{+2}), copper, lead, and cadmium, bismuth can be detected by reactions C, p. 26 or E, p. 28, whose sensitivity is not reduced by these cations. The Hg^{+2} cation interfere with reactions A, p. 23 and B, p. 24, while copper upsets reaction D, p. 27. For the detection of traces of bismuth it is advisable to use reaction B, p. 24, which is very sensitive; but in this case the Hg^{+2} cation must be removed, which can be done in the following manner : precipitate the mercury by means of stannous chloride in an acid solution which reduces the Hg^{+2} cation without precipitating the bismuth; separate the precipitate (Hg_2Cl_2 + Hg) by centrifuging and verify the complete removing of this cation in the solution by means of the diphenylcarbazide reaction. The bismuth can then be investigated by any of the reactions A, B, C or E, p. 23-28. If, in the case of reactions A or B, copper is present, it must be inhibited by means of potassium cyanide.

f. DETECTION OF CADMIUM.

Reaction C, p. 32, enables cadmium to be detected without any previous separation, in the presence of the following ions : Hg^{+2}, Cu^{+2}, Pb^{+2} and Bi^{+3}. The Hg^{+2} cation interferes with reactions A, B and D, p. 29-33, whereas bismuth interferes with reaction A. It is always possible to separate the Hg^{+2} cation of cadmium by treating their sulphides with hot nitric acid ($d = 1.2$). The solution is then neutralized with solid sodium hydroxide; the complete absence of mercury is thus assured so that cadmium can be detected, finally, by means of any of the reactions B, C or D. If reaction A (brucine), p. 29, is to be used, the sulphides must be dissolved in nitric acid, mercury sulphide (HgS) must be separated, the lead hydroxides and bismuth hydroxides precipitated by an excess of ammonia and the solution neutralized with acetic acid before testing for the cadmium.

Elements : As, Sb, Sn, Au and Pt

a. DETECTION OF ARSENIC.

In the presence of large quantities of antimony and tin, arsenic can be identified by means of the three reactions indicated (p. 34-37), without loss of sensitivity.

If gold or platinum is present as well, it is advisable to use the separation of arseniuretted hydrogen in an acid medium (reaction A, p. 34). Reaction B, p. 35, is less sensitive under these circumstances and reaction C, p. 37, is interfered with by the two elements quoted.

b. DETECTION OF ANTIMONY.

Reactions A, p. 38, and C, p. 40, permit the detection of antimony in the presence of large quantities of arsenic, tin and platinum ions and the sensitivity is not reduced. Reaction B, p. 39, is only upset by the Sn^{+2} cation.

Gold causes difficulties; reactions A, p. 38, and C, p. 40, cannot be used and the sensitivity of reaction B, p. 39, is reduced. However, it is easy to eliminate gold ions by means of sulphurous acid, which must afterwards be removed by heating. It is advisable to make sure that no gold is present. Then antimony can be detected by means of reactions A or C.

c. DETECTION OF TIN.

In the presence of large quantities of arsenic or antimony reaction B, p. 42, is best. If gold and platinum are also present, we recommend reaction A, p. 41, although its sensitivity is a little reduced by large quantities of arsenic, notwithstanding the green luminescence produced by gold. If gold is present, but platinum is absent, then gold can be eliminated by means of aluminium and hydrochloric acid 2 N (heating for 5 minutes). After having filtered the solution, one can test for the tin. If required platinum can be eliminated (together with gold) by means of finely divided silver (molecular silver). It is preferable under these circumstances to heat it in the presence of

hydrochloric acid for some minutes. This operation does not reduce the tetravalent tin to the bivalent state. Hereafter tin can be tested for by either reaction B or C, p. 42-44.

d. DETECTION OF GOLD.

Reaction A, p. 45, can always be used, even in the presence of large quantities of arsenic, antimony, tin and platinum. The sensitivity of reaction B, p. 47, is more or less reduced under the same conditions. Reaction C, p. 48, cannot be recommended, as it is interfered with by arsenic and antimony. It is always possible, however, to separate gold from the other ions by repeated extraction with ether. After evaporation of the ether all the reactions indicated can be used; but this extraction is not necessary, if reaction A, p. 45, is used.

e. DETECTION OF PLATINUM.

The reactions of platinum are less interfered with by arsenic antimony and tin, generally speaking, than by gold. Therefore it is advisable to extract gold three times with ether. After having made sure that no gold is present, platinum can be identified by means of all the reactions indicated, but preferably with rubeanic acid (reaction D, p. 61).

Elements : Ru, Rh, Pd, Os, Ir, Pt

When all the elements of this group are present (they are often accompanied by mercury and gold) an analysis is hardly possible without previous separation of osmium (distillation of the tetroxide at 300° in a stream of NO_2 gas) and of ruthenium (distillation of the tetroxide at 700° in a stream of oxygen).

The most frequent cases in practical analysis are :

a. Pt — Ir — Os
b. Pt — Pd
c. Pt — Rh.

In the case of an alloy, the mercury is eliminated by heating, if it is present. Gold is separated in the course of the analysis.

Preparation of the solution.

The principal methods are :

α. Treatment with aqua regia. Rhodium, osmium, and iridium often leave a residue.

β. Heating with a mixture of barium, nitrate and peroxide in a porcelain or silver crucible. All the metals of this group are converted into soluble products. After heating, extract with diluted hydrochloric acid. This method has the advantage that volatilization of osmic acid is avoided.

γ. Fusion with an excess of zinc; dissolve this in hydrochloric acid

which leaves the metals of the platinum group in the state of very fine powder, which is soluble in aqua regia.

The excess of nitric acid is removed by evaporation.

Separation of gold.

Extract the solution with ether; the gold trichloride passes into the ethereal layer, which is evaporated in order to detect gold by means of the reaction with tetramethyldiaminodiphenylmethane (reaction A, p. 45). A threefold extraction is necessary for the total removing of gold.

a. Pt — Ir — Os.

Platinum is detected using the reaction with narcotine (reaction B, p. 59); gold must be removed. The sensitivity is $10^{-4.48}$ ($1 : 3 \cdot 10^4$) with iridium and osmium in a 100 : 1 proportion.

Osmium is detected by heating the solution with thiourea (reaction A, p. 54). The sensitivity is $10^{-4.48}$ ($1 : 3 \cdot 10^4$), in the presence of platinum and iridium in a 100 : 1 proportion.

Iridium is finally detected by means of reaction B, p. 57. Gold interferes. Sensitivity of the reaction : $10^{-3.48}$ ($1 : 3 \cdot 10^3$), in the presence of platinum and osmium in a 100 : 1 proportion.

b. Pt — Pd.

For the detection of platinum there is a choice between the following two reactions :

1. Reaction with potassium chloride (reaction A, p. 59). Gold does not interfere. The sensitivity is $10^{-3.30}$ ($1 : 2 \cdot 10^3$) in the presence of 10 times the quantity of palladium.

2. If only a trace of platinum is present, then the palladium must be eliminated by precipitating it with dimethylglyoxime (reaction Pd, A, p. 51); the gold is then separated by extraction with ether and the platinum is detected by means of narcotine (reaction Pt, B, p. 59); the sensitivity is $10^{-4.30}$ ($1 : 2 \cdot 10^4$), in the presence of palladium in a 1.000 : 1 proportion.

In order to identify palladium reaction A, p. 51, is used (dimethylglyoxime). Gold does not interfere. The sensitivity is $10^{-4.30}$ ($1 : 2 \cdot 10^4$), in the presence of platinum in a 100 : 1 proportion.

c. Pt — Rh.

Platinum is detected by the reaction with potassium chloride (reaction A, p. 59). Gold does not interfere. The sensitivity is $10^{-3.30}$ ($1 : 2 \cdot 10^3$), in the presence of rhodium in a 10 : 1 proportion.

For the detection of rhodium gold must first be removed by extraction with ether and platinum by precipitation with potassium chloride and centrifuging. Rhodium is finally detected by the reaction with stannous chloride (reaction A, p. 40). If there are only traces of this element present then the red colour appears only after a few moments; it is necessary to make a blank test with a solution containing gold and platinum.

General remark.

It is desirable to concentrate all the solutions as much as possible to achieve maximum sensitivity. Only in this way it is possible to identify traces of these elements.

Elements : Se, Te, Ge, Mo, W, V, Nb, Ta

If all these elements are present at the same time, it is not possible to identify them without previous separation. This can easily be achieved if the method of A. A. NOYES and W. C. BRAY (312) is followed in general outline, as it can be adapted to the micro-chemical scale.

The following are the three different groups that can be distinguished :

a. Se — Ge
b. Te — Mo — W — V
c. Nb — Ta

a. Se — Ge.

Place in a micro test tube : 0.1 ml of a solution containing selenium and germanium ions and 0.4 ml of a solution of hydroxylamine hydrochloride (3 mol.). Close the test tube with a rubber stopper to avoid any loss of germanium and heat in a water-bath for 10 minutes until the red precipitate of selenium appears; for small quantities of selenium the heating must last 20 minutes. After some time the precipitate may turn black, but this is of no importance. If the quantity of selenium is large the filtrate must be treated once more with hydroxylamine hydrochloride and centrifuged; the precipitate is then twice washed with 0.1 ml distilled water. This wash water is added to the filtrate.

The red precipitate of selenium does not leave any doubt about the presence of that element. To estimate quickly the quantity of selenium present, dissolve, the precipitate in 0.5 ml concentrated nitric acid, and heat in a water-bath until the solution is clear. Then add mercurous nitrate until precipitation is complete. After centrifuging, the volume of the precipitate is compared with the volume of mercurous selenite, which is obtained from a solution whose selenium content is known.

Acidify the filtrate, which contains germanium, with concentrated sulphuric acid, and saturate with hydrogen sulphide. Close the test tube and heat for 5 minutes in a water-bath, until the white precipitate of germanium sulphide (GeS_2) appears. Estimate the quantity of germanium approximately by comparison with a known volume of precipitated sulphide.

As a qualitative reaction for germanium reaction A, p. 72, can be used.

This separation has been successfully checked by J. GILLIS for the following mixtures : a solution containing 1 g selenium and 0.01 g germanium in 100 ml water and a solution with these concentrations reversed. Using 0.1 ml of these solutions it has been possible to separate and then identify 10 γ germanium in the presence of 1.000 γ selenium and inversely, 10 γ selenium in the presence of 1.000 γ germanium.

On one drop of the solution, e.g. 0.03 ml, the separation is no longer effectual.

Bibliography : 312-313.

b. Te — Mo — W — V.

In a micro test tube evaporate 0.1 ml of the solution containing these four elements to dryness, after adding a few drops of aqua regia or alternatively hydrochloric acid 11 N. Dissolve the residue in hydrochloric acid, 2 N, and boil for some minutes. Tungstic acid forms a yellow precipitate; centrifuge, separate, wash and dissolve in a few drops of concentrated ammonia, 13 N, and evaporate to dryness; after cooling add a drop of a stannous chloride solution, 1 N : in the presence of tungsten a blue colour appears, due to lower oxides (reaction B, p. 84).

Dilute the filtrate of tungstic acid with twice its volume of water and then saturate with hydrogen sulphide; heat in a water-bath for ten minutes, the test tube remaining closed. Then add one third of the volume of water in order that it may again be saturated with hydrogen sulphide; heat for 15 minutes in a water-bath in the same conditions as before. Dissolve the precipitate thus obtained in the minimum quantity of aqua regia and evaporate to dryness. Take up the residue in a few drops of hydrochloric acid, 1 N, and add a few drops of potassium thiocyanate, 1 N and a small quantity of powdered zinc : a red colour indicates molybdenum and a black precipitate indicates tellurium. Evaporate the filtrate after the precipitation of the sulphides to dryness then redissolve in ammonia, 13 N, and saturate with hydrogen sulphide. After some minutes the presence of vanadium $(NH_4)_3VS_4$ is indicated by a purplish red colour.

The detection of vanadium is effected simply in the following manner : place a drop of the filtrate mentioned above on a spot plate with a drop of sulphuric acid, 15-20 N. When hydrogen peroxide, 1 %, is added a rose-pink colour indicates the presence of vanadium (reaction B, p. 87).

This separation has been checked by J. GILLIS for the following mixtures :

Water	W	Mo	Te	V
100 ml	0.05 g	0.5 g	0.5 g	0.5 g
100	0.5	0.05	0.5	0.5
100	0.5	0.5	0.05	0.5
100	0.5	0.5	0.5	0.05

The separation and also the identification are perfectly successful on three drops (0.1 ml) of this mixture. It is no longer feasible with one drop (0.03 ml). It is consequently possible to separate and identify 50 γ of any of these elements in the presence of 500 γ of each of the other three.

Bibliography : 314-316.

c. Nb — Ta (without previous separation).

It is not necessary to separate niobium from tantalum before the analysis, because specific reactions can be used for their ions :

Niobium : pyrocatechol (reaction E, p. 94).
Tantalum : rhodamine B (reaction C, p. 97).

Sensitivity. Nb : D $= \frac{1}{4} 10^{-5}$ ($1 : 10^5$) in the presence of 100 times the quantity of tantalum. Ta : D $= 10^{-4.60}$ ($1 : 4 \cdot 10^4$) in the presence of 100 times the quantity of niobium.

Bibliography : 317-318.

Identification of arsenic, selenium and germanium without previous separation

The detection is possible when using the following reactions :

As (As^{+3} and As^{+5}) potassium hydroxide + aluminium + silver nitrate (see reaction B, p. 35).
Se (Se^{+4} and Se^{+6}) sulphur dioxide (reaction A, p. 62).
Ge (Ge^{+4}) quinalizarin (reaction D, p. 75).

For each test it is necessary to use several drops of the original solution.

Sensitivity. As : D $= 10^{-4.70}$ ($1 : 5 \cdot 10^4$) in the presence of selenium and germanium in a 100 : 1 proportion.

Se : D $= 10^{-5.18}$ ($1 : 1.5 \cdot 10^5$) in the presence of arsenic and germanium in a 100 : 1 proportion.

Ge : D $= 10^{-4}$ ($1 : 10^4$), in the presence of arsenic and selenium in a 100 : 1 proportion.

Bibliography : 319.

25. ALUMINIUM

BY

C. J. VAN NIEUWENBURG

AN 13 **AW 26.97**

A. Al^{+3}, 1.

CAESIUM SULPHATE (PHOTO 12) Cs_2SO_4

BIBLIOGRAPHY : 320-327.

MECHANISM OF REACTION.

Caesium alum,

$$Al_2(SO_4)_3 . Cs_2SO_4 . 24\ H_2O,$$

crystallizes out.

N. SCHOORL (321) and H. YAGODA and H. M. PARTRIDGE (325).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the neutral solution to be analysed and add caesium sulphate crystals, or if necessary caesium chloride and potassium sulphate crystals. Allow to evaporate without heating; after some minutes crystallization sets in at the edge of the drop and colourless octahedra appear, which are always quite distinct although often small.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The cations of iron, chromium and gallium give the same reaction. The crystals resulting from iron and chromium salts are coloured yellow or green when exposed to ammonia vapour. The Hg^{+2} cation and tellurium ions give crystals which resemble the octahedra of alums. The ions of tungsten, strontium and barium give fine precipitates which interfere with the detection of aluminium when they are present in large excess.

When aluminium is present as hydroxide it is preferable to dissolve it only partially in dilute sulphuric acid, so that the solution to be analysed is neutral, when the test can easely be carried out.

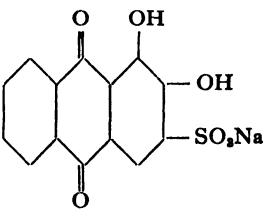
REAGENTS.

1. Solid caesium sulphate or

1*a*. Solid caesium chloride + solid potassium sulphate.

B. Al^{+3}, 23.

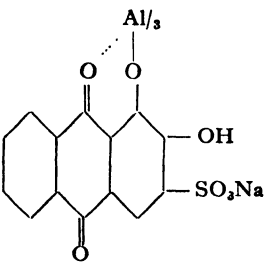
SODIUM 1 : 2-DIHYDROXY-ANTHRAQUINONE-3-SULPHONATE
SODIUM ALIZARIN-3-SULPHONATE
(alizarin S)



BIBLIOGRAPHY : 328-347.

MECHANISM OF REACTION.

A red internal complex is probably formed of the following formula :



F. FEIGL (344).

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the solution to be analysed and then a drop of the reagent solution; develop the stain in ammonia vapour. Even in the absence of aluminium a dark purple colour appears. Wash the stain on a watch-glass with very dilute acetic acid. In the presence of aluminium the purple colour changes to brownish red or to a brick-red colour. It is advisable to make sure that the paper used does not contain any aluminium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The sensitivity is not reduced by the ions of the following elements : Cr, Gl, Zn, Mn, and Ni in a 100 : 1 proportion. The ions of bismuth, titanium and gallium give an analogous reaction, whereas those of Cu, Fe, Ce, rare earths, Zr, Th and Sc give a purplish colour. For the ions of molybdenum, tungsten and vanadium the stain is of a pale yellowish orange colour, for those of cobalt it is pale purple; but there is no interference, even when they are in a 100 : 1 proportion. The UO_2^{+2} cation gives a purplish colour, but generally speaking, the colour of aluminium will be visible at the edge of the stain beside that of the uranium cation. The sensitivity is reduced to 10^{-4} (1 : 10^4) if the uranium cation is in a 100 : 1 proportion.

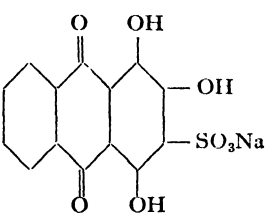
The reaction is sensitive, but it is unfortunately not specific.

REAGENTS.

1. Solution of alizarin sulphonate, 0.2 % in water.
2. Ammonia 11 N.
3. Acetic acid 0.2 N.

C. Al^{+3}, 47.

SODIUM 1 : 2 : 4-TRIHYDROXYANTHRAQUINONE-3-SULPHONATE
SODIUM PURPURIN-3-SULPHONATE
(alizarin red PS)



BIBLIOGRAPHY : 348.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

In a micro test tube.

Place in the test tube a drop of the solution to be analysed, a drop of the reagent solution and a drop of dilute ammonia. Heat this to boiling point and then add 2 drops of dilute acetic acid. A vivid red colour appears and, in ultra-violet light, a yellow fluorescence.

SENSITIVITY AND SELECTIVITY.

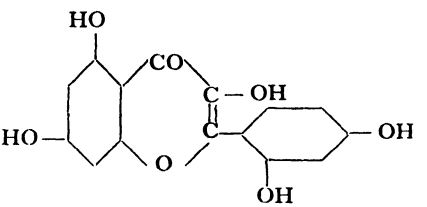
It is difficult to give an exact figure for the sensitivity, as the reagent also produces a weak fluorescence, even in a test tube made of quartz (due to impurities?); it is higher, however, than $D = 10^{-5}$ ($1 : 10^5$). The red colour which is due to aluminium is not selective at all; in fact, a large number of other cations give an identical or rather more brownish colour. The fluorescence, on the other hand, is fairly selective; but the cations of the following elements, viz. Zr, Th, Gl, Sc and Ga give the same effect. The ions of bismuth, gold and iron prevent the reaction, whereas those of titanium do not interfere.

REAGENTS.

1. Solution of sodium purpurin-3-sulphonate, 0.1 %, in water.
2. Ammonia 0.1 N.
3. Acetic acid 0.1 N.

D. Al^{+3}, 42.

3 : 5 : 7 : 2' : 4'-PENTAHYDROXYFLAVONE
(morin)



BIBLIOGRAPHY : 349-363.

MECHANISM OF REACTION.

The fluorescence is attributed to the formation of an aluminium salt of the formula $(C_{15}H_9O_7)_3Al$, but of an unknown structure.

E. SCHANTL (350).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube 1 ml of the solution to be analysed, 1 or 2 drops of hydrochloric acid and 1 drop of the reagent solution. In ultra-violet light a greenish blue fluorescence is observed.

SENSITIVITY AND SELECTIVITY. D = 10^{-5} to 10^{-6} (1 : 10^5 to 1 : 10^6) according to the source of the ultra-violet rays.

The sensitivity is not reduced by the ions of the following elements : Cr, U(UO_2^{+2}), Ce, La, Gl, Zn, Mn, Co and Ni and by the SiO_3^{-2} anion, in a 100 : 1 proportion. The ions of Au, Mo, V and Tl as well as those of iron, which interfere in a 10 : 1 proportion, reduce the fluorescence. The cations of antimony and zinc show a weak fluorescence; that of zinc disappears when 2 more drops of hydrochloric acid are added. The cations of Zr, Th, Sc and Ga give an analogous reaction, although rather yellowish. The ions of titanium interfere in a 100 : 1 proportion, but in a 10 : 1 proportion they reduce the limit of dilution to 10^{-4} (1 : 10^4).

REAGENTS.

1. Hydrochloric acid 2 N.
2. Saturated solution, about 1 %, of morin in methyl alcohol.

26. IRON

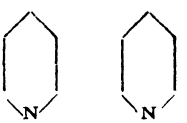
BY

P. E. WENGER

AN 26 **AW 55.85**

A. Fe^{+2}, 72.

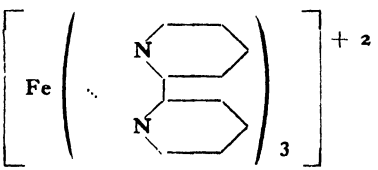
2 : 2'-DIPYRIDYL,
α : α'-DIPYRIDYL



BIBLIOGRAPHY : 364-372.

MECHANISM OF REACTION.

A pink, soluble compound is formed, as described by F. BLAU (364), to which the following structure is attributed :



F. FEIGL and H. HAMBURG (365).

DETAILS OF TEST.

On a spot plate.

Place in a section of the plate, a drop of the solution to be analysed and some hydroxylamine hydrochloride (in order to make the iron change its valency to 2), then a drop of the reagent and a drop of ammonia, so that the medium will be only slightly acid, or even weakly alkaline. In the presence of iron a colour appears which varies between carmine and pink. In the presence of oxidizing agents the quantity of hydroxylamine must be increased so that all the iron is reduced to the bivalent state.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6.18}$ $(1 : 1.5 \cdot 10^6)$.

Very good reaction. As described, the reaction is absolutely selective. The sensitivity is reduced to $10^{-4.48}$ $(1 : 3 \cdot 10^4)$ by the Cu^{+2} and Co^{+2} cations, in a 100 : 1 proportion, the interference by cobalt ions is due to their colour; copper reacts when in high concentrations proportion and better in the presence of hydroxylamine; it is therefore advisable not to use any hydroxylamine in the presence of this cation, but other reducing agents, such as stannous chloride. The ions of the following elements reduce the sensitivity to 10^{-5} $(1 : 10^5)$, when in a 300 : 1 proportion : viz. Rh, Te, (TeO_3^{-2}), Nb, and $Ti(Ti^{+3})$.

The ions of the following elements, in a 5,000 : 1 proportion, do not interfere : Ag, Hg, Pb, Bi, Cd, As, Sb, Sn, Au, Ru, Rh, Pd, Os, Ir, Pt, Se, Mo, W, V, Al, Cr, U, Ce, rare earths, Y, Zr, Th, Gl, Tl, Sc, Ga, In, Zn, Mn, Ni, alkaline-earths and alkali metals.

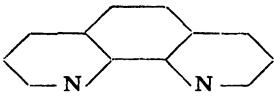
The F^{-1}, PO_4^{-3} anions and the anions of aliphatic hydroxy-acids do not interfere with the detection of iron.

REAGENTS.

1. Solution of $\alpha:\alpha'$-dipyridyl, 0.2 %, in hydrochloric acid 3 N.
2. Solid hydroxylamine hydrochloride.
3. Ammonia 4 N.

B. Fe^{+2}, NR. 1.

o-PHENANTHROLINE



BIBLIOGRAPHY : 373-378.

MECHANISM OF REACTION.

The red colour which appears in the presence of the Fe^{+2} cation is due to a compound of iron of the following formula :

$$\left[Fe(C_{12}H_8N_2)_3\right]^{+2}$$

F. BLAU (373).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the solution to be analysed, which is slightly acid (acidity due to hydrolysis for instance); add some hydroxylamine hydrochloride crystals in order to reduce the iron and one drop of the reagent solution. In the presence of iron a red colour can be observed.

The iron must be in the bivalent state, therefore enough hydroxylamine should be added in the presence of an oxidising agent, to complete the reduction.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6.18}$ ($1 : 1.5 \cdot 10^6$).

The reaction is excellent and very nearly as selective as that of dipyridyl; iridium interferes, however, because it gives a vermilion precipitate.

The sensitivity is reduces to $10^{-4.18}$ ($1 : 1.5 \cdot 10^4$) by the Cu^{+2} cation in a 50 : 1 proportion; the Sb^{+5} and Co^{+2} cations in a 500 : 1 proportion give a sensitivity of $10^{-5.18}$ ($1 : 1.5 \cdot 10^5$). The ions of the following elements, when in a 5,000 : 1 proportion, do not interfere, Ag, Hg, Pb, Bi, Cd, As, Sb (Sb^{+3}), Sn, Au, Ru, Rh, Pd, Os, Pt, Se, Te, Mo, W, V, Nb, Al, Cr, U, Ce, rare earths, Y, Ti, Zr, Th, Gl, Tl, Sc, Ga, In, Zn, Mn, Ni, alkaline-earths and alkali-metals.

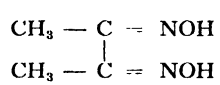
The F^{-1}, PO_4^{-3} anions and those of the aliphatic hydroxy-acids do not interfere with the detection of iron.

REAGENTS.

1. Solution of *o*-phenanthroline in water.
2. Hydroxylamine hydrochloride (solid).

C. Fe^{+2}, 77.

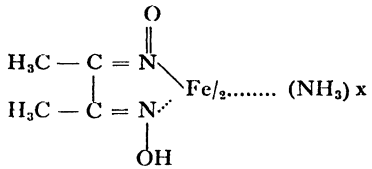
2 : 3-BUTANE DIOXIME, DIMETHYLGLYOXIME



BIBLIOGRAPHY : 379-387.

MECHANISM OF REACTION.

The red, soluble compound which is formed is a complex of bivalent iron, according to the formula :



x = 2 or 3

L. TSCHUGAEFF and B. ORELKIN (382).

DETAILS OF TEST.

On a spot plate.

Place in a section of the plate a drop of the solution to be analysed, to which some hydroxylamine hydrochloride crystals are added in order to ensure that the iron is really in the bivalent state; then add a drop of the reagent solution and a drop of ammonia, so that the medium is definitely alkaline. In the presence of iron a carmine red colour appears. If oxidizing agents are present, one must make sure that the quantity of hydroxylamine hydrochloride is sufficient to bring about the complete reduction of iron to the state of the Fe^{+2} cation, as the Fe^{+3} cation does not react.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ $(1 : 5 \cdot 10^5)$.

The reaction is fairly sensitive, but less selective than the two preceding ones. Nickel reacts under the same conditions and gives

the well-known carmine precipitate, while the cobalt cation gives a brown colour. In the presence of the Au^{+3}, Cr^{+3}, Mn^{+2} and Th^{+4} ions in a 1,000 : 1 proportion the sensitivity is reduced to $10^{-4.70}$ ($1 : 5 \cdot 10^4$). The ions of Rh, Ir, Pt and W only permit the detection of iron with a sensitivity of $10^{-3.70}$ ($1 : 5 \cdot 10^3$), when they are in a 15 : 1 proportion.

The ions of the following elements do not interfere when they are in a 1,500 : 1 proportion : Ag, Hg, Cu, Pb, Bi, Cd, As, Sb, Sn, Pd, Se, Mo, Nb, Ta, Al, U, Ce, rare earths, Y, Ti, Zr, Gl, Tl, Zn, alkaline earths and alkalimetals.

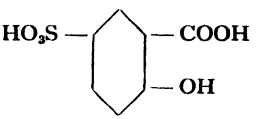
The F^{-1}, PO_4^{-3} anions and those of aliphatic hydroxy-acids do not interfere with the detection of iron.

REAGENTS.

1. Solid hydroxylamine hydrochloride.
2. Ammonia 11 N.
3. Solution of dimethylglyoxime, 1 %, in ethyl alcohol.

D. Fe^{+3}, 87.

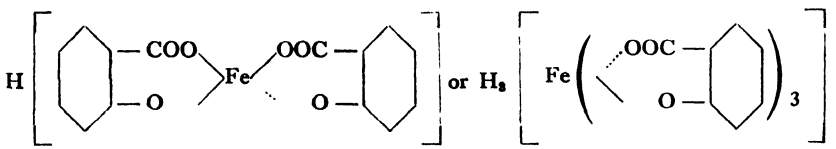
2-HYDROXY-5-SULPHONIC BENZOIC ACID



BIBLIOGRAPHY : 388-393.

MECHANISM OF REACTION.

On analogy of salicylic acid it may be supposed, that the purple colour which salicylsulphonic acid gives with the Fe^{+3} cation is due to the formation of an acid of the disalicylato- or trisalicylatoferrate type :



R. F. WEINLAND and A. HERZ (393),
P. E. WENGER and R. DUCKERT.

DETAILS OF TEST.

On a spot plate.

Place in a section of the plate a drop of the solution to be analysed, which is slightly acid (acidity due to hydrolysis, for example); add some potassium peroxydisulphate (persulphate) crystals in order that the iron may be completely oxidized to a trivalent state and also add a drop of the reagent solution. The presence of iron is indicated by a purple colour. If reducing agents are present, make sure that the quantity of potassium persulphate is sufficient to bring the iron to a valency of 3, as the bivalent cation does not give any reaction.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.48}$ ($1 : 3 \cdot 10^5$).

The reaction is excellent and almost selective, because titanium ions alone mask the reaction of iron. The sensitivity is reduced to 10^{-4} ($1 : 10^4$) by its ions in a 30 : 1 proportion. It is $10^{-4.48}$ ($1 : 3 \cdot 10^4$) in the presence of ions of the following elements : Bi, Sb, Rh, Pd, Ir, Mo, Nb, Cr, Ce, Th and Co in a 100 : 1 proportion. The ions of Ag, Hg, Cu, Pb, Cd, As, Sn, Au, Pt, Se, W, V, Al, U, rare earths, Y, Zr, Gl, Tl, Zn, Mn, Ni, alkaline-earths and alkali-metals do not cause any interference, even in a 1,000 : 1 proportion.

The F^{-1}, PO_4^{-3} anions and those of aliphatic hydroxy-acids mask the Fe^{+3} cation and interfere with the test.

REAGENTS.

1. Solid potassium peroxydisulphate (potassium persulphate).
2. Solution of 2-hydroxy-5-sulphonic benzoic acid, 5 %, in water.

E. Fe^{+3}, NR. 2.

TETRAPOTASSIUM HEXACYANOFERRATE (II), POTASSIUM FERROCYANIDE $K_4[Fe(CN)_6]$

BIBLIOGRAPHY : 394-402.

MECHANISM OF REACTION.

The blue precipitate that is formed is Prussian blue :

$$Fe_4[Fe(CN)_6]_3$$

This reaction is one of the oldest and most universally known.

DETAILS OF TEST.

On a spot plate.

Place in a section of the plate a drop of the acid solution to be analysed (acidity due to hydrolysis) and a drop of the reagent solution. When the iron is not in the trivalent state, especially when the solution contains reducing agents, it must first be oxidized by means of potassium peroxydisulphate (persulphate) crystals. In the presence of iron the formation of a Prussian blue precipitate will be observed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.48}$ ($1 : 3 \cdot 10^4$).

Without being very sensitive or selective, the reaction is very convenient for ordinary analysis.

Numerous ions react; the following give a white precipitate : the ions of Hg, Bi, Cd, Sn, rare earths, Zr, Th, Tl, Zn, Mn, Ni. The Sb^{+5} cation gives a yellow precipitate and niobium gives a yellowish-brown one. The ions of vanadium and of cobalt both give a green precipitate. The UO_2^{+2} cation gives a brown precipitate, the ions of copper (Cu^{+1} and Cu^{+2}) and of molybdenum (Mo^{+6}) give brownish red precipitates.

Besides the Rh^{+3} cation gives a yellowish-brown coloration, W^{+6} a yellow colour and Ti^{+4} gives a pale brownish red colour.

All these reactions, however, do not interfere; the following are the sensitivities :

the sensitivity is not changed by ions of the following elements in a 100 : 1 proportion, viz. As, Sb (Sb^{+3}), Sn, Au, Pd, Te, Nb, Ta, Al, rare earths, Y, Gl, alkaline-earths and alkali-metals.

the sensitivity is 10^{-4} ($1 : 10^4$) in the presence of ions of the following elements : Ag, Pb, Bi, Cd, Rh, Ir, Pt, Se, Cr, Ce, Th, Zn, Mn, and Ni when in a 30 : 1 proportion; it is reduced to $10^{-3.78}$ ($1 : 6 \cdot 10^3$) by ions of the following elements : Hg, Sb (Sb^{+5}), W, V, Ti, Zr, Tl and Co, when in a 20 : 1 proportion; the Sb^{+5} cation which gives a yellow precipitate, will produce a dark-green colour as soon as it is present in a considerable proportion.

Molybdenum (Mo^{+6}) in a 5 : 1 proportion reduces the sensitivity to 10^{-3} ($1 : 10^3$) and lastly the Cu^{+2} and UO_2^{+2} cations, in a 2 : 1 proportion, give a sensitivity of $10^{-2.78}$ ($1 : 6 \cdot 10^2$), that means that

they interfere with the detection of iron in a very marked manner.

It must be noted that the addition of the Zn^{+2} cation, as recommended by J. GUÉRON (398), causes hardly any improvement in the sensitivity.

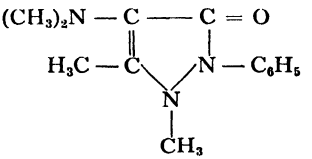
The F^{-1}, PO_4^{-3} anions and those of the aliphatic hydroxy-acids mask the Fe^{+3} cation; therefore they interfere with the detection of iron.

REAGENTS.

1. Solid potassium peroxydisulphate (potassium persulphate).
2. Solution of potassium ferrocyanide, 10 %, in water.

F. Fe^{+3}, 28.

4-DIMETHYLAMINO-1-PHENYL-2 : 3-DIMETHYL-5-PYRAZOLONE, 4-DIMETHYLAMINO-ANTIPYRINE *(pyramidon)*
+ AMMONIUM THIOCYANATE
+ Co^{+2} CATION (PHOTO 13)



+ NH_4CNS + Co^{+2}

BIBLIOGRAPHY : 403-405.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

Under the microscope.

The iron should be in the trivalent state oxidize with some potassium peroxydisulphate (persulphate), if necessary.

Place on a slide a drop of the solution to be analysed and a drop of the cobalt salt solution. Evaporate to dryness over a small burner and leave it to cool down. Then add a drop of the reagent solution and a drop of dilute hydrochloric acid, heat and rub with a glass rod in order to start crystallization. In the presence of iron some pink crystals are obtained, which are formed in rosettes and intermixed with blue crystals originating from the reaction of cobalt only. Small quantities of cobalt improve the crystallization, but an excess interferes.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

The ions of the following elements, in a 1,000 : 1 proportion, do not reduce the sensitivity : Ag, Cu, Pb, Bi, As, Sb, Au, Pd, Pt, W, Ta, Al, Cr, U, Ce, rare earths, Zr, Gl, Mn, Co, Ni, alkaline earths and alkali-metals. It must be noted, however, that cobalt in a proportion larger than 200 : 1, interferes with the detection of iron.

The sensitivity is 10^{-4} ($1 : 10^4$) in the presence of ions of the following elements, in a 100 : 1 proportion, viz. Hg, Cd, Sn, Se, Mo, Nb, Zn. The TcO_3^{-2} anion and the Ti^{+4} cation interfere in a more marked manner and reduce the sensitivity to 10^{-3} ($1 : 10^3$), when they are present in a 10 : 1 proportion. Lastly, the ions of rhodium, iridium and vanadium interfere, giving precipitates that are brownish red, red and purplish red.

The Fe^{-1}, PO_4^{-3} anions and those of the aliphatic hydroxy-acids prevent the detection of iron.

REAGENTS.

1. Solid potassium peroxydisulphate (potassium persulphate).
2. Solution of cobalt (II) chloride, 0.02 %, in water.
3. Saturated solution of pyramidon in a saturated solution of ammonium thiocyanate in water.
4. Hydrochloric acid 0.3 N.

27. CHROMIUM

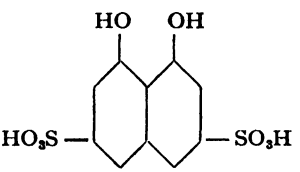
BY

P. E. WENGER

AN 24 **AW 52.01**

A. CrO_4^{-2}, 25.

1 : 8-DIHYDROXYNAPHTHALENE-3 : 6-DISULPHONIC ACID
(chromotropic acid)



BIBLIOGRAPHY : 406-410.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

On a spot plate.

Place in a section of the plate a drop of the solution to be analysed (chromium in the state of alkali-chromate), a drop of the reagent solution and a drop of nitric acid. In the presence of chromate a red colour appears. Among other things the nitric acid is meant to eliminate the reactions of the cations of iron, uranium and titanium. If chromium is in a trivalent state (Cr^{+3}), then the simplest way to oxidise it, is to treat it with sodium peroxide in slightly alkaline medium; the solution is then acidified with nitric acid before the reagent is added and the test is continued as indicated above.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ $(1 : 5 \cdot 10^4)$.

The reaction is excellent and selective, because the colours caused by the Fe^{+2}, Fe^{+3}, UO_2^{+2} and Ti^{+4} cations (green for the first two, brown and pink for the other two) disappear in strongly acid (nitric acid) medium.

The sensitivity is not changed by ions of the following elements, in a 150 : 1 proportion : Ag, Hg, Cu, Pb, Bi, Cd, Sb (Sb^{+5}), Au, Rh, Pd, Ir, Pt, Se (Se^{+6}), Mo (Mo^{+6}), V, Nb, Ta, Al, U, Ce, rare earths, Y, Ti, Zr, Th, Gl, Tl, Zn, Mn, Co, Ni, alkaline earths and alkali-metals. The sensitivity is 10^{-4} $(1 : 10^4)$ in the presence of the following ions : As^{+3}, As^{+5}, TeO_3^{-2} and WO_4^{-2}, in a 30 : 1 proportion. The two Fe cations reduce the sensitivity even down to $10^{-3.70}$ $(1 : 5 \cdot 10^3)$, if they are in a 15 : 1 proportion. Lastly, the Sb^{+3}, Sn^{+2} and Sn^{+4} ions bring the sensitivity to $10^{-3.48}$ $(1 : 3 \cdot 10^3)$, when in a 10 : 1 proportion.

REAGENTS.

1. Solid sodium peroxide.
2. Saturated solution of chromotropic acid in water.
3. Nitric acid 7.5 N.

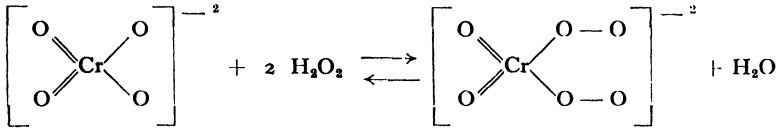
B. CrO_4^{-2}, 40.

HYDROGEN PEROXIDE H_2O_2

BIBLIOGRAPHY : 411-424.

MECHANISM OF REACTION.

It can be represented by the reaction :



in which the blue colour is due to the perchromic anion CrO_6^{-2}.

M. E. RUMPF (411).

DETAILS OF TEST.

In a micro test tube.

Place in the test tube a drop of hydrogen peroxide, a drop of dilute hydrochloric acid and a few drops of ether; then add the solution to be analysed (slightly acid), in which chromium is present in the state of a CrO_4^{-2} anion and avoid any heating of the solution. For high concentrations of chromium the ether is coloured blue; when the concentrations are low a blue ring appears at the surface of separation of the aqueous solution and the ether. This colour does not last long; the ring itself is rather fugitive, and more so if the temperature is higher.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ $(1 : 5 \cdot 10^4)$.

The reaction, which is not extremely sensitive, is very useful because of its selectivity; no other element gives the same reaction and there are few which cause any interference. Reducing agents prevent the reaction, but they are eliminated by the fact, that the reaction is carried out on the CrO_4^{-2} anion, which can easily be obtained starting from the solution of the Cr^{+3} cation by oxidation with sodium peroxide.

The ions of the following elements do not affect the sensitivity,

when in a 100 : 1 proportion : Ag, Hg, Cu, Pb, Cd, Sb, Sn (Sn^{+4}), Au, Rh, Pd, Pt, Se, Mo, W, Nb, Ta, Al, Fe (Fe^{+3}), U, Ce, rare earths, Zr, Th, Gl, Tl (Tl^{+1}), Zn, Mn, Co, Ni, alkaline earths and alkali-metals.

The sensitivity is reduced to $10^{-4.48}$ ($1 : 1.5 \cdot 10^4$) by the ions of the following elements, when in a 15 : 1 proportion : Bi, Ir, Te, Fe (Fe^{+2}), Ti and Tl (Tl^{+3}); the ions of tellurium, iron and titanium give a yellow colour. The ions of arsenic, in a 10 : 1 proportion, lead to a sensitivity 10^{-4} ($1 : 10^4$). Lastly, the V^{+3} and V^{+5} cations interfere with the detection of chromium, even in a 5 : 1 proportion, and give a brownish red colour; the sensitivity is very greatly reduced : it is $10^{-3.70}$ ($1 : 5 \cdot 10^3$).

REAGENTS.

1. Solid sodium peroxide.
2. Solution of hydrogen peroxide, 3 %, in water.
3. Hydrochloric acid 2 N.
4. Pure ether.

C. CrO_4^{-2}, 49.

GUAIACUM RESIN

BIBLIOGRAPHY : 425.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

On a spot plate.

Place in a section of the plate a drop of the solution to be analysed (slightly acid), in which chromium is present in the state of a CrO_4^{-2} anion; add a drop of the reagent solution and a drop of dilute sulphuric acid. The chromic anion causes the formation of a blue precipitate.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 5 \cdot 10^4$).

The reaction is good, although it is disturbed by some elements.

The sensitivity is not reduced by the ions of the following elements,

when present in a 150 : 1 proportion : Ag, Hg, Cu, Pb, Cd, As (As^{+3}), Sn (Sn^{+4}), Rh, Pd, Pt, Se, Te (TeO_3^{-2}), Mo, W, Nb, Ta, Al, Fe (Fe^{+2}), U, Ce (Ce^{+3}), rare earths, Y, Ti, Zr, Th, Gl, Tl, Zn, Mn, Co, Ni, Ca, Sr, Mg and alkali-metals. The Fe^{+3} cation gives the same reaction; but it can be masked by addition of sodium fluoride.

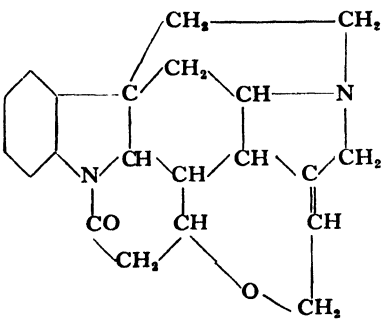
The sensitivity has a value of $10^{-4.18}$ ($1 : 1.5 \cdot 10^4$) in the presence of the Bi^{+3} and As^{+5} ions in a 50 : 1 proportion. It is reduced to a value of $10^{-3.48}$ ($1 : 3 \cdot 10^3$) by the Sn^{+2} and Ba^{+2} ions in a 10 : 1 proportion. Lastly, the ions of the following elements give the same reaction as the chromium anion and prevent its detection, viz. Sb, Au, Ir, V and Ce (Ce^{+4}).

REAGENTS.

1. Solution of guaiacum resin, 1 %, in ethyl alcohol.
2. Sulphuric acid 2 N.
3. Solid sodium fluoride.

D. CrO_4^{-2}, 57.

STRYCHNINE



$= C_{21}H_{22}O_2N_2$

BIBLIOGRAPHY : 426-427.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

In a micro test tube.

Place in the test tube a drop of the solution to be analysed in which

chromium is present in the state of the CrO_4^{-2} anion and add a drop of the reagent solution. The presence of chromium is indicated by the appearance of a pink colour; for tests which are near to the limit of sensitivity one must wait some minutes (about ten to twelve minutes). When the solution to be analysed contains considerable quantities of free hydrochloric acid, it must be neutralized, at least partly, with sodium hydroxide, so as to avoid a decrease in sensitivity.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

The reaction is sensitive. The ions of the following elements, in a 100 : 1 proportion, do not change the sensitivity : Ag, Hg, Cu, Bi, Cd, As, Sb (Sb^{+3}), Sn (Sn^{+4}), Au, Rh, Pd, Ir, Mo, W, Nb, Ta, Al, Ce (Ce^{+3}), rare earths, Y, Ti, Zr, Gl, Tl, Zn, Mn, Ni, alkaline-earths and alkali-metals. The sensitivity is reduced to $10^{-5.48}$ (1 : $3 \cdot 10^5$) in the presence of ions of the following elements, in a 30 : 1 proportion : Pb, Pt, Se, Te, Fe, U, Th and Co; the interference by cobalt is due to the colour of its ion, while a yellow colour is produced in the presence of the elements Te, Fe and Th. The Sb^{+5} cation, in a 10 : 1 proportion, leads to a sensitivity of 10^{-5} (1 : 10^5).

The Sn^{+2} and Ce^{+4} cations prevent the detection of chromium.

It must be observed that slightly soluble chromates and sulphates do not cause any considerable interference, except in the case of lead.

REAGENTS.

1. Sodium hydroxide 3 N.
2. Solution of strychnine, 1 %, in sulphuric acid 35 N.

E. Cr^{+3}, 13.

CAESIUM SULPHATE or CAESIUM CHLORIDE + POTASSIUM HYDROGEN SULPHATE Cs_2SO_4 or $CsCl + KHSO_4$

(PHOTO 14)

BIBLIOGRAPHY : 428-429.

MECHANISM OF REACTION.

Caesium alum crystals are formed, corresponding to the formula :

$$CrCs(SO_4)_2 . 12\ H_2O$$

J. VERMANDE (428) and A MARTINI (429).

DETAILS OF TEST.

Under the microscope.

Place on a slide one drop of the slightly acid solution to be analysed, the chromium being in the state of the Cr^{+3} cation. Add some crystals of the reagent and then heat slightly to concentrate the solution. On cooling the chromium gives isolated pale purple crystals of a trigonal shape, which have the appearance of little triangular plates, truncated at the extreme corners.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.20}$ ($1 : 1.6 \cdot 10^4$).

This reagent allows of a precise detection of the trivalent cation although a large number of other ions also react with caesium salts; but the crystalline forms differ sufficiently so that many ions which give double salts, or even insoluble sulphates or chlorides, only cause slight interference.

The sensitivity is not affected by the ions of the following elements, in a 150 : 1 proportion : Cu, Bi, Cd, As, Sn, Rh, Pd, Pt, Se, Te, Mo, W, Ce, Zr, Th, Tl, Zn, Mn, Ni, alkali-metals. The sensitivity is 10^{-4} ($1 : 10^4$) in the presence of the ions of Hg, Pb, Ir, V and alkaline earths, in a 100 : 1 proportion; it becomes $10^{-3.48}$ ($1 : 3 \cdot 10^3$) in the presence of ions of Sb, Au, Fe (Fe^{+2}) and Gl, in a 30 : 1 proportion. The ions of silver, rare earths and yttrium when in a 15:1 proportion, lead to a sensitivity of $10^{-3.20}$ ($1 : 1.6 \cdot 10^3$) while those of iron (Fe^{+3}), uranium and cobalt, in a 10 : 1 proportion, restrict the sensitivity to 10^{-3} ($1 : 10^3$). Lastly, the Al^{+3} cation interferes with the detection of chromium as soon as it reaches the 5 : 1 proportion.

REAGENTS.

1*a*. Solid caesium sulphate or

1*b*. Solid caesium chloride + solid potassium hydrogen sulphate.

28. URANIUM

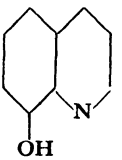
BY

P. E. WENGER

AN 92 AW 238.07

A. UO_2^{+2}, 22.

8-HYDROXYQUINOLINE



BIBLIOGRAPHIE : 430-431.

MECHANISM OF REACTION.

The brown compound formed has the following formula according to F. HECHT and W. REICH-ROHRWIG (431) :

$$(C_9H_6NO)_2UO_2 \cdot C_9H_7NO$$

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the slightly acid solution to be analysed, a drop of the reagent solution and then develop in ammonia gas. A very clear brown stain then appears. The reaction can also be effected on a spot plate, but is then much less selective, as the rare earths react in such a way that they give a yellow precipitate, more or less dark; this does not appear on the filter paper.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ ($1 : 10^4$).

This is a useful reaction which enables us to distinguish uranium from rare earths and from the chief elements contained in its ores, with the exception of iron.

The sensitivity is not changed by the ions of the following elements, in a 50 : 1 proportion : Ag, Hg, Pb, Cd, Sn, Au, Ir, Pt, Se, Te, Mo, W, Al, Cr, Ce (Ce^{+3}), rare earths, Y, Ti, Zr, Gl, Tl, Zn, Mn, Co, Ni, alkaline earths and alkali-metals. The ions of the following elements, when in a 10 : 1 proportion, reduce the sensitivity to $10^{-3.48}$ ($1 : 3 \cdot 10^3$)

viz. Cu, Bi, As, Sb (Sb^{+3}), Rh, Pd, V, Nb, Ta and Th. Lastly, the following ions interfere : Sb^{+5} (orange colour), Fe^{+2} and Fe^{+3} (blackish green colour), and Ce^{+4} (brown colour).

Certain anions, such as F^{-1}, PO_4^{-3} and the anions of aliphatic hydroxyacids entirely prevent uranium from reacting; it is therefore impossible to mask the iron by means of these anions.

REAGENTS.

1. Solution of 8-hydroxyquinoline, 5 %, in alcohol.
2. Ammonia 11 N.

B. UO_2^{+2}, 12.

TETRAPOTASSIUM HEXACYANOFERRATE (II), POTASSIUM FERROCYANIDE $K_4[Fe(CN)_6]$

BIBLIOGRAPHY : 432-436.

MECHANISM OF REACTION.

The brown precipitate obtained has the following formula :

$$(UO_2)_2[Fe(CN)_6]$$

I. A. ATANASIU (432).

DETAILS OF TEST.

On a spot plate.

Place in a section of the plate a drop of the slightly acid solution to be analysed and a drop of the reagent solution. In the presence of uranium a brown precipitate is formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.48}$ ($1 : 3 \cdot 10^4$).

The selectivity of this reaction is not very great.

The sensitivity is not reduced by the ions of the following elements, when in a 100 : 1 proportion : Ag, Hg (Hg^{+1}), Pb, Bi, Cd, Sb (Sb^{+3}), Sn (Sn^{+2}), Au, Pd, Ir, Pt, Se, Te, W, Ta, Al, Cr, Ce, rare earths, Y, Zr, Th, Gl, Tl, Zn, Mn, Ni, alkaline earths and alkali-metals. It must be noted that a very large number of these elements give white precipitates which, fortunately do not interfere with the detection of uranium. The Rh^{+3} cation reduces the sensitivity a little : 10^{-4}

(1 : 10^4), when it is in a 30 : 1 proportion. The Hg^{+2}, As^{+3}, As^{+5}, Sb^{+5}, Sn^{+4}, V^{+3}, Nb^{+5} ions, in a 15 : 1 proportion, lead to a sensitivity of $10^{-3.70}$ (1 : $5 \cdot 10^3$). The cobalt cation reduces the sensitivity even more: $10^{-3.48}$ (1 : $3 \cdot 10^3$), when in a 10 : 1 proportion. Lastly, the Cu^{+2} cation (brownish purple precipitate) and the Fe^{+3} cation (Prussian blue precipitate) interfere with the detection of uranium.

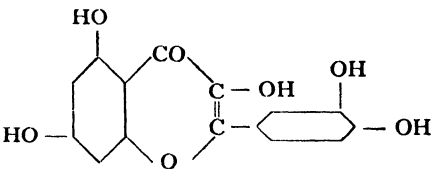
It must again be noted that the UO_2^{+2} cation is totally masked by the following anions : F^{-1}, PO_4^{-3}, CN^{-1} and those of aliphatic hydroxy-acids.

REAGENT.

1. Solution of potassium ferrocyanide, 5 %, in water.

C. UO_2^{+2}, NR. 1.

3:5:7:3':4'-PENTAHYDROXYFLAVONE
(quercetin)



BIBLIOGRAPHY : 437.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the slightly acid solution to be analysed and a drop of the reagent solution; then add a drop of ammonia. The presence of the UO_2^{+2} cation is indicated by a brownish red stain.

In the presence of ions of Ag, Cu, Pb, Bi, Cd, Cr, Ce (Ce^{+3}), rare earths, Y, Tl (Tl^{+3}), Co and Ni the test should be carried out in an acid medium in order to avoid the interference of these ions; instead of a drop of ammonia a drop of dilute nitric acid must be added.

SENSITIVITY AND SELECTIVITY. D = $10^{-4.48}$ (1 : $3 \cdot 10^4$), when in ammoniacal medium; in acid medium D = 10^{-4} (1 : 10^4).

Taking into account both the nature of the medium and the presence

of certain ions quercetin gives a fairly selective test for uranium, especially in the presence of rare elements.

The sensitivity is not altered by ions of the following elements, in a 100: 1 proportion: Hg (Hg^{+2}), Cd, Au, Pd, Ir, Pt, Se, Ta, Cr (CrO_4^{-2}), Ce (Ce^{+3}), Gl, Tl (Tl^{+1}), Zn, alkaline earths and alkali-metals. It is 10^{-4} ($1 : 10^4$) in the presence of ions of the following elements, in a 30 : 1 proportion : Ag, Hg (Hg^{+1}), Pb, As (As^{+3}), Sn, Rh, Te, Mo, W, Al, Cr (Cr^{+3}), rare earths, Y, Zr, Th, Mn, Co and Ni when working in acid medium, as indicated above.

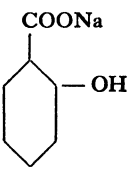
The sensitivity is reduced to $10^{-3.70}$ ($1 : 5 \cdot 10^3$) by the ions of the following elements, in a 15 : 1 proportion : Cu, As (As^{+5}), Sb, V, Nb, Ce (Ce^{+4}), Tl (Tl^{+3}) and Mg. The Bi^{+3} cation, when in a 10 : 1 proportion leads to a sensitivity of $10^{-3.48}$ ($1 : 3 \cdot 10^3$). Lastly, the two cations of iron which give a blackish green colour and that of titanium giving a brown colour interfere with the test for uranium. Among the anions a certain number mask uranium; they are F^{-1}, PO_4^{-3}, CN^{-1} in particular and also the anions of aliphatic hydroxy-acids.

REAGENTS.

1. Solution of quercetin, 0.2 %, in ethyl alcohol.
2. Ammonia 4 N.
3. Nitric acid N.

D. UO_2^{+2}, 36.

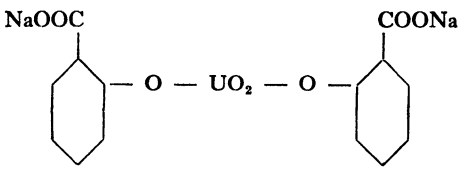
SODIUM 2-HYDROXYBENZOATE, SODIUM SALICYLATE



BIBLIOGRAPHY : 438-439.

MECHANISM AND REACTION.

According to G. CANNERI and L. FERNANDES (439) a disalicylato-uranic acid is formed having the formula :



DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the slightly acid solution to be analysed, a drop of the sodium acetate solution and a drop of the reagent solution. In the presence of uranium an orange colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.78}$ ($1 : 6 \cdot 10^3$).

The reaction is not very sensitive; further, it can only be effected in the absence of free mineral acids.

The sensitivity is not reduced by the ions of the following elements, in a 50 : 1 proportion : Ag, Hg (Hg^{+2}), Pb, Cd, Au, Rh, Ir, Pt, Te, Mo, W, Ce (Ce^{+3}), rare earths, Th, Tl, Zn, Mn, Co, Ni, alkaline earths and alkali-metals. The sensitivity is slightly decreased, $10^{-3.48}$ ($1 : 3 \cdot 10^3$), by the ions of the following elements, in a 10 : 1 proportion : Hg (Hg^{+1}), Cu, Bi, As, Sn, Pd, Se, V, Nb, Ta, Al, Cr (Cr^{+3} and CrO_4^{-2}), Y, Zr, and Gl. Some of these elements give a white precipitate, e.g. Ag, Hg, Bi; copper gives a green colour.

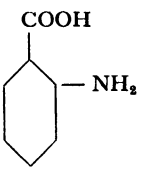
The detection of uranium is rendered impossible by the following cations : Sb^{+3}, Sb^{+5} (brownish green precipitate), Fe^{+2} (red-orange precipitate), Fe^{+3} (purple-red precipitate), Ce^{+4} (brownish green precipitate) and Ti^{+4} (orange-yellow precipitate); also by the following anions : F^{-1}, PO_4^{-3}, CN^{-1} and those of aliphatic hydroxy-acids, which mask the UO_2^{+2} cation.

REAGENTS.

1. Solution of sodium acetate, 10 %, in water.
2. Saturated solution of sodium salicylate in water.

E. UO_2^{+2}, NR. 2.

o-AMINOBENZOIC ACID, ANTHRANILIC ACID (PHOTO 15)



BIBLIOGRAPHY : 440.

MECHANISM OF REACTION.

It is probable that an uranyl salt is formed, but its exact constitution has not yet been established.

P. E. WENGER and R. DUCKERT.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be examined, which is evaporated to dryness; take up the residue in a drop of water in order to have a nearly neutral medium. Add anthranilic acid crystals and heat the mixture so as to dissolve the reagent and start the crystallization. Thin, colourless needles are produced, often grouped in rosettes, that can be easily distinguished from the reagent, which crystallizes in arborescences that are much coarser.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.48}$ $(1 : 3 \cdot 10^4)$.

The reaction is selective.

The sensitivity is not changed by the ions of the following elements, in a 300 : 1 proportion : Ag, Hg (Hg^{+2}), Pb, Cd, Au, Rh, Pd, Ir, Pt, Mo, Al, Cr (Cr^{+3} and CrO_4^{-2}), Cc (Ce^{+3}), rare earths, Y, Ti, Th, Gl, Tl, Zn, Mn, Co, Ni, alkaline-earths and alkali-metals. The sensitivity is slightly decreased by the Hg^{+1} ion (white precipitate) and the Ce^{+4} ion (brown precipitate); it is $10^{-4.18}$ $(1 : 1.5 \cdot 10^4)$.

The ions of the following elements, when in a 100 : 1 proportion reduce the sensitivity to 10^{-4} $(1 : 10^4)$: Cu, Bi, Sn, Se, Te, W, V, Nb, Fe (Fe^{+3}) and Zr. The ions of arsenic and tantalum, in a 15 : 1 proportion, reduce the sensitivity to $10^{-3.18}$ $(1 : 1.5 \cdot 10^3)$. Finally, antimony under both its valencies the F^{-1} and PO_4^{-3} anions and those of aliphatic hydroxy-acids interfere with this test for uranium.

REAGENT.

1. Solid anthranilic acid.

29. RARE EARTHS

BY

P. E. WENGER

AN 57 to 71 **AW 138.92 to 174.99**

The elements of the rare earths form a natural group, which is altogether a special one that can be studied by

itself. Therefore we have deemed it judicious to propose a general reagent for these elements, which will enable us to detect them in the presence of some others with wich they occur in minerals (Nb, Ta, Al, Fe, U, Y, Ti, and Ca).

On the other hand the elements of the rare earths with some others (Th, Sc) form an analytical group, which is well defined and can be isolated in the course of a general analysis of the cations.

Without going into details of systematic analysis, let us observe, that it is possible to separate a group of elements that contains the rare earths as well as cerium, thorium and scandium by following the method of A. A. NOYES and W. C. BRAY (441); see also the methods, which are not very different, in the treatises by F. P. TREADWELL (442) and by P. E. WENGER and G. GUTZEIT (443).

Briefly the process is as follows :

After having eliminated a certain number of elements that are more or less rare by distillation of their bromides (As, Se, Ge) and of their tetroxides (Ru, Os) or by rendering them insoluble (precious metals, W, Nb, Ta, Si) the analysis is continued by a precipitation with hydrogen sulphide in acid solution and finally with a precipitation with ammonium sulphide in ammoniacal solution.

The precipitate of sulphides and hydroxides obtained from the ammoniacal solution contains the elements of the rare earths; it is filtered off in order to separate it from the alkaline-earth elements. After dissolving again in acid, it is treated with sodium hydroxide and sodium peroxide. The following elements are dissolved : V, Al, Cr, U, Gl, In and Zn, whereas Fe, rare earths, Y, Ti, Zr, Th, Sc, Mn, Co, Ni and part of the In are precipitated in the form of hydroxides or hydrated oxides. This precipitate is treated with

hydrofluoric acid, which dissolves the following elements : Fe, Ti, Zr, In, Mn, Co and Ni, while a residue remains containing rare earths cerium, thorium and scandium. This residue can be more minutely examined for the identification of rare earths.

A. RE^{+3}, NR.

OXALIC ACID

BIBLIOGRAPHY : 445-448.

MECHANISM OF REACTION.

The oxalates of elements of the rare earths are precipitated, having the general formula :

$$(C_2O_4)_3Me_2 \cdot xH_2O$$

DETAILS OF TEST.

In a macro test tube.

Place in the test tube a few drops of the slightly acid solution to be analysed and add the reagent solution. In the presence of elements of the rare earths a white crystalline precipitate is formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The sensitivity is approximately the same for each of these elements. Yttrium, thorium and the alkaline earth cations precipitate as well. The thorium precipitate is not soluble in hydrochloric acid, whereas all the others are. The ions of Nb, Ta, Al, Fe, U, Ti, Zr, Ct and Sc do not precipitate.

REAGENT.

1. Saturated solution of oxalic acid in water.

In the field of the group of elements of the rare earths we can only deal with a few simple methods of analysis. The detection is preferably done by a physico-chemical

process (the spark spectrum, for example), as selective chemical reagents are lacking for the most part with regard to ions of the rare earths; the La^{+3}, Ce^{+4} and Eu^{+2} cations are the only exceptions.

The detailed analysis of this group can hardly be anything but a specialist's job and the reader is therefore referred to the works which deal particularly with this subject, and especially to those by G. URBAIN (444).

It is useful, however, to mention two reagents of sub-groups, which allow of an orientation in a more detailed analysis of rare earths.

30. CERIUM EARTHS

BY

P. E. WENGER

AN 57 to 62 **AW 138.92 to 150.43**

Lanthanum, cerium, neodymium, praseodymium, samarium.

A. CE^{+3}, NR.

AMMONIUM ETHANE-1 : 2-DICARBOXYLATE, AMMONIUM SUCCINATE (PHOTO 16)

$$\begin{matrix} CH_2 - COONH_4 \\ | \\ CH_2 - COONH_4 \end{matrix}$$

BIBLIOGRAPHY : 449.

MECHANISM OF REACTION.

Crystallized succinates are formed having the general formula :

$$(C_4H_4O_4)_3Me_2 \,.\, x\ H_2O$$

DETAILS OF TEST.

Under the microscope.

Place on a slide one drop of the solution to be analysed and evaporate o dryness; take up the residue with one drop of distilled water and

add some ammonium succinate crystals. An excess of reagent is required. In the presence of cations of cerium earths some bushy clusters of thin colourless needles are formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-2.52}$ ($1 : 3.3 \cdot 10^2$).

The Fe^{+3} cation gives a brown precipitate. The cations of the elements Nb, U, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Th, Sc and Ca give crystallized precipitates which are appreciably different from those obtained with the cerium earths, with the result that they do not cause any interference in a 10 : 1 proportion. The zirconium cation gives an amorphous precipitate; the tantalum ions do not react.

REAGENT.

1. Solid ammonium succinate.

31. YTTRIUM EARTHS

BY

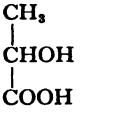
P. E. WENGER

AN 63 to 71 **AW 152.0 to 174.99**

Europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium (cassiopeium).

A. YE^{+3}, NR.

α-HYDROXY-PROPIONIC ACID, LACTIC ACID (PHOTO 17)



BIBLIOGRAPHY : 450.

MECHANISM OF REACTION.

The simple salt of cations of the yttrium earths is formed, having the general formula :

$$(C_3H_5O_3)_3Me.$$

BEHRENS-KLEY (450).

DETAILS OF TEST.

Under the microscope.

Place on a slide: a drop of the solution to be analysed and evaporate to dryness; take up the residue with a drop of water to which the reagent is added. In the presence of cations of yttrium earths colourless prismatic crystals are formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3}$ ($1 : 10^3$).

Scandium reacts in the same way. The cations of the elements Nb, Ta, Fe, U, Ce, La, Nd, Zr, Th and Ca neither react nor interfere, even in a 100 : 1 proportion.

REAGENT.

1. Pure lactic acid.

We indicate here the only reagents that can successfully be used for the detection of three of the rare earths : lanthanum, cerium, and europium.

32. LANTHANUM

BY

P. E. WENGER

AN 57 **AW 138.92**

A. La^{+3}, 6.

IODINE I_2

BIBLIOGRAPHY : 451.

MECHANISM OF REACTION.

The reaction is carried out in the presence of sodium acetate and on heating, which allows of the formation of basic lanthanum salt, which have the property of adsorbing elementary iodine.

D. KRÜGER and E. TSCHIRCH (451).

DETAILS OF TEST.

In a macro test tube.

Place in a test tube one ml of the nearly neutral solution to be analysed, add 0.5 ml of sodium acetate solution, 1 ml. of the iodine solution and finally a few drops of ammonia. In the presence of large quantities of lanthanum a blue flocculent precipitate appears; if the lanthanum is present in low concentration the solution must be heated slowly to the boil.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.18}$ $(1 : 1.5 \cdot 10^3)$.

The reaction is specific for lanthanum in the group of rare earths and related elements of the latter. The reaction is not interfered with by any other ions except the ones that are strongly coloured and trivalent cations which give precipitates of a basic acetate. The alkaline-earth cations do not interfere. Starch gives the same reaction.

Although this reaction is not very sensitive, it allows of a reliable identification of lanthanum in the ores of rare earths.

REAGENTS.

1. Sodium acetate solution, 1 %, in water.
2. Iodine 0.02 N.
3. Ammonia N.

33. CERIUM

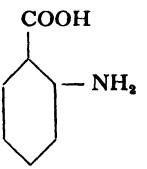
BY

P. E. WENGER

AN 58 **AW 140.13**

A. Ce^{+4}, NR. 1.

o-AMINOBENZOIC ACID, ANTHRANILIC ACID



BIBLIOGRAPHY : 452.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

On a spot plate.

As the Ce^{+3} cation does not react, a previous oxidation must take place with lead (IV) oxide and hot, concentrated nitric acid. Other oxidizing agents which would enable us to obtain the Ce^{+4} cation, cannot be used, because they react with ammonium anthranilate.

Place in a section of the plate a drop of the solution to be analysed which is rendered slightly acid (with nitric acid, for example), and add a drop of the reagent solution. In the presence of cerium a blackish blue precipitate appears, which is very rapidly transformed into a soluble product, which colours the solution brown.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The sensitivity is not changed by the ions of the following elements in a 100 : 1 proportion : Ag, Hg, Pb, Cd, As (As^{+3}), Sb, Sn (Sn^{+4}), Rh, Pd, Ir, Pt, Se (Se^{+6}), Te, Mo, W, Nb, Ta, Al, U, rare earths, Y, Ti, Zr, Th, Gl, Tl, Zn, Mn, Co, Ni, alkaline earths and alkali-metals.

The sensitivity is reduced to $10^{-3.48}$ (1 : $3 \cdot 10^3$) by the following ions in a 10 : 1 proportion : Cu^{+2}, Bi^{+3}, As^{+5}, Fe^{+3} and Cr^{+3}. It must be observed that the Fe^{+3} cation must be masked by the phosphoric anion, without which it absolutely prevents the detection of cerium.

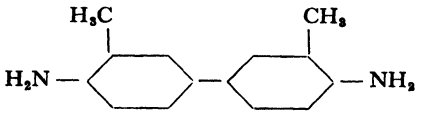
The ions of Au and V, as well as the CrO_4^{-2} anion, give the same reaction, less rapidly, and interfere. The reducing agents, such as Sn^{+2}, Se^{+4} or HCl must be absent, as is the case, presuming that the cerium was oxidized before its identification.

REAGENTS.

1. Solid lead (IV) oxide.
2. Nitric acid $d = 1.4$.
3. Anthranilic acid solution, 5 %, in alcohol.
4. Syrupy phosphorous acid.

B. Ce^{+4}, 26.

4 : 4'-DIAMINO-3 : 3'-DIMETHYL DIPHENYL, *o*-TOLIDINE

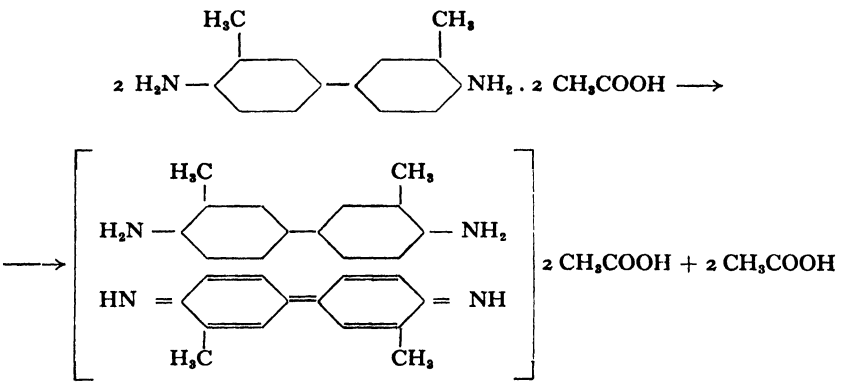


BIBLIOGRAPHY : 453-454.

MECHANISM OF REACTION.

This reaction is of the same type as the well-known one of benzidine with oxidizing agents; the Ce^{+4} cation is reduced to the trivalent state, whilst the amine is oxidized according to the equation :

$$Ce^{+4} + e \longrightarrow Ce^{+3}$$



giving a blue product.

F. FEIGL (453).

DETAILS OF TEST.

On a spot plate.

We must first of all proceed to the oxidation of cerium, since only the tetravalent cation reacts. All oxidizing agents do not allow of a subsequent detection of cerium with *o*-tolidine; we therefore give the following method. Place in a section of the plate a drop of the solution to be analysed and add some grains of sodium peroxide, then add 2 drops of the reagent solution and verify that the medium is nearly neutral. In the presence of cerium a blue colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

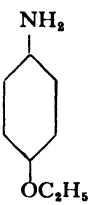
The sensitivity is not reduced by the following elements, in a 300 : 1 proportion : Pb, Bi, Cd, As, Sn, Pt, Se (Se^{+6}), W, Nb, Ta, Al, rare earths, Y, Ti, Zr, Th, Gl, Tl (Tl^{+1}), Zn, Ni, alkaline earths and alkali-metals. The ions of Hg (Hg^{+2}), Mo, Cr (Cr^{+3}) and U lead to a sensitivity of $10^{-4.48}$ ($1 : 3 \cdot 10^4$), when they are present in a 100 : 1 proportion. The ions of Rh, Pd, Te and Fe (Fe^{+3}), in a 30 : 1 proportion, reduce the sensitivity even further, which assumes a value of 10^{-4} ($1 : 10^4$). Finally, a certain number of ions give the same reaction and consequently interfere. They are the ions of the following elements : Ag, Sb, Au, Ir, V (V^{+5}), Cr (CrO_4^{-2}), Tl (Tl^{+3}), Mn and Co. The detection of cerium is also made impossible by the ions : Hg^{+1}, Cu^{+2} and F^{-1}.

REAGENTS.

1. Solid sodium peroxide.
2. Saturated solution of *o*-tolidine in glacial acetic acid.

C. Ce^{+4}, NR. 2.

4-ETHOXY-AMINOBENZENE, *p*-PHENETIDINE



BIBLIOGRAPHY : 455.

MECHANISM OF REACTION.

It is a question of the oxidation of *p*-phenetidine by the Ce^{+4} cation, the mechanism of which has not yet been studied.

P. E. WENGER and R. DUCKERT (455).

DETAILS OF TEST.

On a spot plate.

As only the Ce^{+4} cation reacts, we must carry out a prior oxidation with lead (IV) oxide and hot, concentrated nitric acid : it is not possible to use other oxidizing agents, because they react with *p*-phenetidine in the same way as cerium.

Place in a section of the spot plate a drop of the slightly acid solution to be analysed, to which are added 1 or 2 drops of sodium acetate solution in order to have a medium of *p*H approximately 7, and then add a drop of the reagent solution. In the presence of cerium a purple colour appears and if a strong acid is added this colour changes to blue.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.48}$ (1 : 3 · 10^4).

The sensitivity is not changed by the ions of the following elements, when in a 100: 1 proportion: Ag, Hg, Cu, Pb, Bi, Cd, As, Sn, Rh, Pd, Pt, Se (Se^{+6}), Te, Mo, W, Nb, Ta, Al, Cr (Cr^{+3}), U, rare earths, Y, Ti, Zr, Th, Gl, Tl, Zn, Mn, Co, Ni, alkaline earths and alkali-metals. The Fe^{+3} cation, when in a 100 : 1 proportion and masked by the phosphoric anion, reduces the sensitivity a little, which attains a value of 10^{-4} (1 : 10^4). The ions of Sb, Au, Ir, V (V^{+5}) and Cr (CrO_4^{-2}) give the same reaction as cerium and interfere. Lastly, the F^{-1} anion masks cerium and must therefore be absent.

REAGENTS.

1. Solid lead (IV) oxide.
2. Nitric acid $d = 1.4$.
3. Solution of sodium acetate, 10 %, in water.
4. Saturated solution of *p*-phenetidine in water.

34. EUROPIUM

BY

P. E. WENGER

AN 63 **AW 152.0**

A. Eu^{+2}, NR.

CACOTHELINE + ZINC $C_{21}H_{21}(OH)_3(NO)_2N_2O_3 \cdot HNO_3 + Zn$

BIBLIOGRAPHY : 456.

MECHANISM OF REACTION.

The Eu^{+2} cation is the only one among all the cations of the rare earths, that reduces cacotheline to a violet dyestuff of unknown structure; the Eu^{+2} cation is obtained by reduction of trivalent europium with zinc and hydrochloric acid.

G. BECK (456).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube 1 ml of the solution to be analysed and add some drops of hydrochloric acid and a grain of pure zinc; finally add some drops of the cacotheline solution. In the presence of europium a purple colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.52}$ $(1 : 3.3 \cdot 10^5)$.

The reaction is specific for europium in the group of rare earths. The trivalent ions of Mo, W, V, Nb, U, Ti, Re as well as the Sn^{+2} cation give the same reaction.

REAGENTS.

1. Hydrochloric acid 5 N.
2. Metallic zinc.
3. Solution of cacotheline, 0.25 %, in water.

No reagent is known which could be used for the ions of the following elements : *praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium (cassiopeium).*

35. YTTRIUM

BY

P. E. WENGER

AN 39 AW 88.92

No reagent is known which could be used for the detection of the cations of this element.

36. TITANIUM

BY

C. J. VAN NIEUWENBURG

AN 22 AW 47.90

A. Ti^{+4}, 7.

HYDROGEN PEROXIDE + SULPHURIC ACID $H_2O_2 + H_2SO_4$

BIBLIOGRAPHY : 457-467.

MECHANISM OF REACTION.

The yellow colour of the solution after the reaction with hydrogen peroxide is due to the presence of dihydrogen-dioxydisulphatotitanic acid, which is formed according to the equation :

$$TiOSO_4 + H_2O_2 + H_2SO_4 \longrightarrow H_2[TiO_2(SO_4)_2] + H_2O.$$

R. SCHWARZ (467).

DETAILS OF TEST.

In a micro test tube.

Place in the test-tube 1 ml of the solution to be analysed to which are added 3 or 4 drops of dilute sulphuric acid and 1 drop of hydrogen peroxide. In the presence of titanium an orange yellow colour appears, which is made to disappear by some ammonium fluoride crystals.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

The reaction is doubtful at the limit of $10^{-5.70}$ ($1 : 5 \cdot 10^5$). In the presence of large quantities of Fe^{+3} cations their yellow colour must be eliminated by the addition of some drops of phosphoric acid. The ions of molybdenum and vanadium also give a yellow colour; but it does not disappear when ammonium fluoride is added. However, in the presence of these two ions or other cations that are coloured in the same way, such as Au^{+3}, Pt^{+4} and UO_2^{+2}, two parallel tests are carried out and the ammonium fluoride is only added in one of them. A decrease in colour at the moment when some fluoride is added, indicates the presence of titanium.

The sensitivity is not reduced by the ions of the following elements, when in a 100 : 1 proportion : Al, Fe, Cr, U, Ce, La, Zr, Th, Gl, Ga, neither is it reduced by the SiO_3^{-2} anion.

Some organic anions in large proportions disturb the reaction as for example the formic and acetic anions.

In the presence of ammonium fluoride the reaction is therefore specific for titanium.

REAGENTS.

1. Sulphuric acid 4 N.
2. Solution of hydrogen peroxide, 3 %, in water.
3. Solid ammonium fluoride.
4. Phosphoric acid $d = 1.75$.

B. Ti^{+4}, 28.

ARSENIC ACID + ZIRCONIUM OXYDICHLORIDE, ZIRCONYL CHLORIDE $H_3AsO_4 + ZrOCl_2$

BIBLIOGRAPHY : 468.

MECHANISM OF REACTION.

The zirconium cation precipitates quantitatively in a medium acidified with nitric acid as zirconium arseniate, even in the presence of an excess of reagent; the titanium does not precipitate by itself,

but is entrained in the precipitation by zirconium (induced precipitation), even when a very small amount is present. It will therefore be possible to separate titanium and zirconium by filtration and to effect the detection of titanium by hydrogen peroxide and sulphuric acid according to reaction A; zirconium does not react.

F. FEIGL and E. RAJMANN (468).

DETAILS OF TEST.

In a macro test tube.

Place in the test tube 5 ml of the solution to be analysed, which is about 1 N in hydrochloric acid; add 10 drops of arsenic acid solution and 2 drops of zirconyl chloride solution. Raise to the boil and separate the precipitate by centrifuging, then add 2 ml of sulphuric acid to the precipitate and a drop of the hydrogen peroxide solution. In the presence of titanium an orange yellow colour appears, which disappears when some ammonium fluoride crystals are added. If ions of a yellow colour or molybdenum and vanadium ions are present, it is necessary to wash the precipitate of arseniates with dilute hydrochloric acid to which some drops of arsenic acid solution have been added.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ $(1 : 10^6)$.

The sensitivity is not reduced by the ions of the following elements: Al, Fe, Cr, U, Ce, La, Zr, Th, Gl, Ga, neither is it reduced by the SiO_3^{-2} anion.

The procedure indicated makes the reaction altogether selective and very sensitive.

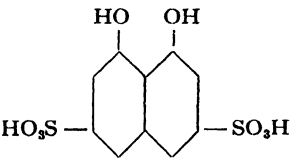
The SO_4^{-2} anion decreases the sensitivity, because it forms complexes which only partially react with arsenic acid.

REAGENTS.

1. Solution of arsenic acid, 20 %, in water.
2. Solution of zirconyl chloride, 1 %, in water.
3. Hydrochloric acid N.
4. Sulphuric acid 4 N.
5. Solution of hydrogen peroxide, 3 %, in water.
6. Solid ammonium fluoride.

C. Ti^{+4}, 44.

1 : 8-DIHYDROXY-NAPHTHALENE-3 : 6-DISULPHONIC ACID
(chromotropic acid)



BIBLIOGRAPHY : 469-476.

MECHANISM OF REACTION.

It has only been studied for phenols and naphthols of a simpler constitution.

O. HAUSER and A. LEWITE (470).

DETAILS OF TEST.

On a filter paper.

The reagent solution is not stable, hence some filter papers are impregnated with the reagent solution and are left to dry in the air; they will keep for some months.

Place on an impregnated filter paper one drop of the solution to be analysed and one drop of dilute sulphuric acid. The presence of titanium is indicated by a purplish-pink colouration.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 5 \cdot 10^4$).

The sensitivity is not reduced by the ions of the following elements, in a 100 : 1 proportion : Al, Fe, Cr, U, Ce, La, Zr, Th, Gl, Ga and by the SiO_3^{-2} anion.

The ions of iron, thorium and scandium in a neutral medium give stains which are pale purple and green, and which disappear when sulphuric acid is added. The ions of gold and vanadium give greenish grey and yellow stains,which do not make it impossible to distinguish the colouration due to titanium.

The reaction is selective and fairly sensitive.

REAGENTS.

1. Reagent paper : filter paper impregnated with a solution of chromotropic acid, 5 %, in water; the paper will keep for some months, but the solution changes rapidly.
2. Sulphuric acid N.

37. ZIRCONIUM

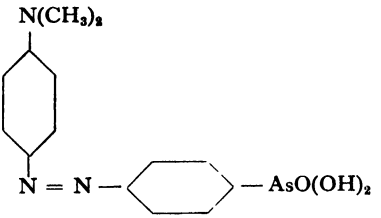
BY

P. E. WENGER

AN 40 AW 91.22

A. Zr^{+4}, 28.

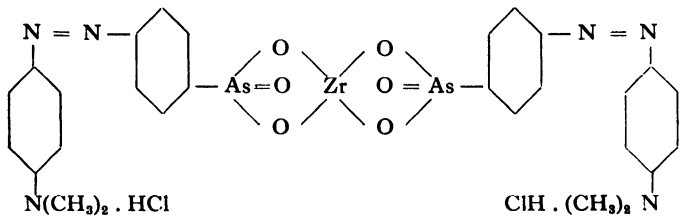
p-DIMETHYLAMINO-4-AZOPHENYLARSONIC ACID



BIBLIOGRAPHY : 477-479.

MECHANISM OF REACTION.

A red brown salt is formed, which according to F. FEIGL, P. KRUMHOLZ and E. RAJMANN (477) has the following formula :



DETAILS OF TEST.

On a filter paper.

Place on a filter paper a drop of the solution to be analysed, then a drop of the reagent solution. Soak the paper for some seconds in a bath of dilute hydrochloric acid, heated to 50-60°. The actual colour of the reagent disappears, but in the presence of zirconium a stain of an orange brown colour persists.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The ions of the following elements do not interfere, when in a 300 : 1 proportion : Ag, Hg, Cu, Pb, Bi, Cd, As, Sb, Sn, Au, Rh, Pd,

Ir, Pt, Se, Te, V, Nb, Ta, Al, Fe, Cr, U, rare earths, Ce, Y, Th, Gl, Tl, Sc, Zn, Mn, Co, Ni, alkaline earths and alkali-metals. The ions of Mo, W, Ti give an analogous reaction; but they react no longer, if a drop of hydrogen peroxide is added after having touched the paper with the solution to be analysed and the reagent. The sensitivity is reduced to $10^{-4.48}$ ($1 : 3 \cdot 10^4$), however, when they are in a 100 : 1 proportion.

REAGENTS.

1. Solution of *p*-dimethylamino-4-azophenylarsonic acid, 2 %, in hydrochloric acid 10 N.
2. Solution of hydrogen peroxide, 30 %, in water.
3. Hydrochloric acid 2 N.

PREPARATION OF REAGENT.

Dissolve 5.5 g arsanilic acid in 50 ml hydrochloric acid N; cool in ice and then diazotise with a concentrated solution (cooled) of 2 g sodium nitrite. Couple with a solution of 3 g dimethylaniline in the minimum quantity of hydrochloric acid 2 N. Allow to stand in the ice chest for some hours. Precipitate by adding solid sodium acetate. Filter, wash and then recrystallize the product from hot hydrochloric acid 2 N.

B. Zr^{+4}, 1.

RUBIDIUM CHLORIDE + AMMONIUM FLUORIDE (PHOTO 18) $RbCl + NH_4F$

BIBLIOGRAPHY : 480.

MECHANISM OF REACTION.

The crystals which are created are formed of rubidium hepta-fluozirconate $Rb_3[ZrF_7]$.

BEHRENS-KLEY (480).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed to which are added a rubidium chloride crystal and a ammonium fluoride crystal. Heat slightly in order to start the crystallization. In the presence of zirconium colourless hexagonal crystals appear.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.78}$ ($1 : 6 \cdot 10^3$).

Many cations react in the same way, but the crystals they give differ considerably from those of zirconium and do not interfere with the detection of this cation; there is only a decrease in sensitivity. They are the ions of the following elements, which reduce the sensitivity to $10^{-2.78}$ ($1 : 6 \cdot 10^2$), when present in a 2 : 1 proportion : Ag, Hg, Cu, Pb, Sn, Se, Te, Mo, Nb, Ta, rare earths, Ce, Ti, Th, Mn.

The ions of the following elements, when in a 20 : 1 proportion, do not interfere : Bi, Cd, As, Sb, Au, Rh, Pd, Pt, W, V, Al, Cr, U, Gl, Tl, Zn, Co, Ni, alkaline earths and alkali-metals.

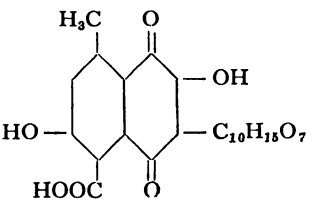
The Fe^{+3} cation interferes.

REAGENTS.

1. Solid rubidium chloride.
2. Solid ammonium fluoride.

C. Zr^{+4}, 27.

CARMINIC ACID



BIBLIOGRAPHY : 481-482.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

On a spot plate.

Place in a section of the plate a drop of the solution to be analysed, which is weakly acid (hydrochloric acid), a drop of the reagents

solution and a drop of concentrated hydrochloric acid. In the presence of zirconium a purple precipitate is formed, which remains, even after addition of the drop of concentrated hydrochloric acid.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.48}$ (1 : $3 \cdot 10^4$).

The sensitivity is not changed by the ions of the following elements in a 100 : 1 proportion : Ag, Hg, Cu, Pb, Bi, Cd, As, Sb, Sn, Au, Rh, Pd, Ir, Pt, Se, Te, Mo, W, V, Ta, Al, Fe, Cr, U, rare earths, Ce, Y, Th, Tl, Zn, Mn, Co, Ni, alkaline-earths and alkali-metals; it must be observed, however, that the Cu^{+2}, Pb^{+2}, and Th^{+4} cations give a purple precipitate, Fe^{+3} gives a black precipitate and UO_2^{+2} gives a green precipitate; but all these precipitates are dissolved when hydrochloric acid is added and hence do not cause any interference.

The ions of Nb, Ce (Ce^{+4}), Gl and Sc, when in a 20 : 1 proportion, reduce the sensitivity to $10^{-3.70}$ (1 : $5 \cdot 10^3$); the Gl^{+2} cation gives a purple precipitate which is soluble in hydrochloric acid. In the presence of the Ce^{+4} cation an excess of reagent is required.

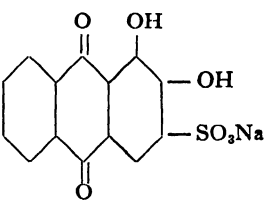
The ions of titanium give a purple precipitate which interferes. Lastly the hydrofluoric anion prevents the detection of zirconium.

REAGENTS.

1. Solution of carminic acid, 1 %, in water.
2. Hydrochloric acid 11 N.

D. Zr^{+4}, 24.

SODIUM 1 : 2-DIHYDROXY-ANTHRAQUINONE-3-SULPHONATE,
SODIUM ALIZARIN-3-SULPHONATE
(alizarin S)



BIBLIOGRAPHY : 483.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

On a spot plate.

Place in a section of the plate a drop of the solution to be analysed, which is slightly acidified (hydrochloric acid), a drop of the reagent solution and a drop of concentrated hydrochloric acid. In the presence of zirconium a red precipitate appears. In distinctly acid medium the reaction is specific of zirconium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.48}$ $(1 : 3 \cdot 10^4)$.

The ions of the following elements in a 100 : 1 proportion do not interfere : Ag, Hg, Pb, Bi, Cd, As, Sb, Sn, Au, Rh, Pd, Ir, Pt, Se, Te, Mo, W, V, Nb, Ta, Al, Fe, Cr, Ce, rare earths, Y, Tl (Tl^{+1}), Zn, Mn, Co, Ni, alkaline-earths and alkali-metals. The ions of the following elements, when in a 20 : 1 proportion, reduce the sensitivity to $10^{-3.70}$ $(1 : 5 \cdot 10^3)$: Cu, U, Ce (Ce^{+4}), Ti, Th, Gl, Tl (Tl^{+3}), Sc.

REAGENTS.

1. Solution of sodium alizarin sulphonate, 1 %, in water.
2. Hydrochloric acid 11 N.

38. CELTIUM (HAFNIUM)

BY

P. E. WENGER

AN 72 **AW 178.6**

A reagent that can be successfully used for the detection of the ions of this element is not yet known.

39. THORIUM

BY

P. E. WENGER

AN 90 AW 232.12

A. Th^{+4}, 1.

AMMONIUM CARBONATE + THALLIUM (I) NITRATE, THALLOUS NITRATE (PHOTO 19) $(NH_4)_2CO_3 + TlNO_3$

BIBLIOGRAPHY : 484-487.

MECHANISM OF REACTION.

The double carbonate which precipitates has the formula :

$$ThTl_6(CO_3)_5.$$

A. ROSENHEIM, V. SAMTER and J. DAVIDSOHN (487).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the neutral or weakly acid solution to be analysed, add a small drop of ammonium carbonate solution and a thallous nitrate crystal. In the presence of thorium rhombic, colourless crystals are slowly formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ $(1 : 10^4)$.

The ions of the following elements in a 30 : 1 proportion do not interfere : Pd, Pt, W, Cr, Na and K. The ions of Cu, Pb, Sn, Mo, Nb, Ta, Al, Fe, rare earths, Y, Ti, Zr, Zn, Mn, Co, Ni, alkaline earths and Li give precipitates under the same conditions as thorium does and reduce the sensitivity to $10^{-3.40}$ $(1 : 2.5 \cdot 10^3)$, when present in a 10 : 1 proportion.

The UO_2^{+2} cation gives the same reaction and interferes.

REAGENTS.

1. Solution of ammonium carbonate, 10 %, in water.
2. Solid thallous nitrate.

B. Th^{+4}, 11.

POTASSIUM IODATE KIO_3

BIBLIOGRAPHY : 488-491.

MECHANISM OF REACTION.

The precipitate which is formed has the following formula :

$$4\ Th(IO_3)_4 . KIO_3 . 18\ H_2O$$

J. A. CHERNIKHOV and T. A. USPENSKAYA (491).

DETAILS OF TEST.

In a macro test tube.

Place in the test tube 5 ml of the weakly acid solution to be analysed, add 5 drops of concentrated nitric acid and a few drops of reagent solution. In the presence of thorium a white precipitate appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.40}$ ($1 : 2.5 \cdot 10^5$).

The ions of the following elements, when in a 20 : 1 proportion, do not interfere : Hg (Hg^{+2}), Cu, Pb, Bi, Cd, As, Sb, Au, Rh, Pd, Ir, Pt, Se, Te, Mo, W, V, Nb, Ta, Al, Fe, Cr (Cr^{+3} and CrO_4^{-2}), U, Ce, rare earths, Y, Gl, Tl, Zn, Mn, Co, Ni, alkaline earths and alkali-metals. The ions of Ag, Hg(Hg^{+1}), Sn, Ti and Zr interfere.

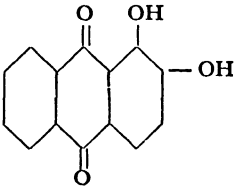
This reagent enables thorium to be distinguished among the rare earths, provided the detection is carried out in a medium acidified with nitric acid.

REAGENTS.

1. Saturated solution of potassium iodate in water.
2. Nitric acid 7.5 N.

C. Th^{+4}, 27.

1 : 2-DIHYDROXY-ANTHRAQUINONE, ALIZARIN



BIBLIOGRAPHY : 492.

MECHANISM OF REACTION.

A lake is formed whose constitution has not yet been established.

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the neutral or very slightly acidified solution to be analysed, add a drop of the reagent solution and a drop of hydrogen peroxide in order to eliminate the reaction of the ions of the following elements : Pb, U, Tl, Zn, Mn, Co and Ni.

In the presence of thorium ions a purple stain appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The ions of the following elements in a 300 : 1 proportion do not interfere : Ag, Hg, Pb, Cd, As, Sb, Sn, Au, Rh, Pd, Ir, Pt, Se, Te, Mo, W, V, Al, Cr, Ce (Ce^{+4}), Gl, Tl, Sc, Zn, Mn, Co, Ni, alkaline earths and alkali-metals. The sensitivity is reduced to 10^{-4} (1 : 10^4) by the ions of Bi, Nb, Ta and Ti (in a 30 : 1 proportion); the ions of titanium give an orange coloration at the moment when hydrogen peroxide is added.

The ions of Cu, Fe, rare earths, Y and Zr prevent the detection of thorium.

REAGENTS.

1. Solution of alizarin, 1 %, in ethyl alcohol.
2. Solution of hydrogen peroxide, 30 %, in water.

40. GLUCINUM (BERYLLIUM)

BY

P. E. WENGER

AN 4 AW 9.02

A. Gl^{+2}, Be^{+2}, 7.

2 : 4-PENTANEDIONE, ACETYLACETONE (PHOTO 20) $CH_3 - CO - CH_2 - CO - CH_3$

BIBLIOGRAPHY : 493-494.

MECHANISM OF REACTION.

The following is most probably formed : $Gl(C_5H_7O_2)_2$ (glucinum acetylacetonate).

A. COMBES (494), P. E. WENGER and R. DUCKERT.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed, which is concentrated by gently heating, and add a drop of acetylacetone. In the presence of glucinum colourless, rhombic and hexagonal crystals are formed at once.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The sensitivity is not reduced by the ions of the following elements in a 30 1 proportion : Ag, Cu, Pb, Sn, Pd, Pt, Se, Te, Mo, W, Nb, Ta, Al, Fe, Cr, U, Ce, rare earths, Y, Ti, Zr, Th, Tl, Zn, Mn, Co, Ni, alkaline earths and alkali-metals. Many of these ions give crystalline precipitates, but they are very different from that obtained with glucinum.

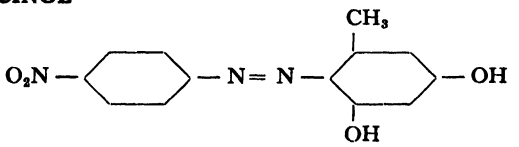
The reaction is specific for glucinum.

REAGENT.

1. Pure acetylacetone.

B. Gl^{+2}, Be^{+2}, 27.

1-(1'-AZO-2'-METHYL-4' : 6'-DIHYDROXYPHENYL)-4-NITROBENZENE, *p*-NITROBENZENE-AZO-ORCINOL



BIBLIOGRAPHY : 495-496.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the slightly acid solution to be analysed, add a drop of reagent solution and a drop of sodium hydroxide solution. In the presence of glucinum an orange red colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The sensitivity is not reduced by the ions of the following elements in a 300 : 1 proportion: Hg (Hg^{+2}), Bi, Cd, As, Sb, Sn, Au, Rh, Pd, Ir, Pt, Se, Te, Mo, W, V, Nb, Ta, Al, Fe, Cr, U, Ce (Ce^{+4}), rare earths, Y, Ti, Zr, Th, Tl, alkaline earths and alkali-metals. Magnesium only interferes if it is present in a very large proportion. The Ag^{+1}, Hg^{+1}, Pb^{+2}, Mn^{+2} and Ni^{+2} ions give precipitates which vary from brown to brownish black; in a 30 : 1 proportion they reduce the sensitivity to 10^{-4} (1 : 10^4).

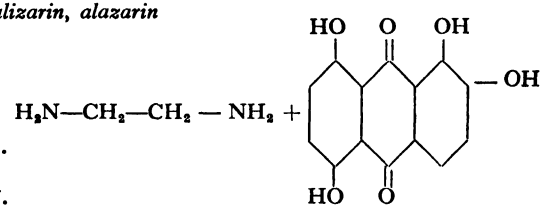
The Cu^{+2} and Zn^{+2} cations give orange red coloured stains and the Co^{+2} cation gives a brownish red one; all three prevent the detection of glucinum as also does the Mg^{+2} cation when present in a large proportion.

REAGENTS.

1. Solution of *p*-nitrobenzene-azo-orcinol, 0.025 %, in sodium hydroxide N. (For preparation of reagent see p. 175).
2. Sodium hydroxide N.

C. Gl^{+2}, Be^{+2}, 25.

1 : 2-DIAMINO-ETHANE, ETHYLENEDIAMINE + 1 : 2 : 5 : 8-TETRAHYDROXY ANTHRAQUINONE *(quinalizarin, alazarin bordeaux)*



$H_2N—CH_2—CH_2—NH_2$ +

BIBLIOGRAPHY : 497-506.

MECHANISM OF REACTION.

The structure of the lake produced has not yet been established.

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the reagent solution and a drop of the neutral or slightly acid solution to be analysed and, finally, a drop of sodium hydroxide N. In the presence of glucinum a blue, flocculent precipitate is formed. It is essential to carry out a blank test, as the colour of the reagent alone is purple.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

The sensitivity is not affected by the ions of the following elements in a 300 : 1 proportion : Hg (Hg^{+2}), Bi, Cd, Sn, Pd, Pt, Se, Te, Nb, Ta, Al, Tl, Zn, alkaline earths and alkali-metals, except Mg.

The sensitivity is reduced to $10^{-4.48}$ ($1 : 3 \cdot 10^4$) by the ions of the following elements in a 100 : 1 proportion: Ag (grey precipitate), As, Sb, Au, Rh (brown precipitate), Ir, Mo, W, Fe (brownish yellow precipitate) Mn (brown precipitate) and Co (brown precipitate). The Hg^{+1} and UO_2^{+2} cations give black and yellowish green precipitates; in a 3 : 1 proportion these two cations lead to a sensitivity of 10^{-3} ($1 : 10^3$).

The ions of Cu, V, Ce, rare earths, Y, Ti, Zr, Th and Mg interfere and prevent the detection of glucinum.

REAGENTS.

1. Solution of quinalizarin, 1 %, in ethyl alcohol + 6 ml ethylenediamine (pure) to 100 ml solution.
2. Sodium hydroxide N.

41. THALLIUM

BY

P. E. WENGER

AN 81 AW 204.39

A. Tl^{+1}, 35.

HEPTAHYDROGEN HEXADIMOLYBDATOPHOSPHORIC ACID, DODECAMOLYBDOPHOSPHORIC ACID, PHOSPHOMOLYBDIC ACID + HYDROBROMIC ACID $H_7\left[P(Mo_2O_7)_6\right] + HBr$

BIBLIOGRAPHY : 507-508.

MECHANISM OF REACTION.

With phosphomolybdic acid alone a yellow coloured salt of thallium (I) is precipitated; but in the presence of hydrobromic acid thallium is oxidized to the trivalent bromide $TlBr_3$; whereas molybdenum, whose redox potential is increased by its coordination with phosphorus, is reduced to a blue oxide.

F. FEIGL (508).

DETAILS OF TEST.

On a filter paper.

Place on a filter paper a drop of the slightly acid solution to be analysed, a drop of phosphomolybdic acid solution and a drop of hydrobromic acid. In the presence of thallium a blue colour appears. The Tl^{+3} cation does not react.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

The sensitivity is not modified by the ions of the following elements in a 300 : 1 proportion : Ag, Hg (Hg^{+2}), Cu, Pb, Bi, Cd, As, Sb (Sb^{+5}), Sn, Au, Rh, Pd, Ir, Pt, Se, Te, Mo, W, V, Al, Cr, U, Ce, rare earths, Y, Ti, Zr, Th, Gl, Zn, Mn, Co, Ni, alkaline earths, Mg and Li.

The ions of Nb, Ta, Fe (Fe^{+3}), Rb as well as the NH_4^{+1} cation in a 100 : 1 proportion reduce the sensitivity to $10^{-3.08}$ ($1 : 1.2 \cdot 10^3$).

The Hg^{+1}, Sb^{+3} and Fe^{+2} cations give the same reaction and interfere with the detection of thallium.

REAGENTS.

1. Saturated solution of phosphomolybdic acid in water.
2. Solution of hydrobromic acid, 50 %, in water.

B. Tl^{+1}, NR. 1.

BISMUTH NITRATE + SODIUM IODIDE $Bi(NO_3)_3 + NaI$

BIBLIOGRAPHY : 509.

MECHANISM OF REACTION.

The precipitate that is formed is probably an iodobismuthate of thallium whose formula has not yet been exactly determined.

P. E. WENGER, Y. RUSCONI and R. DUCKERT (509).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the slightly acid solution to be analysed and add a drop of the bismuth nitrate solution and a drop of the sodium iodide solution. In the presence of the Tl^{+1} cation a red precipitate appears.

The Tl^{+3} cation does not react.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 5 \cdot 10^4$).

The ions of the following elements do not affect the sensitivity in a 150 : 1 proportion : Cd, As (As^{+3}), Sb (Sb^{+3}), Sn, Mo, W, V, Ge, Nb, Ta, Al, Fe (Fe^{+2}), Cr, Ti, Zr, Gl, Zn, Mn, Co, Ni, alkaline earths and alkali-metals. The Pt^{+4}, Fe^{+3} and Ce^{+4} cations react also, but after a drop of a sodium thiosulphate solution has been added, they no longer prevent the detection of thallium, even when they are

present in a 150 : 1 proportion. The ions of Ag, Au, Rh and Pd reduce the sensitivity to $10^{-3.48}$ ($1 : 3 \cdot 10^3$), when they are present in a 10 : 1 proportion. The same is true for the ions of Hg, Cu, As (As^{+5}) and Sb (Sb^{+5}) after a drop of sodium thiosulphate solution has been added.

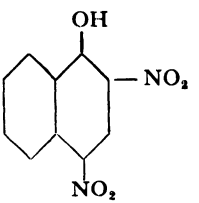
The ions of selenium and tellurium prevent the detection of thallium because they give an abundant black precipitate.

REAGENTS.

1. Solution of bismuth nitrate, 0.4 %, in nitric acid 20 %.
2. Solution of sodium iodide, 10 %, in water.
3. Saturated solution of sodium thiosulphate in water.

C. Tl^{+3}, NR. 2.

2 : 4-DINITRO-1-NAPHTHOL
(Martius yellow) (PHOTO 21)



BIBLIOGRAPHY : 510.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the slightly acid solution to be analysed and add a drop of the reagent solution. In the presence of the Tl^{+3} cation rhombic crystals and yellowish orange coloured needles are formed.

The Tl^{+1} cation does not react.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.52}$ ($1 : 3.3 \cdot 10^4$).

The ions of the following elements in a 300 : 1 proportion do not affect the sensitivity: Ag, Cu, Bi, Cd, As, Au, Pd, Pt, Se, Mo, W, Nb, Ta, Al, Ce, rare earths, Y, Gl, Zn, Mn, Ni, alkaline earths and alkali-metals; a certain number of these ions give precipitates, namely those

of the following elements : Cu, Bi, Ce, rare earths and Y. The ions of Hg, Pb, Sb, Sn, Te, Fe, Cr and U give crystallized precipitates and reduce the sensitivity to $10^{-3.22}$ ($1 : 1.66 \cdot 10^3$), when they are present in a 15 : 1 proportion.

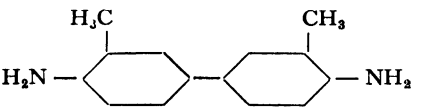
Finally, the ions of cobalt give the same reaction as thallium and prevent the detection of this element.

REAGENT.

1. Saturated solution of Martius yellow in pyridine to which 3 vols. of water are added.

D. Tl^{+3}, 39.

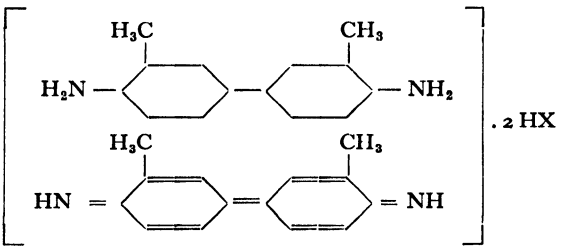
4 : 4'-DIAMINO- 3 : 3' DIMETHYL DIPHENYL, *o*-TOLIDINE



BIBLIOGRAPHY : 511-513.

MECHANISM OF REACTION.

The Tl^{+3} cation oxidizes *o*-tolidine to a colouring agent which is analogous to benzidine blue (see p. 58, 73 and 89), and is itself reduced to the monovalent state.



F. FEIGL (512).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the slightly acid solution to be analysed and add a drop of the *o*-tolidine solution and a drop of sodium hydroxide solution. In the presence of the Tl^{+3} cation a blue colour appears. The monovalent cation does not react.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The ions of the following elements in a 300 : 1 proportion do not affect the sensitivity : Hg(Hg^{+2}), Pb, Cd, Se, Te, Mo, W, Nb, Ta, Al, Fe (Fe^{+2}), rare earths, Y, Ti, Zr, Th, Gl, Zn, Ni, alkaline earths and alkali-metals. The ions of Bi, As, Sn, Cr and U in a 100 : 1 proportion reduce the sensitivity to $10^{-4.48}$ (1 : $3 \cdot 10^4$). The ions of rhodium and palladium reduce the sensitivity even further; it attains the value of 10^{-4} (1 : 10^4). They give orange colorations. Finally, a series of cations react in the same way as thallium; accordingly they prevent its detection. They are the ions of the following elements : Ag, Hg (Hg^{+1}), Cu, Sb, Au, Ir, Pt, V, Fe (Fe^{+3}), Ce (Ce^{+4}), Mn and Co as well as the anions with a high oxidizing power, such as VO_4^{-3}, CrO_4^{-2}, etc. It should be noted, that the reaction of copper and cobalt is probably not due to oxidation of *o*-tolidine.

REAGENTS.

1. Saturated solution of *o*-tolidine in glacial acetic acid.
2. Sodium hydroxide 2 N.

42. SCANDIUM

BY

P. E. WENGER

AN 21 **AW 45.10**

A. Sc^{+3}, NR. 1.

COCHINEAL

BIBLIOGRAPHY : 514.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

In a macro test tube.

Place in a test tube 5 ml of the solution to be analysed; add a few

drops of the reagent solution and a few drops of a sodium hydroxide solution until a purple colour appears. Heat gently and add about 10 drops of glacial acetic acid.

In the presence of scandium a dark blue precipitate is formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 5 \cdot 10^4$).

As several cations of the hydrogen sulphide group react, it is advisable to precipitate them before the detection of scandium is carried out; they are particularly the cations of Ag, Hg, Cu, Sn, Au and V.

The ions of the following elements in a 10 : 1 proportion do not affect the sensitivity : Pb, Cd, Nb, Ta, Al, Cr, Ce, rare earths, Y, Gl, Tl, Zn, Mn, Co, Ni, alkaline earths and alkali-metals. The Fe^{+3} cation gives a brown precipitate, which reduces the sensitivity of the scandium reaction. The UO_2^{+2}, Zr^{+4}, Ti^{+4} and F^{-1} ions prevent the detection of scandium; the three cations give purple precipitates.

REAGENTS.

1. Commercial tincture of cochineal.
2. Sodium hydroxide 2 N.
3. Glacial acetic acid.

B. Sc^{+3}, NR. 2.

HEXAMMINOCOBALT (III) NITRATE, LUTEOCOBALTIC NITRATE + SODIUM FLUORIDE (PHOTO 22)

$$\left[Co(NH_3)_6\right](NO_3)_3 + NaF$$

BIBLIOGRAPHY : 515.

MECHANISM OF REACTION.

The crystals which are formed consist of hexamminocobalti-hexafluoscandate.

$$\left[Co(NH_3)_6\right]\left[ScF_6\right]$$

G. BECK (515).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the slightly acid solution to be analysed which is evaporated to dryness. The residue is taken up in a drop of saturated sodium fluoride solution, to which the solid cobalt complex is added.

In the presence of scandium small hexagonal plates and pale yellow prisms are formed.

SENSITIVITY OF SELECTIVITY. $D = 10^{-3.30}$ $(1 : 2 \cdot 10^3)$.

The ions of the following elements do not interfere in a 20 : 1 proportion : Al, Zr, Tl, alkaline earths and alkali metals. Those of Fe, Cr, Zn, Mn, Co and Ni in a 10 : 1 proportion reduce the sensitivity to 10^{-3} $(1 : 10^3)$. The ions of the rare earths, thorium and glucinium prevent the detection of scandium.

REAGENTS.

1. Saturated solution of sodium fluoride in water.
2. Solid luteocobaltic nitrate.

43. GALLIUM

BY

P. E. WENGER

AN 31 AW 69.72

A. Ga^{+3}, 3.

CAESIUM CHLORIDE + POTASSIUM HYDROGEN SULPHATE $CsCl + KHSO_4$

(PHOTO 23)

BIBLIOGRAPHY : 516-518.

MECHANISM OF REACTION.

The hexagonal crystals which are formed consist of an alum of caesium and gallium, corresponding to the formula :

$$Ga_2(SO_4)_3 \cdot Cs_2SO_4 \cdot 24\ H_2O$$

A. A. BENEDETTI-PICHLER and W. F. SPIKES (518).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed, add a caesium chloride crystal and a potassium hydrogen sulphate crystal. After gentle heating colourless crystals appear of hexagonal form, identical with those produced by aluminium with the same reagent.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.30}$ $(1 : 2 \cdot 10^3)$.

A large number of cations react as well, but they give crystals of different shapes. They are the ions of Ag, Hg, Cu, Pb, Bi, Cd, As, Sb, Sn, Au, Rh, Pd, Ir, Pt, Se, Te, Mo, W, V, Fe, U, Ce, Y, Zr, Th, Gl, Tl, Sc, Zn, Mn, Co, Ni, alkaline earths and alkali-metals.

The ions of aluminium, chromium and indium prevent the detection of gallium, because they give an identical reaction.

REAGENTS.

1. Solid caesium chloride.
2. Solid potassium hydrogen sulphate.

B. Ga^{+3}, 12.

MANGANESE (II) CHLORIDE, MANGANOUS CHLORIDE + POTASSIUM BROMATE + TETRAPOTASSIUM HEXACYANOFERRATE (II), POTASSIUM FERROCYANIDE $MnCl_2 + KBrO_3 + K_4[Fe(CN)_6]$

BIBLIOGRAPHY : 519-520.

MECHANISM OF REACTION.

The Ga^{+3} cation gives a hexacyanoferrate (II) which is only slightly

soluble but which is colourless. On the other hand manganous salts in the presence of an oxidizing agent (e.g. potassium bromate) give a brown precipitate of manganese hexacyanoferrate (II); if the solution is very dilute the precipitate is not produced, but the solution assumes a brown colour. As the gallium cation is still present in this brown solution gallium hexacyanoferrate (II) is precipitated, and is coloured brown by the induced precipitation of the hexacyanoferrate (III) of manganese (II) or of the hexacyanoferrate (II) of manganese (III).

N. S. POLUEKTOFF (519).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the reagent solution and add a drop of the solution to be analysed. In the presence of gallium cations a brownish red precipitate is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.88}$ ($1 : 7.5 \cdot 10^3$).

The sensitivity is not affected by the ions of the following elements in a 100 : 1 proportion : Hg (Hg^{+2}), Bi, Cd, As, Sb, Sn, Rh, Pd, Ir, Pt, Te, W, Nb, Ta, Al, rare earths, Y, Zr, Th, Gl, Tl (Tl^{+3}), In, Zn, Mn, Ni, alkaline earths and alkali metals. The Ag^{+1}, Hg^{+1} and Pb^{+2} cations give a black precipitate which does not interfere very much.

The ions of Cu, Mo, V, Cr, U, Ce (Ce^{+4}), Ti, Sc and Co give the same reaction as the gallium cation and prevent its detection; the same is true for the ions of selenium and thallium (Tl^{+1}) which give a purple colouration and those of iron which give bluish green precipitates.

REAGENT.

1. Mixture of 120 ml of a 5 % solution of manganous chloride in hydrochloric acid 7 N + 30 ml of a solution of potassium ferrocyanide, N + 1 ml of potassium bromate 0.1 N.

44. INDIUM

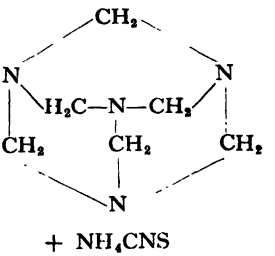
BY

P. E. WENGER

AN 49 AW 114.76

A. In^{+3}, 17.

HEXAMETHYLENETETRAMINE *(urotropine)* **+ AMMONIUM THIOCYANATE**
(PHOTO 24)



+ NH_4CNS

BIBLIOGRAPHY : 521-523.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the slightly acid solution to be analysed and add a few urotropine crystals and some ammonium thiocyanate crystals. In the presence of indium cations rose-pink hexagonal crystals are formed, which are sometimes arranged in crosses or in rosettes.

For very low indium concentrations it is advisable to heat gently in order to start the crystallization, meanwhile stirring with a glass rod.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.52}$ $(1 : 3.33 \cdot 10^3)$.

The ions of the following elements in a 100 : 1 proportion do not affect the sensitivity : Cu, Cd, As, W, Al, Cr, Zn, Mn, Ni, alkaline earths and alkali metals. It is reduced to 10^{-3} $(1 : 10^3)$ by the ions

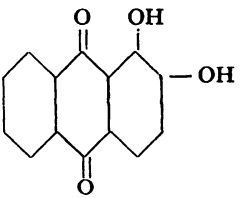
of Pb, Sn, Fe (Fe^{+3}) and Sc, when present in a 10 : 1 proportion. Finally the cobalt cation gives pink crystals, which can be easily mistaken for those of indium; it therefore interferes.

REAGENTS.

1. Solid urotropine.
2. Solid ammonium thiocyanate.

B. In^{+3}, 19.

1 : 2-DIHYDROXY-ANTHRAQUINONE, ALIZARIN



BIBLIOGRAPHY : 524.

MECHANISM OF REACTION.

A lake is formed whose composition is not yet known.

DETAILS OF TEST.

On a filter paper.

Place on a filter paper a drop of alizarin solution and a drop of the slightly acid solution to be analysed; develop over concentrated ammonia and steep the paper in a bath containing boric acid solution for some seconds. In the presence of indium cations a purplish red colour appears at the moment of development over ammonia, which persists in the boric acid bath. The reagent alone is coloured purple in alkaline medium and it becomes yellow by washing in boric acid.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ (1 : 5 · 10^5).

The sensitivity is not affected by the ions of As, W, Tl (Tl^{+1}) and Mg in a 1,000 : 1 proportion.

A large number of cation prevent the detection of indium more or less, although some of those that give a lake with alizarin can be

masked. The sensitivity is reduced to $10^{-4.78}$ ($1 : 6 \cdot 10^4$) by the ions of Zr, Ti, Gl and Sc in a 200 : 1 proportion, after being masked by the hydrofluoric ion. It becomes $10^{-4.48}$ ($1 : 3 \cdot 10^4$) in the presence of ions of the following elements : Fe(Fe^{+3}), rare earths, Ce, Y and alkaline earths in a 100 : 1 proportion (Fe and the rare earths being masked by the hydrofluoric anion). The ions of Ag, Hg, Cu, Cd, Zn, Mn, Co and Ni give purple lakes and prevent the detection of indium. The ions of Ag, Hg, Zn, Co and Ni in a 200 : 1 proportion, however, lead to a sensitivity of $10^{-4.70}$ ($1 : 5 \cdot 10^4$), after masking by means of potassium cyanide. The Cu^{+2}, Cd^{+2} and Mn^{+2} cations in a 100 : 1 proportion reduce the sensitivity to $10^{-4.48}$ ($1 : \cdot 10^4$).

The aluminium cation gives a lake which has a brick-red colour and which prevents the detection of indium; but it can be masked by sodium fluoride; in that case the sensitivity is $10^{-4.48}$ ($1 : 3 \cdot 10^4$), if aluminium is present in a 100 : 1 proportion.

Indium diffuses in the presence of the chromium cation and the sensitivity of the reaction is considerably reduced; in this case it is advisable to touch the paper with sodium hydroxide solution, which precipitates indium hydroxide, before adding the solution to be analysed. Chromium in a 100 : 1 proportion gives a sensitivity of $10^{-4.48}$ ($1 : 3 \cdot 10^4$).

The ions of Pb, Bi, Pd, Pt, U and Ga prevent the detection of indium.

It is always preferable first to separate the elements of the hydrogen sulphide group.

REAGENTS.

1. Saturated solution of alizarin in ethyl alcohol 96 %.
2. Ammonium hydroxide 11 N.
3. Saturated solution of boric acid in water.
4. Saturated solution of sodium fluoride in water.
5. Solution of potassium cyanide, 10 %, in water.
6. Sodium hydroxide 0.5 N.

45. ZINC

BY

P. E. WENGER

AN 30 AW 65.38

A. Zn^{+2}, 41. $(NH_4)_2[Hg(CNS)_4] + CuSO_4$

DIAMMONIUM TETRATHIOCYANATOMERCURATE (II), AMMONIUM MERCURITHIOCYANATE + COPPER (II) SULPHATE, CUPRIC SULPHATE

(PHOTO 25)

BIBLIOGRAPHY : 525-528.

MECHANISM OF REACTION.

The two cations Cu^{+2} and Zn^{+2} give a mixed crystalline precipitate, which is coloured purple :

$$Cu[Hg(CNS)_4] \cdot Zn[Hg(CNS)_4]$$

whereas the copper complex by itself is olive green and that of zinc is colourless.

R. MONTEQUI (525).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the solution to be analysed, which is slightly acid (preferably sulphuric acid), a drop of cupric sulphate solution and a drop of ammonium mercurithiocyanate solution. In the presence of zinc cations a blackish purple precipitate appears; the shape of the crystals depends on the foreign elements that are present in the solution and accordingly it is advisable to carry out a blank test.

At the limit of dilution one must wait several minutes and stir with a glass rod in order to start the precipitation.

The reaction can also be carried out under the microscope.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ ($1 : 10^4$) on the spot plate and $10^{-5.48}$ ($1 : 3 \cdot 10^5$) under the microscope.

The reaction is selective. The sensitivity is not affected by the ions of the following elements in a 100 : 1 proportion : Hg (Hg^{+2}), Bi, Cd, Sn, Au, Rh, Pd, Ir, Pt, Se, Te, Mo, W, V, Nb, Ta, Al, Fe, Cr, U, rare earths, Ce, Y, Zr, Th, Gl, Ni, alkaline earths and alkali metals. The ions of Ag, Cu, Pb, As, Sb, Tl, Mn and Co in a 10 : 1 proportion reduce the sensitivity to $10^{-3.48}$ ($1 : 3 \cdot 10^3$).

REAGENTS.

1. Solution of cupric sulphate, 0.1 %, in water.
2. Solution of 2.7 g mercuric chloride + 3 g ammonium thiocyanate in 100 ml water.

B. Zn^{+2}, 44.

DIAMMONIUM TETRATHIOCYANATOMERCURATE (II), AMMONIUM MERCURITHIOCYANATE + COBALT (II) CHLORIDE $(NH_4)_2[Hg(CNS)_4] + CoCl_2$

(PHOTO 26)

BIBLIOGRAPHY : 529-533.

MECHANISM OF REACTION.

The cobalt cation is precipitated only partially by ammonium mercurithiocyanate; but in the presence of zinc cations it is carried down and the precipitation becomes complete. Crystals are produced of a mixture of the two salts :

$$Co[Hg(CNS)_4] \cdot Zn[Hg(CNS)_4]$$

This reaction can be used for the detection of zinc as well as for that of cobalt.

P. KRUMHOLZ and J. VASQUEZ SANCHEZ (530).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed, which is slightly acid (preferably sulphuric acid). Add a drop of the cobalt chloride solution and a drop of the ammonium mercurithiocyanate solution. In the presence of zinc cations blue prisms are formed, which are arranged as rosettes. The shape of the crystals can be affected by the presence of certain cations and accordingly a control test is advisable.

For tests near the limit one should concentrate a little by heating in order to start the crystallization.

The reaction can also be carried out on a spot plate.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.48}$ ($1 : 3 \cdot 10^5$).

The reaction is selective, although the cobalt cation in very large proportion interferes, while the Cu^{+2} cation causes precipitation of blackish purple crystals (see the preceding reaction).

The sensitivity is not reduced by the ions of the following elements in a 1,000 : 1 proportion : Hg (Hg^{+2}), Pb, Bi, Cd, As, Sb, Sn, Au, Rh, Pd, Pt, Se, Te, Mo, W, V, Nb, Ta, Al, Fe, Cr, U, rare earths, Ce, Y, Th, Gl, Co, Ni, alkaline earths and alkali metals. The cobalt cation in a 1,000 : 1 proportion affects the sensitivity only a little. The Ag^{+1}, Hg^{+1}, Tl^{+1} and Zr^{+4} cations in a 100 : 1 proportion reduce the sensitivity to $10^{-4.30}$ ($1 : 2 \cdot 10^4$), because they give white precipitates. Finally, the Mn^{+2} cation in a 10 : 1 proportion reduces the sensitivity to 10^{-3} ($1 : 10^3$).

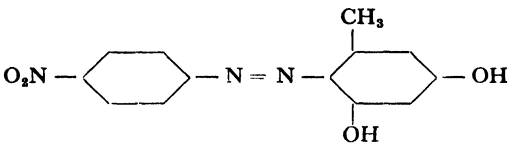
REAGENTS.

1. Solution of cobalt (II) chloride, 0.02 %, in water.
2. Solution of 2.7 g mercury (II) chloride + 3 g ammonium thiocyanate in 100 ml water.

C. Zn^{+2}, 77.

1-(1'-AZO-2'-METHYL-4' : 6'-DIHYDROXYPHENYL)-4-NITROBENZENE, *p*-NITROBENZENE-AZO-ORCINOL

BIBLIOGRAPHY : 534.



MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

On a filter paper.

Place on a filter paper a drop of the slightly acid solution to be analysed and add a drop of the reagent solution and a drop of sodium hydroxide solution.

In the presence of zinc cations a reddish orange coloured stain appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.48}$ ($1 : 3 \cdot 10^3$).

The ions of the following elements in a 10 : 1 proportion do not affect the sensitivity : Hg (Hg^{+2}), Pb, Bi, Cd, As, Sb, Sn, Au, Rh, Pd, Ir, Pt, Se, Te, Mo, W, V, Nb, Ta, Al, Fe (Fe^{+3}), Cr (Cr^{+3}), U, rare earths, Ce, Y, Ti, Zr, Th, Gl, Ba, Sr, Ca and alkali metals.

Some cations react and give colourations which differ from that of zinc; a reduction in sensitivity is the result, however. That applies to the Ni^{+2} and Mn^{+2} cations in a 3 : 1 proportion, which lead to a sensitivity of 10^{-3} ($1 : 10^3$) (brown colouration). The Ag^{+1} cation in a 2 : 1 proportion gives a sensitivity of $10^{-2.78}$ ($1 : 6 \cdot 10^2$) (blackish brown colouration). The Hg^{+1} cation by its blackening reduces the sensitivity even more, it becomes $10^{-2.30}$ ($1 : 3 \cdot 10^2$), when it is present in a proportion equal to that of zinc.

The cations of copper and cobalt interfere by their reddish orange colour, as well as those of glucinum and magnesium (when the latter

is present in a large quantity), because they react in the same way as zinc.

REAGENTS.

1. Saturated solution of *p*-nitrobenzene-azo-orcinol in ethyl alcohol 96 %.
2. Sodium hydroxide 2 N.

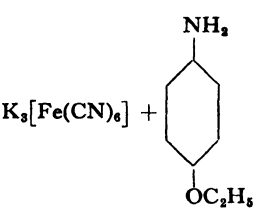
PREPARATION OF REAGENT.

Dissolve 1.38 g of *p*-nitroaniline in the smallest possible quantity of hydrochloric acid. Cool this solution to O° in order to diazotise with an aqueous solution of 0.85 g potassium nitrite, which is also cooled to O°. In this way a solution of *p*-nitrobenzene diazonium-chloride is obtained, to which is added under vigorous stirring a solution of 1.42 g orcinol in water made slightly alkaline with sodium carbonate (this solution is also cooled to O°). On acidifying a flocculent precipitate is obtained (bright red), which is filtered and washed, first of all with acid water and then with pure water. After desiccation of the dyestuff a dark red powder is obtained, which dissolves in alkali hydroxide solutions to give a yellow coloured solution.

A. S. KOMAROWSKY and N. S. POLUEKTOFF (534).

D. Zn^{+2}, NR.

TRIPOTASSIUM HEXACYANOFERRATE (III), POTASSIUM FERRICYANIDE
4-ETHOXY-AMINOBENZENE, *p*-PHENETIDINE



BIBLIOGRAPHY : 535-536.

MECHANISM OF REACTION.

The hexacyanoferrate (III) anion has a fairly low oxidation potential, which depends in solution on the concentration of the hexacyano-

ferrate (II) anion. For very low concentrations of this latter anion the oxidation potential is practically nil, with the result that the change of a coloured redox indicator cannot be obtained. But if the ferrocyanide anions are rendered inactive, for instance by precipitation using the Zn^{+2} cation, then the oxidation potential of the ferricyanide anion will reappear and a redox indicator, such as *p*-phenetidine, will assume a colour. This change in colour serves to identify the zinc cation.

L. SZEBELLEDY and ST. TANAY (535).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the potassium ferricyanide solution a drop of the *p*-phenetidine solution, a drop of sulphuric acid solution and finally a drop of the slightly acid solution to be analysed.

In the presence of zinc cations a purple to blue colour appears. For tests near the limit it is advisable to compare with a blank test.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The ions of the following elements do not affect the sensitivity in a 300 : 1 proportion : Al, Cr, rare earths, Ce (Ce^{+3}), Y, Gl, Tl (Tl^{+1}), alkaline earths and alkali metals.

The ions of the following elements react and prevent the detection of zinc : Fe (Fe^{+3}), U, Ce (Ce^{+4}), Zr, Th, Tl (Tl^{+3}), Mn, Co and Ni. It is essential to eliminate the cations of the hydrogen sulphide group as well, as a large number of them give a reaction which is identical with that of zinc (that is especially the case with copper).

This reaction is of interest if one intends to detect the zinc cation in the presence of the ions of aluminium, glucinum and magnesium.

REAGENTS.

1. Solution of potassium ferricyanide, 2 %, in water.
2. Solution of *p*-phenetidine hydrochloride, 1 %, in water.
3. Sulphuric acid 0.3 N.

46. MANGANESE

BY

P. E. WENGER

AN 25 AW 54.93

A. Mn^{+2}, 39.

POTASSIUM PEROXYDISULPHATE, POTASSIUM PERSULPHATE + SILVER NITRATE $K_2S_2O_8 + AgNO_3$

BIBLIOGRAPHY : 537-556.

MECHANISM OF REACTION.

The action of a persulphate on a manganous salt leads to the formation of manganese dioxide; only a few permanganic anions are formed. The silver cation on the other hand catalyses this reaction with the result that the dioxide stage is passed and the permanganic anion is formed, which imparts a purple colour to the solution. It is obvious, that anions which make the silver cation change to the state of an insoluble salt, prevent the catalytic reaction.

The reactions can be formulated as follows :

$$2\,(NH_4)_2S_2O_8 + 2\,H_2O \longrightarrow 2\,(NH_4)_2SO_4 + 2\,H_2SO_4 + O_2$$

$$7\,AgNO_3 + 3\,(NH_4)_2S_2O_8 + 6\,H_2O \longrightarrow AgNO_3 \cdot 3\,Ag_2O_2 + 3\,(NH_4)_2SO_4 + 3\,H_2SO_4 + 6\,HNO_3$$

$$4\,AgNO_3 + O_2 + 2\,H_2O \longrightarrow 2\,Ag_2O_2 + 4\,HNO_3$$

A. TRAVERS (547).

$$2\,Mn(NO_3)_2 + 5\,Ag_2O_2 + 6\,HNO_3 \longrightarrow H_2Mn_2O_8 + 10\,AgNO_3 + 2\,H_2O$$

A. KROPF (546).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the solution acidified with nitric acid, add some potassium persulphate crystals and a drop of silver nitrate solution. The reaction takes place even in the cold, but it is preferable to heat with a red-hot platinum wire, especially for tests near the limit. In the presence of manganese cations a purple colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ ($1 : 5 \cdot 10^5$).

The reaction is specific for manganese in its various stages of valency.

The sensitivity is not affected by the ions of the following elements in a 1,000 : 1 proportion : Ag, Hg, Cu, Pb, Bi, Te, Mo, W, Al, Fe, U, rare earths, Ce (Ce^{+3}), Y, Ti, Zr, Th, Gl, Tl, Zn, Re, Co, Ni, alkaline earths and alkali metals. It should be noted, that in the presence of reducing cations (Fe^{+2} for example) a large excess of reagent must be added. The Cr^{+3} and Ce^{+4} cations in a 300 : 1 proportion reduce the sensitivity to 10^{-5} ($1 : 10^5$).

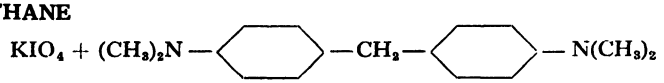
The hydrochloric anion prevents the reaction, because it precipitates silver. In certain cases one may succeed by adding an excess of silver, which will render the detection of manganese possible. The chromate anion interferes; it gives a red precipitate of silver chromate.

REAGENTS.

1. Nitric acid N.
2. Solid potassium persulphate.
3. Solution of silver nitrate, 1 %, in water.

B. Mn^{+2}, 43.

POTASSIUM PERIODATE
+ BIS-(*p*-DIMETHYLAMINOPHENYL)-METHANE
***p*-TETRAMETHYLDIAMINO-**
DIPHENYLMETHANE



BIBLIOGRAPHY : 557-563.

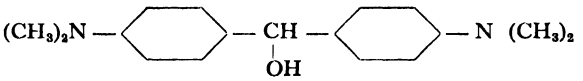
MECHANISM OF REACTION.

The Mn^{+2} cation is oxidized (hot) by alkaline periodates to a permanganic anion according to the following equation :

$$2\ Mn(NO_3)_2 + 5\ KIO_4 + 3\ H_2O \longrightarrow 2\ HMnO_4 + 5\ KIO_3 + 4\ HNO_3.$$

ST. R. BENEDICT (557), H. H. WILLARD and L. H. GREATHOUSE (558).

In order to increase the sensitivity, the permanganic anion is made to react on a base such as *p*-tetramethyldiaminodiphenylmethane, which is oxidized to its corresponding hydrol, having the following formula :



and whose salts are coloured blue.

A. TRILLAT (563).

DETAILS OF TEST.

On a filter paper.

Place on a filter paper a drop of the very slightly acid solution to be analysed, then a drop of potassium periodate solution and a drop of the nitrogenous base solution. In the presence of manganese cations a blue stain appears. Near the limit it is advisable to compare with a blank test.

SENSITIVITY AND SELECTIVITY. $D = 10^{-7.48}$ ($1 : 3 \cdot 10^7$).

The ions of the following elements in a $10^5 : 1$ proportion do not affect the sensitivity : Hg (Hg^{+2}), Cu, Pb, Bi, Cd, As, Sb, Sn, Pd, Pt, Se, Te, Mo, W, Al, Fe, U, rare earths, Ce (Ce^{+3}), Y, Ti, Zr, Th, Gl, Tl, Zn, Re, Co, Ni, alkaline earths and alkali metals. The Ag cation gives a brown colour and it reduces the sensitivity to $10^{-5.48}$ ($1 : 3 \cdot 10^5$), when it is in a 1,000 : 1 proportion. The Hg^{+1} cation in a $10^4 : 1$ proportion leads to a sensitivity of $10^{-6.48}$ ($1 : 3 \cdot 10^6$).

Finally, the ions of Au, Rh, Ir, V, Cr and Ce (Ce^{+4}) prevent the detection of manganese, because they give an identical reaction.

REAGENTS.

1. Saturated solution of potassium periodate in water.

2. Saturated solution of *p*-tetramethyldiaminodiphenylmethane in glacial acetic acid.

C. Mn^{+2}, 42.

POTASSIUM NITRATE + SODIUM CARBONATE $KNO_3 + Na_2CO_3$

BIBLIOGRAPHY : 564-567.

MECHANISM OF REACTION.

The oxidising fusion of all manganese compounds (the metal itself included, although with greater difficulty) leads to the formation of alkali manganate, according to the equation :

$$MnO + Na_2CO_3 + 2\,KNO_3 \longrightarrow Na_2MnO_4 + 2\,KNO_2 + CO_2$$

P. E. WENGER and G. GUTZEIT (567).

DETAILS OF TEST.

In a micro capsule or on a strip of platinum foil.

Place on one of the pieces of apparatus mentioned a drop of the solution to be analysed; evaporate to dryness and add to the residue a few small potassium nitrate crystals and a tipful of the micro spatula of anhydrous sodium carbonate. Heat to fusion over the blowpipe.

In the presence of manganese the molten mass assumes a green colour after cooling.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ $(1 : 10^6)$.

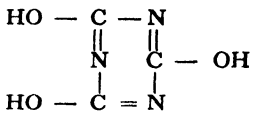
The sensitivity is slightly reduced by the ions of the following elements in a 1,000 : 1 proportion : Pb, Cd, As, Se, Mo, W, Al, rare earths, Y, Ti, Gl, Zn, Re, alkaline earths and alkali metals. The sensitivity is reduced to $10^{-4.70}$ $(1 : 5 \cdot 10^4)$ by the ions of Fe, Cr and U in a 100:1 proportion. Finally, the ions of copper, cobalt and nickel, which give black oxides, reduce the sensitivity still more; it is 10^{-4} $(1 : 10^4)$ when they are in a 30 : 1 proportion.

REAGENTS.

1. Solid potassium nitrate.
2. Anhydrous sodium carbonate.

D. Mn^{+2}, 7.

CYANURIC ACID (PHOTO 27)



BIBLIOGRAPHY : 568.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the neutral solution to be analysed and a drop of the reagent solution. In the presence of manganese (II) cations and even in the cold state characteristic small colourless needles are formed. For low concentrations in cations it is essential to heat a little in order to facilitate crystallization.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.52}$ ($1 : 3.3 \cdot 10^4$).

The sensitivity is not affected by the ions of Mo, Al, rare earths, Ce, Y, Ti, Gl, Re and Ni in a 300 : 1 proportion. It is reduced to 10^{-4} ($1 : 10^4$) by the ions of Fe, Cr, U, Zn, Co, alkaline earths and by the hydrochloric anion in a 100 : 1 proportion.

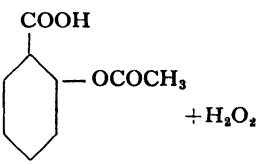
The Mg^{+2} cation interferes because the crystals it gives may be mistaken for those of manganese.

REAGENT.

1. Saturated solution of cyanuric acid in ammonia N.

E. Mn^{+2}, 63.

ACETYLSALICYLIC ACID
(aspirin)
+ HYDROGEN PEROXIDE



BIBLIOGRAPHY : 569.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the neutral or slightly acid solution to be analysed, add a drop of the reagent solution and a drop of hydrogen peroxide. In the presence of manganese (II) cations a reddish colour appears, or even a brown precipitate for strong concentrations.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ ($1 : 5 \cdot 10^5$).

The sensitivity is not reduced by ions of the following elements in a 1,000 : 1 proportion : Hg (Hg^{+2}), Bi, Cd, As, Sb Ir Pt, Se, Te, Mo, W, Nb, Ta, Al, Cr (CrO_4^{-2}), rare earths, Y, Zr, Th, Gl, Zn, alkaline earths and alkali metals. The ions of Sn, Cr (Cr^{+3}), U and Tl in a 100 : 1 proportion reduce the sensitivity to $10^{-4.70}$ ($1 : 5 \cdot 10^4$). The ions of Ag, Hg (Hg^{+1}), Cu, Pb, Au, V, Fe, Ti, Co and Ni (the latters in large proportions) prevent the detection of manganese.

REAGENTS.

1. Saturated solution of acetylsalicylic acid in ammonia 15 %.
2. Solution of hydrogen peroxide, 15 %, in water.

F. MnO_4^{-1}, NR.

RUBIDIUM NITRATE + POTASSIUM PERCHLORATE (PHOTO 28) $RbNO_3 + KClO_4$

BIBLIOGRAPHY : 570.

MECHANISM OF REACTION.

Mixed crystals are formed of rubidium perchlorate and rubidium permanganate, which are pale purple.

I. M. KORENMAN (570).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed and add a few rubidium chloride and potassium perchlorate crystals. In the

presence of permanganic anions prisms and lozenges are formed, which are bright rose violet in colour. The reaction takes place at room temperature, but for tests near the limit it is advisable to heat a little.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

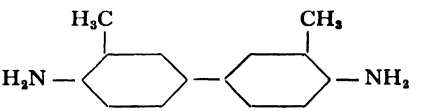
The cations of Cu, Sn, Al, Fe, Cr, U, rare earths, Y, Ti, Zr, Gl, Tl, Zn, Co, Ni, alkaline earths and alkali metals as well as the following anions AsO_4^{-3}, SeO_4^{-2}, MoO_4^{-2}, WO_4^{-2}, VO_3^{-1}, CrO_4^{-2} and ReO_4^{-1} in a 1,000 : 1 proportion do not prevent the detection of manganese.

REAGENTS.

1. Solid rubidium chloride.
2. Solid potassium perchlorate.

G. MnO_4^{-1}, 61.

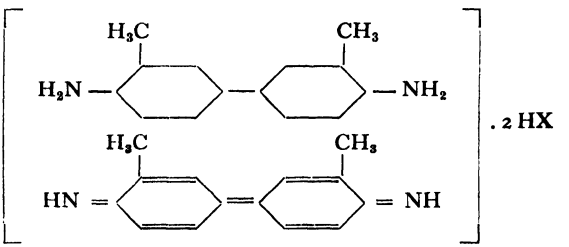
4 : 4'-DIAMINO-3 : 3'-DIMETHYL DIPHENYL, *o*-TOLIDINE



BIBLIOGRAPHY : 571-572.

MECHANISM OF REACTION.

The permanganic anion oxidizes *o*-tolidine to a blue mesiquinoid dyestuff having the following formula :



L. M. KUL'BERG (572).

DETAILS OF TEST.

On a filter paper.

Place on a filter paper a drop of the neutral solution to be analysed and a drop of the reagent solution. In the presence of permanganic anions a blue colour appears.

Originally the reagent was benzidine, but with the aid of *o*-tolidine a better sensitivity is attained.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.78}$ $(1 : 6 \cdot 10^5)$.

The ions of the following elements in a 1,000 : 1 proportion do not affect the sensitivity : Hg, Cu, Pb, Cd, As, Sb, Sn, Rh, Pd, Se, Te, Mo, W, Nb, Ta, Al, Fe, Cr (Cr^{+3}), U, rare earths, Y, Ti, Zr, Th, Gl, Tl, Zn, Re, Co, Ni, alkaline earths and alkali metals.

The following ions prevent the detection of the permanganic anion, because they react in an analogous way : Ag^{+1}, Bi^{+3}, Au^{+3}, Ir^{+4}, Pt^{+4}, Ce^{+4}, VO_3^{-1} and CrO_4^{-2}.

REAGENT.

1. Saturated solution of *o*-tolidine in glacial acetic acid.

47. RHENIUM

BY

P. E. WENGER

AN 75 **AW 186.31**

A. Re^{+3}, ReO_4^{-1}, 21.

TIN (II) CHLORIDE, STANNOUSCHLORIDE + SODIUM TELLURATE $SnCl_2 + Na_2TeO_4$

BIBLIOGRAPHY : 573-574.

MECHANISM OF REACTION.

Tin (II) chloride reduces the perrhenic anion to the state of trivalent rhenium, while the latter reduces the tellurium anion to black elementary tellurium, which the Sn^{+2} cation does not do.

N. S. POLUEKTOV (573), P. E. WENGER and R. DUCKERT.

DETAILS OF TEST..

In a spot plate.

Place on the plate a drop of the slightly acid solution to be analysed and add a drop of sodium tellurate solution and a drop of tin (II) chloride solution. In the presence of rhenium a black precipitate appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6.30}$ $(1 : 2 \cdot 10^6)$.

The sensitivity is not reduced by the ions of the following elements in a 5,000 : 1 proportion : Pb, Bi, Cd, As, Sb, Sn, Te, V, Nb, Ta, Fe, Al, Cr, U, rare earths, Ce, Y, Zr, Th, Gl, Tl, Zn, Mn, Co, Ni, alkaline earths and alkali metals. The ions of Cu, Ir and Pt reduce the sensitivity to $10^{-4.70}$ $(1 : 5 \cdot 10^4)$, when they are in a 150 : 1 proportion. The ions of selenium give a red precipitate and the tungsten anion gives a blue precipitate; when they are in a 30 : 1 proportion, they lead to a sensitivity of 10^{-4} $(1 : 10^4)$.

Finally, the ions of some elements prevent the detection of rhenium, because they give precipitates; they are : mercury (black), silver (black), gold (black), rhodium (greenish black), palladium (greenish black), molybdenum (VI) (brownish black) and titanium (black).

REAGENTS.

1. Solution of sodium tellurate, 1 %, in water.
2. Solution of tin (II) chloride, 50 %, in hydrochloric acid 10 N.

For the detection of rhenium in the presence of molybdenum, which is frequently required, molybdenum must be separated previously, because it reacts in the same way as rhenium. Accordingly treat a ml of the solution to be analysed with an excess of solid potassium ethylxanthate in a micro test tube, add 0.5 ml chloroform and shake energetically until the supernatant solution becomes colourless. The molybdenum xanthate, which is purplish red, enters the chloroform (lower layer), whereas the rhenium remains in the aqueous solution (top layer). For the detection of rhenium use a drop of the aqueous solution.

B. Re^{+3}, ReO_4^{-1}, 29.

TIN (II) CHLORIDE, + 2 : 3-BUTANE DIOXIME, DIMETHYLGLYOXIME

$$SnCl_2 + \begin{matrix} CH_3 - C = NOH \\ | \\ CH_3 - C = NOH \end{matrix}$$

BIBLIOGRAPHY : 575.

MECHANISM OF REACTION.

Stannous chloride reduces the perrhenic anion to the trivalent cation, which in its turn reacts with dimethylglyoxime, giving a red product whose structure is not yet known.

B. TOUGARINOFF (575).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the dimethylglyoxime solution, add a few stannous chloride crystals and then a drop of concentrated hydrochloric acid and a drop of the slightly acid solution to be analysed. In the presence of rhenium a red or brownish-red precipitate is formed.

If molybdenum is present the method as indicated for reaction Re A, must be followed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ $(1 : 5 \cdot 10^4)$.

The ions of the following elements in a 100 : 1 proportion do not reduce the sensitivity : Ag, Pb, Cd, As, Sb, Sn, Nb, Ta, Al, Fe, Cr, U, rare earths, Y, Ti, Zr, Th, Gl, Tl, Zn, Mn, Co, Ni, alkaline earths and alkali metals. The ions of copper and vanadium reduce the sensitivity, which assumes a value of 10^{-4} $(1 : 10^4)$, when they are in a 30 : 1 proportion. The sensitivity is $10^{-3.70}$ $(1 : 5 \cdot 10^3)$ in the presence of bismuth cations, in a 20 : 1 proportion. It is even further reduced by the tungsten anion in a 3 : 1 proportion to 10^{-3} $(1 : 10^3)$.

Finally the ions of Hg, Au, Rh, Pd, Ir, Pt, Te and Mo interfere with the detection of rhenium.

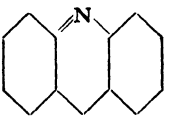
REAGENTS.

1. Saturated solution of dimethylglyoxime in ethyl alcohol 96 %.
2. Solid stannous chloride.
3. Hydrochloric acid 10 N.

C. ReO_4^{-1}, 17.

ACRIDINE HYDROCHLORIDE

(PHOTO 29)



BIBLIOGRAPHY : 576-577.

MECHANISM OF REACTION.

A perrhenate of the organic base is formed, whose structure is not exactly known.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the neutral or slightly acid solution to be analysed, heat a little in order to concentrate the solution and add a drop of the reagent solution. In the presence of perrhenic anions some yellow needles are formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ $(1 : 5 \cdot 10^4)$.

The ions of the following elements in a 500 : 1 proportion do not affect the sensitivity : Cu, Sn, Al, Fe, Cr (Cr^{+3}), rare earths, Y, Ti, Gl, Zn, Mn (Mn^{+2}), Co, Ni, alkaline earths and alkali metals. The molybdenum and tungsten anions give yellow precipitates which reduce the sensitivity a little : $10^{-4.30}$ $(1 : 2 \cdot 10^4)$, for a 100 : 1 proportion.

The chromic and permanganic anions as well as the uranium cation give an identical reaction and accordingly interfere with the detection of rhenium.

REAGENT.

1. Saturated solution of acridine hydrochloride in water.

48. COBALT

BY

P. E. WENGER

AN 27 AW 58.94

A. Co^{+2}, 19.

DIAMMONIUM TETRATHIOCYANATOMERCURATE (II), AMMONIUM MERCURITHIOCYANATE + ZINC CATION (PHOTO 30) $(NH_4)_2[Hg(CNS)_4] + Zn^{+2}$

BIBLIOGRAPHY : 578-586.

MECHANISM OF REACTION.

A crystalline blue precipitate is formed, which is a mixture of the two zinc and cobalt salts, according to the formula :

$$Co[Hg(CNS)_4] \cdot Zn[Hg(CNS)_4]$$

The cobalt cation alone reacts also to give blue crystals, but the reaction is less sensitive than in the presence of zinc cations.

I. M. KORENMAN (581).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the slightly acid solution to be analysed and a drop of the zinc solution. Evaporate partly if the drop spreads too much and add a drop of the cold reagent solution. In the presence of cobalt cations are formed rosettes of very dark blue crystals, or for lower concentrations some thick needles which are grouped together in small numbers. Crystallization sets in spontaneously, but it is often slow; it is advisable to wait 10 to 15 minutes.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ ($1 : 5 \cdot 10^5$).

The reaction is excellent and specific, because only cobalt gives such dark crystals, which are so well defined morphologically.

A fairly large number of cations precipitate more or less completely or produce crystals, but they do not cause any interference in the detection under the microscope, even in a 100 : 1 proportion. They are the cation of lead, barium, strontium and calcium, which precipitate as sulphates; the ions of Ag, Hg, Pb, Cd, As, Sb, Sn, Os, Se, Te, Mo, W and Zn, which give a white precipitate; the ions of Bi, Rh, Pt, Cr (Cr^{+3}), Ce and Zr, which give pale purple precipitates; the ions of Au and Ir, which give a pale brown precipitate; the UO_2^{+2} cation which gives a pale yellow precipitate; the V^{+5} and Fe^{+2} ions which cause a grey muddiness; the nickel cation which gives a pale green precipitate and the copper (II) cation which gives very characteristic arborescences, which are olive green. The ions of rare earths, Y, Ti, Gl, Zn, Mn, Re and alkali metals do not precipitate and do not affect the sensitivity, even in a 200 : 1 proportion.

It should be noted that in certain cases the sensitivity is increased by the presence of a large quantity of a cation; the blue colour of the crystals always subsists, even if the form of the latter is a little affected. It is necessary to increase the quantity of reagent if an abundant precipitation is produced.

The red colour produced by the Fe^{+3} cation hardly interferes, it can be eliminated, however, by adding an alkaline fluoride solution, or the same salt in a solid state.

REAGENTS.

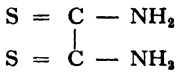
1. Solution of zinc sulphate, 0.5 %, in water.

2. Solution of 2.7 g mercury (II) chloride + 3 g ammonium thiocyannate in 100 ml water.

3. Solution of sodium fluoride, 10 %, in water, or solid sodium fluoride.

B. Co^{+2}, 41.

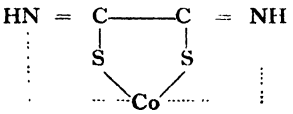
1 : 2-ETHANEDITHIAMIDE, DITHIO-OXAMIDE *(rubeanic acid)*



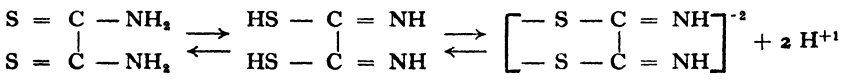
BIBLIOGRAPHY : 587-592.

MECHANISM OF REACTION.

An internal complex is formed, which is reddish brown and has the following structure :



the three forms of rubeanic acid being given in equilibrium :



P. RÂY (586).

DETAILS OF TEST.

On a filter paper.

Place on a filter paper a drop of the slightly acid solution to be analysed and a drop of ammonia in order to have a medium that is as near to neutral as possible. Dry rapidly over a flame and add a drop of the reagent solution. A reddish brown stain is produced in the presence of cobalt cations.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

The sensitivity is not affected by the ions of Al, Cr, Zn and Re in a 100 : 1 proportion; the Mn^{+2} cation in the same proportions reduces it to $10^{-4.70}$ (1 : $5 \cdot 10^4$). The Fe^{+3} cation, after being masked by the hydrofluoric anion, gives a sensitivity of 10^{-5} (1 : 10^5) for the detection of cobalt. The silver cation gives a yellow colour, which gradually changes to brown, so that it interferes if it is present in a considerable proportion. The nickel cation gives a dark blue

colour, which masks that of cobalt, if the drop on the filter paper is not left to diffuse sufficiently. The Cu^{+2} cation gives a very dark greenish black precipitate which interferes with the detection of cobalt.

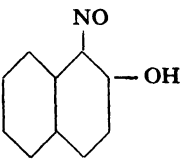
The other ions of the analysis do not react.

REAGENTS.

1. Ammonia 2 N.
2. Saturated solution of rubeanic acid in ethyl alcohol 96 %.
3. Solid sodium fluoride.

C. Co^{+2}, 27.

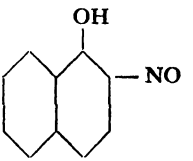
1-NITROSO-2-NAPHTHOL,
α-NITROSO-β-NAPHTHOL



or

Co^{+2}, 33.

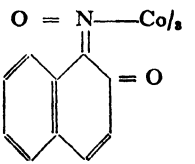
2-NITROSO-1-NAPHTHOL,
β-NITROSO-α-NAPHTHOL



BIBLIOGRAPHY : 593-609.

MECHANISM OF REACTION.

An internal complex of cobalt is formed, to which the structure of a derivative from the trivalent cation has been attributed (W. H. CHAPIN [595]), as well as that of a derivative of the bivalent cation (I. BELLUCCI [608]). It is the tautomeric quinoxime which reacts :



F. FEIGL (604).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the solution to be analysed, which is slightly acid (acidity of hydrolysis) and add 1 or 2 drops of the reagent solution, avoiding an excess. In the presence of cobalt cations a wine red precipitate is produced, which is totally different from the reagent which is rendered insoluble. For low concentrations of the cation the precipitation should be started by stirring with a glass rod and waited for 5 to 10 minutes.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.48}$ $(1 : 3 \cdot 10^5)$.

The sensitivity is not affected by the ions of the following elements in a 300 : 1 proportion : Cd, As, Sb, Sn, Au, Rh, Os, Ir, Pt, Se, Te, Mo, W, Cr, rare earths, Ce (Ce^{+3}), Ti, Th, Gl, Tl, Mn, Re and alkali metals.

A certain number of ions produce precipitates or turbidities which interfere with the detection of cobalt. The ions of Ag, Pb, Bi, V(V^{+3}), Al, Zr and alkaline-earths give a yellow, more or less brownish muddiness, the UO_2^{+2} and Ce^{+4} cations produce a browner precipitate, Hg^{+1}, V^{+5}, Ti^{+3} and Ni^{+2} have a brownish red precipitate and finally Hg^{+2} yields a red precipitate which is nearly identical with that of cobalt. The ions of copper give an abundant precipitate, which is brownish red and hides everything. Fe ions react also : a greenish black precipitate for the bivalent cation and a brownish black precipitate for the trivalent cation. The trivalent cation can be masked with an alkaline fluoride and also the bivalent cation after oxidation (with hydrogen peroxide or nitric acid).

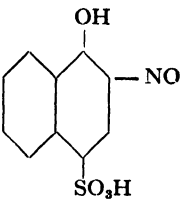
The colours mentioned refer to 1-nitroso 2-naphtol. The isomer reacts in nearly the same way and without any considerable difference in the sensitivity and selectivity of the reactions. 2-Nitroso-4-sulfo-1-naphthol has two advantages over these two reagents; it is much more soluble and it does not precipitate at the same time as cobalt (see the following reaction).

REAGENTS.

1. Solution of nitrosonaphthol, 0.5 %, in ethyl alcohol 96 %.
2. Solid sodium fluoride.

D. Co^{+2}, NR.

2-NITROSO-1-NAPHTHOL-4-SULPHONIC ACID



BIBLIOGRAPHY : 610.

MECHANISM OF REACTION.

It is probable that the compound which is formed, has a structure which is analogous to that of the complex obtained with simple nitro-naphthols. An exact investigation on this subject has not yet been made.

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the neutral solution to be analysed (buffered with sodium acetate). Add 2 or 3 drops of the reagent solution. In the presence of cobalt cations a red colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ ($1 : 5 \cdot 10^5$).

The ions of the following elements in a 100 : 1 proportion do not affect the sensitivity : Hg (Hg^{+2}), Pb, Bi, Cd, As, Sb, Sn, Au, Os, Ir, Pt, Se, Te, V, Al, Cr (Cr^{+3}), U, rare earths, Ce (Ce^{+3}), Ti, Th, Gl, Zn, Mn, Re, Ni, alkaline earths and alkali metals. The Fe^{+2} and Fe^{+3} cations give a green and greenish brown colour; they can be effectively masked with the hydrofluoric anion, the same sensitivity being maintained when the one or the other is present in a 100 : 1 proportion (after oxidation of the bivalent cation).

A certain number of ions precipitate and prevent the detection of cobalt. They are those of Ag, Mo, W, Zr and Tl, as well as the chromium anion, which give a yellow precipitate; they interfere as soon as they are present in the same proportion as cobalt. The Hg^{+1}, Cu^{+1}, Cu^{+2} and Ce^{+4} cations interfere in the same manner giving an orange coloured precipitate. Finally, the rhodium and palladium cations give purple precipitates, which border on brown or on black.

REAGENTS.

1. Solution of sodium acetate, 10 %, in water.
2. Solution of 2-nitroso-4-sulfo-1-naphthol, 1 %, in water.
3. Solid sodium fluoride.

E. Co^{+2}, 88.

POTASSIUM CYANATE KCNO

BIBLIOGRAPHY : 611-614.

MECHANISM OF REACTION.

The complex salt $K_2[Co(CNO)_4]$ is formed, which is blue.

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube a few drops of the neutral or slightly acid solution to be analysed and add the solid reagent. A blue complex is formed, which can be extracted by means of amyl alcohol and is characteristic of the cobalt (II) cation.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The sensitivity is not affected by the ions of the following elements in a 200 : 1 proportion : Hg, As, Sb, Sn, Au, Rh, Pd, Os, Pt, Se, Te, Mo, W, V, Al, Fe (Fe^{+3}), Cr, U, Ti, Gl, Zn, Mn, Re, Ni, alkaline earths and alkali metals.

The Fe^{+2} cation gives a pale yellow colour, but it does not interfere. Other coloured ions interfere with the detection of cobalt because of their colour, as soon as they are present in considerable proportions; viz. the ions of copper, of the platinum group, of vanadium and chromium.

If the sensitivity of the cobalt test mentioned above is to be maintained, it is essential to effect the extraction with amyl alcohol. A certain number of cations produce a white precipitate; such is the case for the ions of the following elements : Ag, Pb, Bi, Cd, rare earths, Ce (Ce^{+3}), Zr and Th.

REAGENTS.

1. Solid potassium cyanate.
2. Amyl alcohol.

F. Co^{+2}, 81.

POTASSIUM THIOCYANATE KCNS

BIBLIOGRAPHY : 615-650.

MECHANISM OF REACTION.

The blue colour is due to the cobalt complex of formula : $K_2[Co(CNS)_4]$, which is soluble in amyl alcohol or in acetone.

A. ROSENHEIM and R. COHN (617).

DETAILS OF TEST.

In a micro test tube.

Place a few drops of the neutral or slightly acid solution to be analysed in a micro test tube and add the solid reagent.

In the presence of cobalt cations a blue complex is formed which can be extracted by means of amyl alcohol.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

The sensitivity is not affected by the ions of the following elements in a 1,000 : 1 proportion : Cd, As, Sb (Sb^{+3}), Sn, Se, Te, Al, Fe (Fe^{+2}), rare earths, Ce (Ce^{+3}), Ti, Zr, Th, Gl, Ga, Zn, Mn, Re (ReO_4^{-1}), Ni, alkaline earths and alkali metals.

Several cations of the hydrogen sulphide group give very marked colours with the thiocyanic anion; viz. Cu^{+1} (brownish red), Cu^{+2} (greenish brown), Bi^{+3} (red), Sb^{+5} (reddish yellow), Os^{+4} (yellow), Pt^{+4} (red), Mo^{+3} (red), W^{+3} (orange) and the ions of vanadium (purple); it is obvious that these ions must be eliminated before the detection of cobalt to avoid their interference. The Cr^{+3}, UO_2^{+2} and Ce^{+4} cations interfere because of their own colour.

The Fe^{+3} cation gives the well-known red colour; to avoid its

interference it can be reduced to the bivalent cation, or (and that is more simple) masked by means of the hydrofluoric anion. In this way it does not affect the sensitivity of the cobalt reaction, even in a 100 : 1 proportion.

REAGENTS.

1. Solid potassium thiocyanate.
2. Amyl alcohol.
3. Solid sodium fluoride.

49. NICKEL

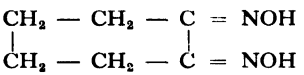
BY

P. E. WENGER

AN 28 **AW 58.69**

A. Ni^{+2}, 35.

***o*-CYCLOHEXANEDIONEDIOXIME**



BIBLIOGRAPHY : 651-654.

MECHANISM OF REACTION.

It has not been studied precisely, but we suppose that the red complex which is formed has a structure which is identical with that of the equivalent complex of dimethylglyoxime (see reaction B).

O. WALLACH and A. WEISSENBORN (652).

DETAILS OF TEST.

On a spot plate.

Place on the plate some drops of the solution to be analysed, made definitely alkaline with ammonia. Withdraw a drop of the alkaline solution by filtration with the capillary pipette. Place a drop of this solution in another compartment of the spot plate and add a drop of the reagent solution. In the presence of nickel cations a red

precipitate is obtained, which appears only after 10 to 15 minutes for high dilutions.

The reaction can also be carried out on filter paper, but with a slightly lower sensitivity.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.48}$ ($1 : 3 \cdot 10^5$).

The ions of palladium give a yellow precipitate, which is not very abundant and does not interfere when the test is carried out on filter paper. The Cu^{+2} cation causes a slightly green colouration which does not itself interfere, but the sensitivity is somewhat reduced by it; for a 100 : 1 proportion the sensitivity is $10^{-4.48}$ ($1 : 3 \cdot 10^4$); in a 10 : 1 proportion there is no interference.

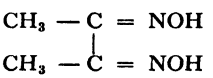
All the other elements of the analysis do not affect the sensitivity at all, even in a 100 : 1 proportion. In the case of Fe cations there is no reduction in sensitivity either, even when they are in a 2,000 : 1 proportion.

REAGENTS.

1. Ammonia 7.5 N.
2. Solution of cyclohexanedionedioxime, 0.02 %, in water.

B. Ni^{+2}, 28.

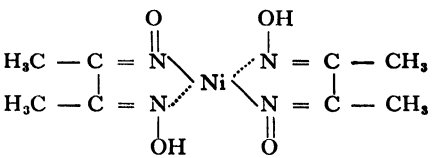
2 : 3-BUTANE DIOXIME, DIMETHYLGLYOXIME



BIBLIOGRAPHY : 655-704.

MECHANISM OF REACTION.

The red complex which is formed during the detection of nickel has the following structure :



L. TSCHUGAEFF (655 and 656), F. FEIGL (666).

DETAILS OF TEST.

On a spot plate.

Place on the plate a few drops of the solution to be analysed, made definitely alkaline with ammonia. Filter one or two drops of the solution by means of a capillary pipette and place them in another compartment of the spot plate. Then add a drop of the reagent solution. In the presence of nickel cations a bright pink colour is produced and then a more or less heavy carmine-coloured precipitate. In the case of tests near the limit it is advisable to wait some minutes.

The reaction can also be carried out on filter paper.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.48}$ $(1 : 3 \cdot 10^5)$.

If the ammoniacal solution is not filtered, the precipitate of hydroxide of the cations which accompany nickel, considerably reduce the sensitivity which becomes $10^{-4.48}$ $(1 : 3 \cdot 10^4)$.

The reaction is excellent and almost specific.

The only cations which react are the following : Pd^{+2} (yellow precipitate) Fe^{+2} (red colour) and Co^{+2} (brownish red colour). In the presence of palladium in a 100 : 1 proportion the sensitivity is $10^{-4.48}$ $(1 : 3 \cdot 10^4)$ and it is necessary to use a larger quantity of the reagent. The solution can also be reduced with zinc and hydrochloric acid 10 %, which causes some increase in sensitivity.

The Fe^{+2} cation must be oxidized to the Fe^{+3} cation in order to prevent reaction; hydrogen peroxide can be used for example. If the work is done on a filter paper oxidation will take place of its own accord in the air. The sensitivity of the nickel test is not reduced in the presence of cations of bivalent or trivalent iron in a 2,000 : 1 proportion.

The ions of cobalt, even when they are precipitated as hydroxides, give a solubility which is large enough to interfere by their colour.

The sensitivity is reduced to $10^{-4.48}$ $(1 : 3 \cdot 10^4)$, when they are in a 100 : 1 proportion.

The Cu^{+2} cation always interferes and reduces the sensitivity very considerably; in a 10 : 1 proportion it is $10^{-3.48}$ $(1 : 3 \cdot 10^3)$.

All the other ions of the analysis even in a 100 : 1 proportion do not interfere at all.

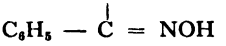
The sensitivity of the nickel test is $10^{-5.48}$ ($1 : 3 \cdot 10^5$) in the presence of Al^{+3}, Zn^{+2}, Mn^{+2} cations as well as of CrO_4^{-2} and ReO_4^{-1} anions in a 1,000 : 1 proportion.

REAGENTS.

1. Ammonia 7.5 N.
2. Saturated solution of dimethylglyoxime in ethyl alcohol 96 %.

C. Ni^{+2}, 32.

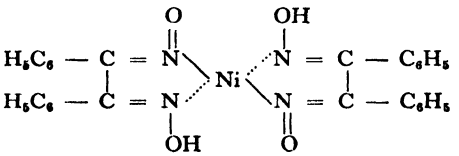
α:β-DIPHENYLETHANE-α:β-DIOXIME, DIPHENYLGLYOXIME *(α-benzil dioxime)*



BIBLIOGRAPHY : 705-710.

MECHANISM OF REACTION.

It is in every respect similar to that of the reaction with dimethylglyoxime. The nickel complex has the following formula :



F. W. ATACK (705).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube a drop of the very slightly acid solution to be analysed and make slightly alkaline with ammonia; add 3 to 5 drops of the reagent solution and heat to 80°-100°. In the presence of nickel cations an orange-red precipitate is produced, fairly bright in colour.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ ($1 : 10^6$).

The reaction is excellent and selective with the exception of cobalt.

It is obvious that the alkaline medium causes the precipitation of a series of hydroxides, which must be filtered before the reagent is

added. The procedure indicated above, for dimethylglyoxime for example, can be followed (see Ni, B).

The ions of cobalt give a yellow colour which does not markedly reduce the sensitivity, but which makes the interpretation of the test more difficult.

The ions of chromium and cobalt in a 10 : 1 proportion reduce the sensitivity to $10^{-5.70}$ ($1 : 5 \cdot 10^5$); these ions do not react in a visible manner, however.

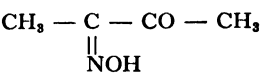
The other elements of the analysis more particularly the cations of aluminium, iron, zinc and manganese do not affect the sensitivity of the nickel test, even when they are present in a 100 : 1 proportion. Copper reduces the sensitivity (without any reaction) to 10^{-5} ($1 : 10^5$), when it is present in a 10 : 1 proportion.

REAGENTS.

1. Ammonia 7.5 N.
2. Solution (saturated by heating) of diphenylglyoxime in ethyl alcohol 96 %.

D. Ni^{+2}, 55.

2 : 3-BUTANONE MONOXIME, DIACETYLMONOXIME



BIBLIOGRAPHY : 711.

MECHANISM OF REACTION.

Not yet been studied.

DETAILS OF TEST.

On a spot plate.

Separate first of all by capillary filtration the hydroxides precipitated by ammonia (see Ni, B). Place a drop of the filtered solution on the spot plate together with a drop of the reagent solution. In the presence of nickel cations a red precipitate is formed, often after a few minutes.

The test can also be carried out on filter paper.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.48}$ (1 : 3 · 10^5).

The reaction is very good.

The Pd^{+2} cation gives a yellow precipitate which does not interfere.

The cobalt ions produce a yellow, slightly brown colour, but they do not cause any interference.

Copper ions react and interfere with the test therefore they must be eliminated, before the detection of nickel is undertaken.

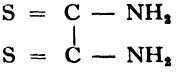
All the other elements of the analysis even when present in a 100 : 1 proportion do not cause any decrease in the sensitivity.

REAGENTS.

1. Ammonia 7.5 N.
2. Solution of diacetylmonoxime, 4 %, in ethyl alcohol 96 %.

E. Ni^{+2}, 41.

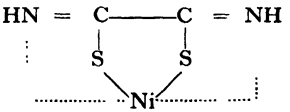
1 : 2-ETHANEDITHIAMIDE, DITHIOOXAMIDE *(rubeanic acid)*



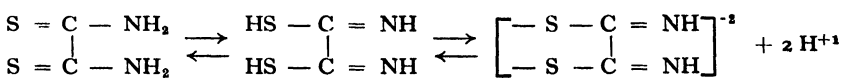
BIBLIOGRAPHY : 712-719.

MECHANISM OF REACTION.

The blue complex which is formed has the following structure :



the three forms of rubeanic acid (in equilibrium) being given :



P. RÂY (713).

DETAILS OF TEST.

On a filter paper.

Place on a filter paper a drop of the solution to be analysed, which is slightly acid or, preferably, buffered with sodium acetate. Add a drop of the reagent solution. In the presence of nickel cations a dark blue stain is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

The sensitivity is not affected by the ions of the following elements in a 100 : 1 proportion : Pb, Bi, Cd, As, Sb, Sn, Au, Pt, Se, Te, Mo, W, V, Al, Cr, Tl, Zn, Re (ReO_4^{-1}), alkaline earths and alkali metals.

The ions of cobalt give a brownish red colour which does not interfere. Those of copper (II) on the other hand, which give a blackish green precipitate, prevent the detection of nickel. The same is true for the cations Ag^{+1} and Hg^{+1}, which give a black precipitate.

The Fe^{+3} cation must be masked by the hydrofluoric anion; in these conditions and when it is present in a 100 : 1 proportion, the sensitivity of the nickel test is 10^{-5} (1 : 10^5).

REAGENTS.

1. Sodium acetate solution, 10 %, in water.
2. Saturated solution of rubeanic acid in ethyl alcohol 96 %.
3. Solid sodium fluoride.

F. Ni^{+2}, 4.

AMMONIUM MOLYBDATE (PHOTO 31) $(NH_4)_2MoO_4$

BIBLIOGRAPHY : 720-721.

MECHANISM OF REACTION.

Not yet been studied.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the slightly acid solution to be analysed and a drop of the reagent solution. In the presence of nickel cations small colourless cubes are formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.70}$ $(1 : 5 \cdot 10^3)$.

Most of the cations of the ammonium sulphide group give amorphous precipitates, which make it difficult to detect nickel, although the sensitivity of the test is not affected; this applies to the cations of aluminium, cerium, thallium and manganese. The Fe^{+3} cation must be masked by the hydrofluoric anion.

The ions of cobalt and rhenium (ReO_4^{-1}) do not react.

This reagent makes it possible to distinguish rapidly between nickel and cobalt.

REAGENTS.

1. Aqueous solution, saturated with ammonium molybdate (freshly prepared).
2. Solid sodium fluoride.

QUALITATIVE SEPARATION OF ELEMENTS OF THE AMMONIUM SULPHIDE GROUP

A large number of ions among the elements of this group have fairly similar properties, so that it is not desirable to try to carry out an analysis directly on the mixture; it is preferable therefore to effect a separation into sub-groups.

It is obvious that certain elements possess reagents which are entirely selective and allow of a certain and sensitive identification in the presence of all the elements of the ammonium sulphide group and even of elements of other groups of the analysis. That is most particularly the case for the following elements :

Iron. Reaction A, p. 112: $\alpha\alpha'$-dipyridyl; reaction B, p. 114: *o*-phenanthroline, both for the bivalent cation, and reaction D, p. 116 : 5-salicylsulphonic acid; in the latter case the detection is not possible in the presence of titanium ions.

Chromium. Reaction A, p. 120 : chromotropic acid and reaction B, p. 122 : hydrogen peroxide; both are meant for the detection of the chromic anion, but can serve for the detection of the trivalent cation (after oxidation) for which there is no specific reagent.

Titanium. Reaction B, p. 145 : arsenic acid + zirconyl chloride; the separation of titanium arseniate by this method allows of a specific identification by means of hydrogen peroxide; reaction C, p. 147 : chromotropic acid, with less security.

Zirconium. Reaction A, p. 148 : *p*-dimethylamino-4-azophenylarsonic acid.

Glucinum (beryllium). Reaction A, p. 156 : acetylacetone; it is obvious that the shape of the crystals must be carefully examined.

Thallium. Reaction B, p. 160 : bismuth nitrate + sodium iodide; apart from the reduction of selenium and tellurium the reaction is perfectly specific.

Zinc. Reaction A, p. 171 : ammonium mercurithiocyanate + cupric sulphate and reaction B, p. 172 : ammonium mercurithiocyanate + cobalt (II) chloride; these two reactions must preferably be carried out under the microscope if zinc is to be detected in any mixture of cations.

Manganese. Reaction A, p. 177 : potassium persulphate + silver nitrate; only the hydrochloric and chromic anions interfere with the detection of

manganese. Reaction C, p. 180 : potassium nitrate + sodium carbonate; the sensitivity is clearly reduced when cations are present which give black oxides.

Cobalt. Reaction A, p. 188 : ammonium mercurithiocyanate + zinc cation. Reaction B, p. 190 : rubeanic acid; this reagent is not really selective, but working on filter paper and with a little skill the cobalt can be detected for certain in the presence of interfering ions (Cu^{+2} and Ni^{+2}).

Nickel. Reaction A, p. 196 : *o*-cyclohexanedionedioxime. Reaction B, p. 197 : dimethylglyoxime; the selectivity is a little less and the Fe^{+2} cation must be oxidized to Fe^{+3}. Reaction C, p. 199 : diphenylglyoxime. These last two oximes do not allow of a sensitive detection of nickel in the presence of copper under its two valencies.

The indications given in the description of the reactions suffice to guide the analyst.

To accomplish the detection of all the ions of this group and especially of those which have no specific reagent we recommend a separation into three sub-groups according to a classical method, as follows : after separating the elements which are precipitated by hydrogen sulphide, the group of rare earths is first isolated by precipitation by means of oxalic acid in a slightly acid medium (hydrochloric acid). This group contains rare earths (with the exception of the Ce^{+4} cation), yttrium, thorium (the alkaline earths elements may also be carried down by the precipitation).

A series of hydroxides of trivalent and tetravalent cations is then precipitated by means of ammonia and ammonium chloride. They are : aluminium, iron, chromium, cerium (IV), titanium, zirconium, hafnium, thallium, scandium, gallium and indium, as well as uranium and glucinum.

Finally ammonium sulphide in ammoniacal medium makes it possible to separate the last cations of this large group, viz. zinc, manganese, rhenium, cobalt and nickel.

We shall therefore study the detection of the elements, taking this preliminary separation as a basis.

Rare earths group : Rare earths, Y, Th

We do not revert to the separation of the rare earths elements into their two sub-groups (cerium and yttrium sub-groups), which is described on page 132. On the same place we also mentioned the few reagents of lanthanum, cerium and europium, which are specific in this group.

For the other rare earths no reagent can be indicated; the same is true for yttrium.

Cerium can be detected by means of its three reactions, p. 138-142, of the tetravalent cation.

The identification of thorium in the presence of rare earths can be effected by means of reaction B, p. 154 : potassium iodate, provided the work is done in a medium acidified with nitric acid.

Ammonia sub-group : Al, Fe^{+3}, Cr, U, Ce^{+4}, Ti, Zr, Ct, Gl, Tl, Sc, Ga, In

It is advisable to convert iron to the trivalent state, so that it can be completely precipitated.

Difficulties in detection are not lacking in this group, most particularly for the rare elements and aluminium. It must be pointed out at once, that no reagent can be proposed for celtium.

Very fortunately some cations have reagents, which are selective to a wide extent. These, moreover, have already been mentioned above.

DETECTION OF ALUMINIUM.

Reaction A, p. 108: caesium sulphate makes the detection of aluminium possible in the presence of other cations of the group with the exception of those of iron, chromium and gallium. By means of reaction B, p. 109: sodium alizarin-3-sulphonate, aluminium and chromium can be distinguished, but a series of other ions cause serious disturbances. Reaction C, p. 110: sodium purpurin-3-sulphonate can be used to distinguish between aluminium and iron provided the fluorescence is taken into account; in this case the ions of Zr, Th, Gl, Sc and Ga still interfere. The detection of aluminium in the presence of titanium causes hardly any trouble; reactions A and C give a sensitivity of 10^{-5} ($1 : 10^5$) in the presence of titanium in a 100 : 1 proportion. Finally, gallium and aluminium cannot be distinguished from each other by means of the reagents mentioned.

DETECTION OF IRON.

For the bivalent cation reaction A, p. 112: $\alpha\alpha'$-dipyridyl, and reaction B, p. 114: *o*-phenanthroline are excellent and specific. The reagents we have indicated are not really selective for the trivalent cation, as titanium nearly always interferes. The best among them is 2-hydroxy-5-sulphonic benzoic acid (Fe, D, p. 116), in the absence of titanium. It will always be possible to reduce the trivalent cation to the bivalent cation in order to carry out a test which is absolutely selective, even in the presence of titanium (Fe, A and Fe, B, p. 112-114).

DETECTION OF CHROMIUM.

Reaction A, p. 120 : chromotropic acid and reaction B, p. 122 : hydrogen peroxide allow of a selective detection of the chromium anion and consequently of the trivalent cation after oxidation, as mentioned above. Reaction C, p. 123 : guaiacum resin, is only possible in the absence of cerium (IV); the same is true for reaction D, p. 124 : strychnine. For the trivalent cation (reaction E, p. 125 : caesiumsulphate) there exists no possibility of a sensitive test, particularly in the presence of the ions of aluminium and iron.

DETECTION OF URANIUM.

It is very difficult to carry out a reliable test for uranium in the presence of Fe^{+2}, Fe^{+3} and Ce^{+4} ions; often the ions of titanium interfere as well. The

only reagent allowing of a selective detection in the sub-group is anthranilic acid (reaction E, p. 131) and solely under the microscope. Iron and zirconium only reduce the sensitivity. Reactions A, p. 127; 8-hydroxyquinoline, C, p. 129 : quercetin, and D, p. 130 : sodium salicylate, can only be effected in the absence of iron, cerium and titanium; reaction B, p. 128 : potassium ferrocyanide, on the other hand is not disturbed by cerium.

DETECTION OF CERIUM (IV).

The greatest difficulty consists in the detection of this cation in the presence of chromium, in point of fact the oxidation of cerium to the tetravalent state, in the majority of cases causes the formation of chromic anions, which react as well. In the presence of chromium it will therefore be preferable to keep cerium in the trivalent state so that it may pass into the group of rare earths; the three reactions indicated are then selective. Reactions A, p. 141, anthranilic acid, and C, p. 138, *p*-phenetidine can be used, if care is taken to mask iron (Fe^{+3}) by the phosphoric anion; the chromic anion gives the same reaction. Chromium (VI) and thallium (III) prevent the detection of cerium by reaction B, p. 140, *o*-tolidine.

DETECTION OF TITANIUM.

A selective test can be carried out by means of hydrogen peroxide, as the tetravalent cation can be separated by precipitation as arseniate in the presence of zirconium (Ti, B, p. 145). The three reactions indicated make it possible to detect titanium in the presence of aluminium in a 100 : 1 proportion.

DETECTION OF ZIRCONIUM.

Reaction A, p. 148 : *p*-dimethylamino-4-azophenylarsonic acid, makes it possible to carry out a test which is entirely selective, as the titanium reaction is eliminated by hydrogen peroxide. The other three reactions are less precise, as several cations of the ammonia sub-group either react in the same way or disturb the test. The ions of iron and titanium are particularly to be feared.

DETECTION OF GLUCINUM (BERYLLIUM).

Acetylacetone, reaction A, p. 156, is a specific reagent, when the test is carried out under the microscope and the shape of the crystals is taken into account. It should be noted neither the alkaline earth elements nor magnesium react. Reaction B, p. 157 : 1-(1'-azo-2'-methyl-4' : 6'-dihydroxyphenyl)-4-nitrobenzene is also very useful in the absence of magnesium. Reaction C, p. 158 : alizarin bordeaux is much less selective.

DETECTION OF THALLIUM.

Reaction B, p. 160 : bismuth nitrate + sodium iodide, is selective, providing allowance is made for a certain number of masking reactions which are mentioned in the text. Reaction A, p. 159 : phosphomolybdic acid + hydrobromic acid, is also very good; the ions of iron, however, interfere (Fe^{+2}) or appreciably reduce the sensitivity (Fe^{+3}). Reaction C, p. 161 : Martius yellow, has a sensitivity which is very markedly diminished by the ions of the

sub-group. As regards reaction D, p. 162 : *o*-tolidine, this cannot be carried out in the presence of iron and cerium ions.

DETECTION OF SCANDIUM.

The two reagents indicated are not very satisfactory for the detection of this element, although they are the best that can be recommended. With reaction A, p. 163: cochineal, scandium can be distinguished from aluminium, chromium, cerium, glucinum and thallium. Unfortunately titanium and iron, in particular, interfere. Reaction B, p. 164 : luteocobaltic nitrate eliminates the reactions with iron and with zirconium, but it re-establishes that with glucinum. Reagent A will always be very useful because glucinum and the rare earths do not react it is these elements which constantly accompany scandium.

DETECTION OF GALLIUM.

The two reagents are not very sensitivity. Reaction B, p. 166 : manganous-chloride + potassium bromate + tetrapotassium hexacyanoferrate (II), makes the detection of gallium possible in the presence of the elements which accompany it most frequently (Al, In, Zn, Mn); it is especially very important that it can be distinguished from aluminium. Reagent A, p. 165 : caesium chloride + potassium hydrogen sulphate, must be referred to when iron is present. The chromic cation is the only ion of this sub-group which disturbs both reactions.

DETECTION OF INDIUM.

Reaction A, p. 168 : urotropine + ammonium thiocyanate is reliable for the detection of indium in the presence of Al, Fe, Cr and Sc. Zinc does not react either, which is very important, because indium always accompanies this element in ores. On the other hand recourse must be had to reagent B, p. 169 : alizarin in order to provide a wider selectivity in the group; with the aid of various masking reactions indicated in the text, one can succeed in detecting indium in the presence of cations of the following elements : Al, Fe, Cr, Ce, Ti, Zr, Gl, Tl, and Sc; this reaction B is also much more sensitive than the other one. It is hardly possible to distinguish gallium from indium.

Ammonium sulphide sub-group : Zn, Mn, Re, Co, Ni

It is not difficult to detect each of these elements, because selective and sensitive reagents are not wanting.

DETECTION OF ZINC.

Reaction B, p. 172 : diammonium tetrathiocyanatomercurate (II) provides a very sensitive test for zinc in the presence of cobalt and nickel; manganese always reduces the sensitivity whichever reagent may have been chosen. Reaction C, p. 174 : *p*-nitrobenzene azo-orcinol, must not be used in the presence of cobalt; finally reaction D, p. 175 : potassium ferricyanide + *p*-phenetidine, is clearly less selective.

DETECTION OF MANGANESE.

Reaction A, p. 177 : potassium persulphate + silver nitrate, and reaction B, p. 178 : potassium periodate + *p* - tetramethyldiaminodiphenylmethane, have a high sensitivity in the presence of all the cations of the sub-group. For reaction C, p. 180 : potassium nitrate + sodium carbonate a reduction in sensitivity is caused by cobalt and nickel. These first three oxidation-reduction reactions do not make it possible to specify the particular cation in question but reaction D, p. 181 : cyanuric acid, and reaction E, p. 181 : acetylsalicylic acid + hydrogen peroxide, enable us to detect the bivalent cation alone. The sensitivity of reaction D is diminished by zinc and cobalt ions; as regards reaction E, this is highly selective.

The permanganic anion can be detected in a way which is quite selective and sensitive by means of reaction F, p. 182 : rubidium nitrate + potassium perchlorate, which is much preferable to reaction G, p. 183 : *o*-tolidine.

DETECTION OF RHENIUM.

The three reactions are selective in the presence of the elements of the sub-group and the detection of rhenium does not offer great difficulties. As this element is very frequently associated with molybdenum, we have indicated a very practical means for the separation of their ions; an almost selective test for rhenium can accordingly be made in the ores containing it, making use of reactions A, p. 184 : stannous chloride + sodium tellurate and B, p. 186 : stannous chloride + dimethylglyoxime.

DETECTION OF COBALT.

Reaction A, p. 188 : ammonium mercurithiocyanate, effected with the microscope is very widely selective. Reaction B, p. 190 : rubeanic acid, is also very good, but its sensitivity is reduced by the presence of manganese and iron (after masking of the latter). The well-known nitrosonaphthols cannot be used with any certainty in the presence of nickel (reaction C, p. 191). On the other hand, 2-nitroso-1-naphtol-4-sulphonic acid (reaction D, p. 193) cannot be used with any great sensitivity in the presence of zinc, manganese and nickel. Finally, reaction E, p. 194 : potassium cyanate, and reaction F, p. 195 : potassium thiocyanate, are also suitable for the detection of cobalt in the presence of the elements mentioned above.

DETECTION OF NICKEL.

Reaction A, p. 196 : *o*-cyclohexanedionedioxime, is quite selective, and in the presence of all the elements of the analysis, moreover. Reaction B, p. 197 : dimethylglyoxime, and reaction C, p. 199 : diphenylglyoxime, have their sensitivity reduced by the ions of cobalt; but they can be used if that element is not present in a large proportion. Reaction D, p. 200 : diacetyl-monoxime, and reaction E, p. 201 : rubeanic acid, are quite unmistakeable and very selective, as are the preceding ones. Finally, reaction F, p. 202 : ammonium molybdate makes it possible to distinguish between nickel and cobalt very quickly. It is never difficult to detect nickel accurately.

50. RADIUM

BY

P. E. WENGER

AN 88 **AW 226.05**

A. Ra^{+2}, NR.

AMMONIUM CARBONATE + POTASSIUM CHROMATE $(NH_4)_2CO_3 + K_2CrO_4$

BIBLIOGRAPHY : 722.

It is possible to distinguish barium from radium by means of the different precipitations of these two cations in the concentrated solutions of the reagents indicated.

The operation can only be effected under well defined conditions of mutual concentrations of the two cations. We therefore refer the reader to the original article by B. A. NIKITIN (722).

Radio-active elements belong to various analytical groups. We only mention here the most important among them, radium. In point of fact, up to the present this element alone can be detected with a chemical reagent. All the other radio-active elements are identified by the classical physico-chemical methods, which are outside the scope of this report.

51. BARIUM

BY

C. J. VAN NIEUWENBURG

AN 56 **AW 137.36**

A. Ba^{+2}, 31.

POTASSIUM CHROMATE K_2CrO_4

BIBLIOGRAPHY : 723-740.

MECHANISM OF REACTION.

The yellow precipitate which is formed is barium chromate, $BaCrO_4$.

DETAILS OF TEST.

Under the microscope or on a spot plate.

Place on a slide a drop of the solution to be analysed, acidified with dilute acetic acid, and add a drop of the reagent solution. A bright yellow precipitate of barium chromate is produced which crystallises in squares or rectangles. If strong mineral acids are present, the solution must be buffered with sodium acetate.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.78}$ ($1 : 6 \cdot 10^5$), under the microscope.

The Ca^{+2}, Sr^{+2} and Mg^{+2} ions in a 100 : 1 proportion only reduce the sensitivity to $10^{-5.70}$ ($1 : 5 \cdot 10^5$). The ions of Hg (Hg^{+2}), Pb, Bi, and Tl give analogous precipitates; the Hg^{+1} cation gives a red precipitate and the Ag^{+1} cation gives a reddish brown precipitate. All these ions interfere with the detection of barium.

On the spot plate the sensitivity is only $10^{-4.30}$ ($1 : 2 \cdot 10^4$). It is preferable to use a black plate.

REAGENTS.

1. Acetic acid N.
2. Solution of potassium chromate, 5 %, in water.
3. Solution of sodium acetate, 10 %, in water.

E. Ba^{+2}, NR.

POTASSIUM PERMANGANATE + SULPHURIC ACID $KMnO_4 + H_2SO_4$

BIBLIOGRAPHY : 741-742.

MECHANISM OF REACTION.

The precipitate of barium sulphate which is formed adsorbs potassium permanganate from the solution and assumes a purple colour, the reducing agents reduce the MnO_4^{-1} anion of the solution, which becomes colourless, but they do not affect the manganese which is fixed to the barium sulphate by adsorption, and remains purple.

H. E. WOHLERS (741).

DETAILS OF TEST.

In an Emich tube (micro-tube of a centrifuge).

Place in an Emich tube a drop of the neutral solution to be analysed, add a drop of potassium permanganate solution and then a drop of dilute sulphuric acid and, without delay a quantity of sulphurous acid solution sufficient to decolourize the permanganate. In the presence of barium a purple precipitate remains, which can be separated in the centrifuge and observed under a magnifying glass against a background of white paper.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.70}$ $(1 : 5 \cdot 10^3)$.

The Ca^{+2}, Sr^{+2} and Mg^{+2} cations scarcely affect the sensitivity, when they are present in a 10 : 1 proportion, but in a 100 : 1 proportion they reduce it to approximately half. The reaction is selective for Pb^{+2} and Ba^{+2} cations; the lead precipitate is reddish brown.

REAGENTS.

1. Solution of potassium permanganate, 5 %, in water.
2. Sulphuric acid N.
3. Saturated solution of sulphurdioxide in water.

C. Ba^{+2}, 3.

DIAMMONIUM HEXAFLUOSILICATE, AMMONIUM SILICOFLUORIDE (PHOTO 32) $(NH_4)_2[SiF_6]$

BIBLIOGRAPHY : 743-751.

MECHANISM OF REACTION.

Colourless crystals of barium hexafluosilicate are formed, of formula $Ba[SiF_6]$.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the neutral solution to be analysed, add a drop of dilute acetic acid or dilute hydrochloric acid and a few

reagent crystals. After some moments—and if necessary, the above must be heated slightly—lenticular barium fluosilicate crystals are seen to take shape, often arranged in crosses, clusters or rosettes.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.78}$ ($1 : 6 \cdot 10^3$).

The Mg^{+2}, Ca^{+2} and Sr^{+2} cations in a 10 : 1 proportion reduce the sensitivity to $10^{-3.48}$-$10^{-3.60}$ ($1 : 3 \cdot 10^3$-$1 : 4 \cdot 10^3$). In a 100 : 1 proportion these same cations lead to a sensitivity of 10^{-3}-$10^{-3.48}$ ($1 : 10^3$-$1 : 3 \cdot 10^3$). The ions of Mo, W, Al and Mn prevent the detection of barium; the Al^{+3} cation even in a 1 : 1 proportion makes it difficult to distinguish between the crystals. The ions of platinum give yellow triangles, hexagons and rhombs, which do not interfere. The Zr^{+4} cation, which does not visibly react prevents the formation of the barium fluosilicate precipitate.

REAGENTS.

1. Acetic acid 0.2 N or
1*a*. Hydrochloric acid 0.1 N.
2. Solid ammonium fluosilicate.

52. STRONTIUM

BY

C. J. VAN NIEUWENBURG

AN 38 **AW 87.63**

A. Sr^{+2}, 25.

COPPER (II) NITRATE, CUPRIC NITRATE + POTASSIUM NITRITE $Cu(NO_3)_2 \cdot KNO_2$ (PHOTO 33)

BIBLIOGRAPHY : 752.

MECHANISM OF REACTION.

The triple nitrite of copper, strontium and potassium is precipitated.

DETAILS OF TEST.

Under the microscope.

Evaporate on a slide a drop of the solution to be analysed; take up the residue in a drop of the cupric nitrate solution and evaporate once more to dryness. Take up, finally, in 2 drops of very dilute acetic acid in order to obtain a clear solution, and add a few potassium nitrite crystals. After several minutes dark greenish-blue cubes of triple nitrite of copper, strontium and potassium are formed, which formation can be accelerated, if crystallization is started on the outer edge of the drop by gentle heating.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ ($1 : 10^4$).

The sensitivity is not reduced by the Mg^{+2} cation, even in a 100 : 1 proportion. The Ca^{+2} and Ba^{+2} cations also give green crystals, those of calcium have a hexagonal form and those of barium have a rectangular or rhombic shape, which shapes are imperfectly developed; in both cases the crystals are birefringent.

This reaction is not very useful distinguishing between strontium and barium. In any case it is necessary to note that the crystals are the cubic form of the complex strontium nitrite.

The Pb^{+2} cation gives very dark red cubes. The ions of Au, Pd, Se, Te, Mo, W and V give products which cannot be dissolved in acetic acid which makes the reaction practically unusable. The other cations do not interfere.

REAGENTS.

1. Solution of copper (II) nitrate, 2 %, in water.
2. Acetic acid 0.1 to 0.05 N.
3. Solid potassium nitrite.

B. Sr^{+2}, 3.

NITRIC ACID (PHOTO 34) HNO_3

BIBLIOGRAPHY : 753-759.

MECHANISM OF REACTION.

The crystalline precipitate is formed of strontium nitrate $Sr(NO_3)_2$.

DETAILS OF TEST.

Under the microscope.

Evaporate on a slide a drop of the solution to be analysed to dryness; redissolve the residue in dilute nitric acid, and again evaporate to dryness. Then take up in a drop of nitric acid and heat until crystallization begins at the edge of the drop. Skeletons are produced of octahedrahexagons and triangles of strontium nitrate.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.08}$ $(1 : 1.2 \cdot 10^4)$.

The sensitivity is reduced to 10^{-4} $(1 : 10^4)$ by the Ca^{+2} and Mg^{+2} ions in a 100 : 1 proportion. The Pb^{+2} and Ba^{+2} cations give analogous crystals and interfere with the reaction. The ions of Mo, W and Nb give white precipitates, which more or less interfere with the detection of strontium. The ions of the other elements do not interfere.

REAGENT.

1. Nitric acid 6 N ($d = 1.2$).

53. CALCIUM

BY

C. J. VAN NIEUWENBURG

AN 20 **AW 40.08**

A. Ca^{+2}, 2.

SULPHURIC ACID (PHOTO 35) H_2SO_4

BIBLIOGRAPHY : 760-767.

MECHANISM OF REACTION.

The crystals which are formed are those of calcium sulphate dihydrate $CaSO_4 . 2\ H_2O$.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed and evaporate to dryness. Take up the residue with a drop of water to which is added a small drop of dilute sulphuric acid. Heat until on the edges of the drop crystallization sets in; needles of calcium sulphate are produced, often grouped together in little bundles, or sometimes prisms with oblique terminal planes, showing oblique extinction.

The reaction is excellent.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.48}$ $(1 : 3 \cdot 10^5)$.

The sensitivity is considerably reduced by the Sr^{+2}, Ba^{+2} and Mg^{+2} ions :

Mg : Ca	1 : 1	$D = 10^{-5.48}$	$(1 : 3 \cdot 10^5)$
	10 : 1	$D = 10^{-4.90}$	$(1 : 8 \cdot 10^4)$
	100 : 1	$D = 10^{-3.78}$	$(1 : 6 \cdot 10^3)$
Sr or Ba : Ca	1 : 1	$D = 10^{-4.70}$	$(1 : 5 \cdot 10^4)$
	10 : 1	$D = 10^{-4}$	$(1 : 10^4)$
	100 : 1	no reaction for calcium.	

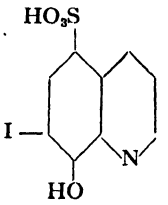
The Pb^{+2} cation does not interfere, unless it is present in very large proportion with regard to calcium. The ions of Ce, La, Th and Sc give analogous crystals and prevent the identification of calcium. The Fe^{+3} and Cr^{+3} cations modify the crystal habit because they produce mixed crystals. Accordingly we obtain tiny rectangular rods (Fe^{+3}) or rodlets, hexagons and rhombs (Cr^{+3}) which are always mixed with the normal needles of calcium sulphate.

REAGENT.

1. Sulphuric acid 2 N.

B. Ca^{+2}, 43.

7-IODO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID *(loretine)*



(PHOTO 36)

BIBLIOGRAPHY : 768.

MECHANISM OF REACTION.

The compound which is formed has not yet been described.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the nearly neutral solution to be analysed, and add a drop of the reagent solution. Start the crystallization on the edges of the drop by heating gently, when orange coloured needles are produced, often grouped together in bundles.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.95}$ $(1 : 9 \cdot 10^4)$.

The Sr^{+2} and Ba^{+2} ions give exactly the same reaction. The Mg^{+2} cation does not interfere, but it reduces the sensitivity :

Mg : Ca	10 : 1	$D = 10^{-4.30}$ $(1 : 2 \cdot 10^4)$.
	100 : 1	$D = 10^{-3.70}$ $(1 : 5 \cdot 10^3)$.

The ions of Ag, Hg, Pb, Sb, Sn, Fe and Zr give precipitates, which make it impossible to distinguish the needles of calcium. The ions of Cu, Cd, Zn, Mn, Co and Ni interfere because they give similar needles, although they are not orange coloured. The ions of the alkali metals interfere more or less. The ammonium cation does not interfere.

REAGENT.

1. Saturated solution of 7-iodo-8-hydroxyquinoline-5-sulphonic acid in water.

54. MAGNESIUM

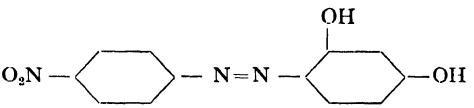
BY

C. J. VAN NIEUWENBURG

AN 12 AW 24.32

A. Mg^{+2}, 45.

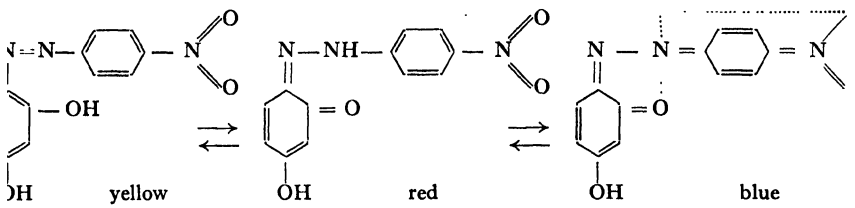
1-(1'-AZO-2' : 4'-DIHYDROXYPHENYL)-4-NITROBENZENE, *p*-NITROBENZENE-AZO-RESORCINOL
(magneson)



BIBLIOGRAPHY : 769-787.

MECHANISM OF REACTION.

The precipitation of magnesium hydroxide is accompanied by a phenomenon of adsorption; the azo dyestuff is fixed on the hydroxide to which it imparts a blue colour, whereas it would have a red shade in a solution of the same *p*H. The following tautomeric equilibria should be considered :



K. SUITSU and K. OKUMA (769), R. PATRIZIETTI (784, 785).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the neutral or slightly acid solution to be analysed and add a drop of the reagent solution and 1 or 2 drops of potassium hydroxide in dilute solution. In the presence of magnesium either a blue colour or a blue precipitate is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.60}$ (1 : $4 \cdot 10^4$).

The Ba^{+2}, Sr^{+2} and Ca^{+2} ions do not interfere and even in a 100 : 1 proportion they only reduce the sensitivity in a negligable manner.

The Ni^{+2} cation gives a purple precipitate, with the result that in its presence the reaction with magnesium gives a dark blue colour. The Co^{+2} cation gives a dark blue precipitate, which prevents the identification of magnesium. Finally, the Cd^{+2} cation, which gives a brown precipitate, makes the precipitate of magnesium assume a purple colour. As the reaction of magnesium is due to the adsorption of the dyestuff on magnesium hydroxide, the presence of ammonium salts must be avoided (eliminating them by calcination at 400°-500°), because they would prevent the precipitation of that hydroxide.

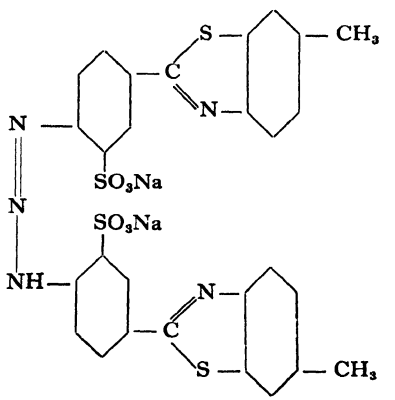
REAGENTS.

1. Solution of *p*-nitrobenzene-azo-resorcinol, 0.1 %, in alcohol 50 %.
2. Potassium hydroxide 0.1 N.

B. Mg^{+2}, 46.

SODIUM DEHYDROTHIO-*p*-TOLUIDINESULPHO-*p*-DIAZOAMINO-DEHYDROTHIO-TOLUIDINE SULPHONATE

(thiazole yellow, titan yellow, titan yellow G)



BIBLIOGRAPHY : 788-802.

MECHANISM OF REACTION.

It is in every way comparable with that described for *p*-nitrobenzene-azo-resorcinol (reaction A), except the tautomeric equilibria.

E. EEGRIWE (791).

DETAILS OF TEST.

In a macro test tube.

Place in a test tube 1 ml of the neutral or slightly acid solution to be analysed and add 0.5 ml of the reagent solution and 1 ml of potassium hydroxide solution. In the presence of magnesium a vivid red precipitate is formed; if this ion is present in very small quantity only a red colouration appears. This colour should not be confused with that which the reagent produces in an alkaline solution. A little heating tends to coagulate the precipitate.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ ($1 : 10^6$).

The Ba^{+2}, Sr^{+2} and Ca^{+2} ions reduce the sensitivity only slightly; if they are present in a 100 : 1 proportion, it assumes a value of $10^{-5.30}$ ($1 : 2 \cdot 10^5$). The ions of Ag, Hg, Cu, Cd, Mn, Co and Ni give analogous precipitates and interfere. The ions of Bi, Fe, Cr and U, which give coloured precipitates with potassium hydroxide, reduce the sensitivity without altogether preventing the detection of magnesium.

As the reaction is due to the adsorption of the dyestuff on magnesium hydroxide, the presence of ammonium salts should be avoided (eliminating them by calcination at 400°-500°), because they would prevent the precipitation of that hydroxide.

REAGENTS.

1. Solution of titan yellow, 0.05 %, in alcohol.
2. Potassium hydroxide 0.1 N.

C. Mg^{+2}, 38.

POTASSIUM HYPOIODITE KIO

BIBLIOGRAPHY : 803-819.

MECHANISM OF REACTION.

The brown colour is due to the adsorption of iodine on the precipitate of magnesium hydroxide.

SCHLAGDENHAUFEN (803) and P. REMY-GENNETÉ (818).

DETAILS OF TEST.

In a macro test tube.

Place in a macro test tube 1 ml of the reagent solution and add a dilute solution of potassium hydroxide until the liquid exhibits only a pale yellow colour; finally add 1 ml of the solution to be analysed. In the presence of magnesium a dark brown, flocculent precipitate is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.18}$ ($1 : 1.5 \cdot 10^4$).

The sensitivity is reduced to $10^{-4.15}$ ($1 : 1.4 \cdot 10^4$) by the ions of calcium in a 100 : 1 proportion. It is reduced by the ions of strontium to $10^{-3.90}$ ($1 : 8 \cdot 10^3$) in a 100 : 1 proportion; it is only $10^{-3.30}$ ($1 : 2 \cdot 10^3$) in the presence of barium ions in a 100 : 1 proportion.

The ions of Hg (Hg^{+2}), Bi, Fe (Fe^{+3}), Mn, Co and Ni give analogous precipitates. The Hg^{+1}, Al^{+3} and NH_4^{+1} cations prevent the precipitation of magnesium. The ions of Pb, Cd, V, U, Ce and La interfere more or less.

REAGENTS.

1. Potassium hydroxide 0.1 N.
2. Solution of 3 g potassium iodide + 1.5 g iodine in 100 ml water.

QUALITATIVE SEPARATION OF ELEMENTS OF THE ALKALINE-EARTH GROUP

The case of radium has not been considered.

When the four elements are present in normal quantities, magnesium can be identified by means of the three reactions indicated (p. 218-221). Barium can be detected using either the reaction with potassium chromate (Ba, A, p. 210) or the reaction with potassium permanganate (Ba, B, p. 211). For the identification of barium and strontium it is preferable to eliminate the barium, precipitating it as chromate, and to separate the strontium from the calcium by nitric acid ($d = 1.4$), as indicated below (vide *b*).

As regards the detection of traces of each of these elements the following four cases must be considered :

a. DETECTION OF TRACES OF Ba^{+2}, Sr^{+2} AND Ca^{+2} CATIONS IN THE PRESENCE OF LARGE PROPORTIONS OF Mg^{+2} CATION

The Ba^{+2} cation can be identified using the reaction with potassium chromate (Ba, A, p. 210) of which the sensitivity is $10^{-5.70}$ ($1 : 5 \cdot 10^5$), magnesium being present in a 100 : 1 proportion. The other reagents are less sensitive and for same proportion of magnesium the following values are obtained :

Reaction Ba, B, p. 211 : potassium permanganate : $D = 10^{-3.40}$ ($1 : 2.5 \cdot 10^3$)
Reaction Ba, C, p. 212 : ammonium fluosilicate : $D = 10^{-3.48}$ ($1 : 3 \cdot 10^3$).

The Sr^{+2} cation is identified by means of the reaction with cupric nitrate and potassium nitrite (Sr, A, p. 213) of which the sensitivity is 10^{-4} ($1 : 10^4$) for a magnesium proportion of 100 : 1.

The Ca^{+2} cation is detected as the hydrated sulphate (Ca, A, p. 215); the sensitivity is $10^{-3.78}$ ($1 : 6 \cdot 10^3$), magnesium being present in a 100 : 1 proportion.

b. DETECTION OF TRACES OF Ba^{+2}, Sr^{+2} and Mg^{+2} CATIONS IN THE PRESENCE OF PROPORTIONS OF Ca^{+2} CATION

Barium is detected by means of potassium chromate (Ba, A, p. 210) : sensitivity $D = 10^{-5.70}$ ($1 : 5 \cdot 10^5$) for a calcium proportion of 100 : 1. The other reagents are less sensitive (vide *a*, the values being practically the same).

The Sr^{+2} cation can be identified by means of its reaction with cupric nitrate and potassium nitrite (Sr, A, p. 213). The formation of non-birefringent cubes should be taken as a basis (Sr, A, p. 213). It is preferable to eliminate the excess of calcium by evaporation to dryness, treating it afterwards with nitric acid ($d = 1.4$), which dissolves calcium nitrate, but not strontium nitrate.

The Mg^{+2} cation is identified by means of one of its three reactions (p. 218-221). For a calcium proportion of 100 : 1 the sensitivities of the three reagents are : $10^{-4.60}$ ($1 : 4 \cdot 10^4$), $10^{-4.30}$ ($1 : 2 \cdot 10^4$) and $10^{-4.15}$ ($1 : 1.4 \cdot 10^4$).

c. DETECTION OF TRACES OF Ba^{+2}, Ca^{+2} AND Mg^{+2} CATIONS IN THE PRESENCE OF LARGE PROPORTIONS OF Sr^{+2} CATION

The barium cation is identified by means of the reaction with potassium chromate (Ba, A, p. 210), the other reagents being less sensitive. In solutions in which strontium is present in a 100 : 1 proportion the sensitivities are : potassium chromate (Ba, A, p. 210) : $10^{-5.70}$ ($1 : 5 \cdot 10^5$); potassium permanganate (Ba, B, p. 211) : $10^{-3.40}$ ($1 : 2.5 \cdot 10^3$); ammonium fluosilicate (Ba, C) : 10^{-3} ($1 : 10^3$, p. 212).

Calcium is detected by means of sulphuric acid (Ca, A, p. 215); but the test is impossible if strontium is present in a 100 : 1 proportion. In a 10 : 1 proportion on the other hand the sensitivity of the reaction will still be 10^{-4} ($1 : 10^4$).

The Mg^{+2} cation is detected by means of one of the three reagents mentioned (p. 218-221). If strontium is present in a 100 : 1 proportion the sensitivities become : magneson (Mg, A, p. 218) : $10^{-4.60}$ ($1 : 4 \cdot 10^4$); titan yellow (Mg, B, p. 219) : $10^{-5.30}$ ($1 : 2 \cdot 10^5$); potassium hypoiodite (Mg, C, p. 220) : $10^{-3.90}$ ($1 : 8 \cdot 10^3$). For the elimination of strontium see *b*.

d. DETECTION OF TRACES OF Sr^{+2}, Ca^{+2} AND Mg^{+2} CATIONS IN THE PRESENCE OF LARGE PROPORTIONS OF Ba^{+2} CATION

The Sr^{+2} cation can be detected by means of the reaction with cuprous nitrate and potassium nitrite (Sr, A, p. 213). If barium is present in a very considerable proportion, the sensitivity is not great and it will be useful to eliminate this cation beforehand, precipitating it as a chromate in an acid medium (acetic acid).

The Ca^{+2} cation is identified as the sulphate (Ca, A, p. 215); the sensitivity of the reaction is the same as in case *c*. Barium can be eliminated as nitrate by evaporating the solution to dryness and treating it with nitric acid ($d = 1.4$), which dissolves only calcium nitrate.

The Mg^{+2} cation is detected by means of one of the three reagents mentioned (p. 218-221). If barium is present in a 100 : 1 proportion, the sensitivities become : magneson (Mg, A, p. 218) : $10^{-4.60}$ ($1 : 4 \cdot 10^4$); titan yellow (Mg, B, p. 219) : $10^{-5.30}$ ($1 : 2 \cdot 10^5$); potassium hypoiodite (Mg, C, p. 220) : $10^{-3.30}$ ($1 : 2 \cdot 10^3$).

RECAPITULATION :

The three reactions indicated for barium are useful, but the reaction with potassium chromate (Ba, A, p. 210) is the most sensitive. The other reactions are also interesting, because they have the advantage of being more selective and are therefore more convincing.

The two reactions of strontium are not very sensitive. That of the triple nitrite (Sr, A, p. 213) is fairly selective (in the absence of the Ba^{+2} cation), but it is more or less capricious. Hence it is useful to use the other reaction as well (nitric acid : Sr, B, p. 214), the more so because strontium will be present already in the form of nitrate after the separation of calcium.

The reaction of calcium with sulphuric acid (Ca, A, p. 215) is excellent, if the Ba^{+2} and Sr^{+2} cations are not present in a large proportion; but if the opposite is the case it is necessary to eliminate these two cations by means of nitric acid ($d = 1.4$). The reaction with loretine (Ca, B, p. 217) is only useful for the detection of calcium in the presence of large quantities of Mg^{+2} cation and in the absence of the other two alkaline-earth cations.

55. LITHIUM

BY

J. GILLIS

AN 3 AW 6.940

A. Li^{+1}, 1.

AMMONIUM CARBONATE (PHOTO 37) $(NH_4)_2CO_3$

BIBLIOGRAPHY : 820-827.

MECHANISM OF REACTION.

A precipitate of crystallized lithium carbonate, Li_2CO_3, is formed.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed, which is partly evaporated. After cooling, a few grains of sodium carbonate or of ammonium carbonate are added. Some lithium carbonate crystals are formed at once, which occur under three different aspects : they resemble gypsum crystals, or they are in the form of either hexagonal stars or plates. These crystals can easily be distinguished from those of the other salts which crystallize at the same time because of their low solubility.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ ($1 : 10^4$).

The Na^{+1} cation in a 10 : 1 proportion reduces the sensitivity to $10^{-3.48}$ ($1 : 3 \cdot 10^3$). The K^{+1} cation in the same proportion as sodium gives a sensitivity of $10^{-3.78}$ ($1 : 6 \cdot 10^3$). The Rb^{+1} and Cs^{+1} cations do not interfere. The alkaline-earth cations, which react with ammonium carbonate, interfere and must be separated beforehand.

REAGENTS.

1. Solid sodium carbonate or

1*a*. Solid ammonium carbonate.

B. Li^{+1}, 2.

DISODIUM HYDROGEN PHOSPHATE, SODIUM BIPHOSPHATE Na_2HPO_4

BIBLIOGRAPHY : 828-834.

MECHANISM OF REACTION.

The Li^{+1} cation gives a white precipitate of phosphate according to the formula : Li_3PO_4.

DETAILS OF TEST.

In a macro test tube.

Place in a test tube 1 ml of the solution to be analysed, add a drop of ammonia and 0.1 ml of the alkali phosphate solution. Then add alcohol in a quantity sufficient to obtain a syrupy precipitate, which only disappears when the test tube is shaken. On heating to the boil a white precipitate is formed in the presence of lithium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.30}$ $(1 : 2 \cdot 10^5)$.

The Na^{+1}, Rb^{+1} and Cs^{+1} cations do not interfere. The K^{+1} and NH_4^{+1} cations lead to the following sensitivities : $10^{-4.26}$ $(1 : 1.8 \cdot 10^4)$ and $10^{-4.08}$ $(1 : 1.2 \cdot 10^4)$, when they are present in a 1,000 : 1 proportion. The alkaline-earth cations interfere.

REAGENTS.

1. Ammonia 8 N.
2. Sodium biphosphate 0.2 N (2.4 g of $Na_2HPO_4 . 12\ H_2O$ dissolved in 100 ml of water).
3. Ethyl alcohol 96 %.

C. Li^{+1}, NR.

COMPLEX PERIODATE OF IRON (III) $KIO_4 + FeCl_3 + KOH$

BIBLIOGRAPHY : 835-838.

MECHANISM OF REACTION.

The white precipitate which is formed has the formula : $KLiFeIO_6$.

O. Pročke and A. Šlouf (838).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube a drop of the solution to be analysed (lithium being in the form of chloride), and 2 drops of the ferric periodate solution. Shake, and immerse the test tube in a boiling water-bath for 20 seconds. A white precipitate indicates the presence of lithium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.6}$ $(1 : 3 \cdot 10^4)$.

The Na^{+1} cation and the K^{+1} cation in a 500 : 1 proportion do not reduce the sensitivity. The Rb^{+1} cation and the Cs^{+1} cation in a 15,000 : 1 proportion do not interfere with the detection of lithium.

REAGENT.

1. Solution of ferric periodate prepared in the following manner : dissolve 2 g of potassium periodate in 10 ml of potassium hydroxide 2 N, dilute with water to 50 ml, add 3 ml of chloride of iron (III) solution, 10 %, and dilute to 100 ml with potassium hydroxide 2 N.

56. SODIUM

BY

J. GILLIS

AN 11 **AW 22.997**

A. Na^{+1}, 18.

URANYL ACETATE (PHOTO 38) $(CH_3CO_2)_2UO_2$

BIBLIOGRAPHY : 839-849.

MECHANISM OF REACTION.

The sodium uranyl acetate which crystallizes out has the formula :

$$(CH_3CO_2)_2UO_2 \cdot CH_3CO_2Na$$

W. LENZ and N. SCHOORL (842).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed and evaporate to dryness. After cooling add a drop of the reagent solution to the residue, which dissolves completely. After some moments in the presence of sodium tetrahedra with a high refractive index are formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The K^{+1} cation in a 1,300 : 1 proportion reduces the sensitivity to $10^{-4.30}$ (1 : $2 \cdot 10^4$). The NH_4^{+1} cation leads to a sensitivity of $10^{-4.18}$ (1 : $1.5 \cdot 10^4$), if present in a 90 : 1 proportion. Ag^{+1}, Li^{+1}, Rb^{+1}, Cs^{+1} cations and inorganic acids interfere.

REAGENT.

1. Saturated solution of uranyl acetate in acetic acid 6 N + an equal volume of acetic acid 6 N.

B. Na^{+1}, 19.

MAGNESIUM URANYL ACETATE $(CH_3CO_2)_2UO_2 . (CH_3CO_2)_2Mg$

(PHOTO 39)

BIBLIOGRAPHY : 850-860.

MECHANISM OF REACTION.

The product which crystallizes out has the following formula :

$$3\ (CH_3CO_2)_2UO_2 . (CH_3CO_2)_2Mg . CH_3CO_2Na . 9\ H_2O$$

A. STRENG (850).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed, which is concentrated by evaporation, and add a drop of the reagent solution. At the end of a more or less prolonged interval of time and in the presence of sodium crystallization can be started by rubbing with a glass rod, when yellow octahedral or tetrahedral crystals are produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The ions of alkaline earth elements do not interfere, neither does the NH_4^{+1} cation. The K^{+1} cation interferes, if it is present in a 100 : 1 proportion. The Li^{+1}, Rb^{+1} and Cs^{+1} ions crystallize in the same way as sodium and they interfere as well as the cations of Ag, Hg, Sb and the anions : PO_4^{-3}, AsO_4^{-3}, $[SiF_6]^{-2}$, $[Fe(CN)_6]^{-4}$ and $C_2O_4^{-2}$.

REAGENT.

1. Magnesium uranyl acetate in a solution prepared in the following manner :

Mix in equal parts the two solutions :

a. 100 g uranyl acetate + 60 g glacial acetic acid + 1,000 ml distilled water.

b. 333 g magnesium acetate + 100 g glacial acetic acid + 1,000 ml distilled water.

Allow to settle for some time after mixing and filter in order to eliminate all the sodium salts which may have precipitated.

C. Na^{+1}, 20.

ZINC URANYL ACETATE (PHOTO 40) $(CH_3CO_2)_2UO_2 . (CH_3CO_2)_2Zn$

BIBLIOGRAPHY : 861-878.

MECHANISM OF REACTION.

The precipitate of monoclinic yellow crystals has the formula :

$$3\ (CH_3CO_2)_2UO_2 . (CH_3CO_2)_2Zn . CH_3CO_2Na . 9\ H_2O$$

I. M. KOLTHOFF (863).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed (sodium in the state of chloride) and evaporate to dryness. Add a drop of the reagent solution to the dry residue. Large yellow crystals, which are monoclinic and twinned, and appear octahedral, indicate the presence of sodium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6.30}$ (1 : $2 \cdot 10^6$).

The K^{+1} cation in a 130 : 1 proportion reduces the sensitivity to $10^{-5.08}$ (1 : $1.2 \cdot 10^5$). Li^{+1}, Rb^{+1} and Cs^{+1} cations only interfere when they are present in very large proportions. The NH_4^{+1} cation does not interfere.

REAGENT.

1. Saturated solution of zinc uranyl acetate in acetic acid N (filter the solution).

D. Na^{+1}, 21.

BISMUTH NITRATE + POTASSIUM NITRITE + CAESIUM NITRATE $Bi(NO_3)_3 + KNO_2 + CsNO_3$

BIBLIOGRAPHY : 879-881.

MECHANISM OF REACTION.

The pale yellow precipitate which is formed has the formula :

$$5\ Bi(NO_2)_3 \cdot 6\ NaNO_2 \cdot 9\ CsNO_2$$

W. C. BALL (879).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed, evaporate it and add a drop of the reagent solution. In the presence of sodium a white-yellow precipitate is formed, which is more easily observed against a black background.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The K^{+1} cation does not interfere, whereas the Li^{+1}, Rb^{+1}, Cs^{+1} and NH_4^{+1} ions interfere with the detection of sodium as soon as they are present in a proportion higher than 10 : 1. The ions of Ag, Co and Ni also interfere.

REAGENTS.

1. The reagent solution is prepared as follows : dissolve 50 g potassium nitrite in 100 ml water, neutralize with nitric acid 2 N, add 10 g pulverized bismuth nitrate. After filtering, add a solution of caesium nitrate, 10 %, in water until the yellow precipitate (due to sodium) ceases to be formed. Filter after some hours and continue to add caesium salt solution until precipitation stops altogether. Approximately 2.5 g caesium nitrate are required and a total volume of about 150 ml is obtained. Finally acidify with a few drops of nitric acid 6 N.

57. POTASSIUM

BY

J. GILLIS

AN 19 **AW 39.096**

A. K^{+1}, 40.

TRISODIUM HEXANITRITOCOBALTATE (III), SODIUM COBALTINITRITE $Na_3[Co(NO_2)_6]$

BIBLIOGRAPHY : 882-897.

MECHANISM OF REACTION.

The yellow precipitate which is formed, has the following formula :

$$K_2Na[Co(NO_2)_6]$$

L. L. BURGESS and O. KAMM (887).

DETAILS OF TEST.

Under the microscope.

Put on a slide (which is placed against a black background) a drop of the solution to be analysed and a drop of the reagent solution. With high potassium concentrations the precipitate can be observed with the naked eye, with low concentrations the crystals must be examined through the microscope.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.18}$ ($1 : 1.5 \cdot 10^5$).

The Na^{+1} cation does not interfere, whereas the Li^{+1}, Rb^{+1}, Cs^{+1}, NH_4^{+1} and NO_3^{-1} ions do.

IMPROVED TEST.

The sensitivity and the selectivity can be clearly improved, if the following technique is adopted. Place on a slide a drop of the solution to be analysed, a drop of alcohol and a drop of the reagent solution. In the presence of potassium yellow crystals are formed immediately.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ ($1 : 10^6$).

The Li^{+1} cation in a 1 : 1 proportion reduces the sensitivity to $10^{-4.30}$ ($1 : 2 \cdot 10^4$). The Na^{+1}, Rb^{+1}, Cs^{+1} and NH_4^{+1} cations do not interfere.

REAGENTS.

1. Solution of 0.5 g sodium cobaltinitrite in 3 ml water.
2. Ethyl alcohol.

B. K^{+1}, 41.

DIHYDROGEN HEXACHLOROPLATINIC (IV) ACID, CHLOROPLATINIC ACID $H_2[PtCl_6]$ (PHOTO 41)

BIBLIOGRAPHY : 898-906.

MECHANISM OF REACTION.

The potassium salt $K_2[PtCl_6]$, which is orange-yellow, is precipitated.

DETAILS OF TEST.

Under the microscope.

Place side by side on a slide a drop of the solution to be analysed and a drop of the reagent solution. Bring the two drops into contact

with each other by means of a thin glass rod. In the presence of potassium a crystalline precipitate is formed which is coloured orange-yellow.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.28}$ ($1 : 1.9 \cdot 10^3$).

The Na^{+1} cation in a 15 : 1 proportion reduces the sensitivity to $10^{-2.70}$ ($1 : 5 \cdot 10^2$). The NH_4^{+1} cation gives an identical reaction and it must therefore be eliminated beforehand. The Tl^{+1}, Rb^{+1}, Cs^{+1} ions, hydriodic acid, sulphuric acid and nitric acid, amines and certain alkaloids interfere with the detection of potassium. The Li^{+1} cation does not interfere.

REAGENT.

1. Solution of chloroplatinic acid, 10 %, in water.

C. K^{+1}, 44.

LEAD ACETATE + COPPER (II) ACETATE, CUPRIC ACETATE + SODIUM NITRITE

(PHOTO 42) $(CH_3CO_2)_2Pb + (CH_3CO_2)_2Cu + NaNO_2$

BIBLIOGRAPHY : 907-911.

MECHANISM OF REACTION.

Black cubes and red crystals of a complex nitrite are formed :

$$K_2[PbCu(NO_2)_6]$$

J. KISSER (908).

DETAILS OF TEST.

Under the microscope.

Evaporate to dryness on a slide a drop of the solution to be analysed; after cooling, take up in a drop of the reagent solution. In the presence of potassium black cubes are observed (or red ones if the crystals are fine) in a green coloured solution.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.89}$ (1 : $7.7 \cdot 10^4$).

The Na^{+1} cation in a large proportion (75 : 1) prevents the formation of crystals, which appear only after dilution. Tl^{+1}, Rb^{+1}, Cs^{+1} and NH_4^{+1} cations interfere. The Li^{+1} cation does not interfere.

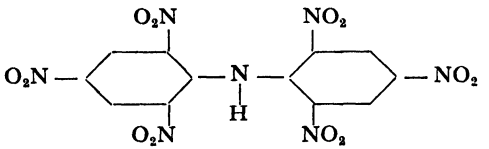
REAGENT.

1. Solution of 16.2 g lead acetate + 9.1 g cupric acetate + 20 g sodium nitrite + 2 ml glacial acetic acid in 150 ml distilled water.

D. K^{+1}, 68.

2 : 4 : 6 : 2' : 4' : 6'-HEXANITRODIPHENYLAMINE, DIPICRYLAMINE

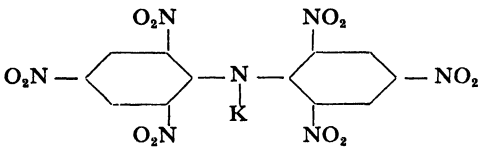
(PHOTO 43)



BIBLIOGRAPHY : 912-918.

MECHANISM OF REACTION.

The potassium salt of the following formula is probably formed :



P. E. WENGER and R. DUCKERT.

DETAILS OF TEST.

a. On filter paper.

Place on a filter paper a drop of the solution to be analysed and a drop of the reagent solution. Acidify by means of a few drops of dilute hydrochloric acid. An orange coloured stain indicates the presence of potassium.

b. Under the microscope.

Evaporate to dryness on a slide a drop of the solution to be analysed, and after cooling, add a drop of the reagent solution, made slightly

alkaline. For high potassium concentrations a crystallization with arborescences is obtained and for low concentrations some well-shaped hexagonal crystals.

SENSITIVITY AND SELECTIVITY.

a. On filter paper : $D = 10^{-3}$ ($1 : 10^3$).

b. Under the microscope : $D = 10^{-5.70}$ ($1 : 5 \cdot 10^5$).

The ions of Hg (Hg^{+2}), Pb, Zr, Gl, Tl, Rb, Cs as well as the NH_4^{+1} cation interfere. The Mg^{+2}, Li^{+1} and Na^{+1} cations do not interfere.

REAGENTS.

1. Solution of 200 mg dipicrylamine + 2 ml sodium carbonate N in 20 ml water.
2. Hydrochloric acid 2 N.

E. K^{+1}, NR.

TRIPLE NITRITE OF LEAD, COBALT AND SODIUM (PHOTO 44) $Na_2Pb[Co(NO_2)_6]$

BIBLIOGRAPHY : 919.

MECHANISM OF REACTION.

Black crystals of a complex nitrite are formed :

$$K_2[PbCo(NO_2)_6]$$

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed and evaporate to dryness. Take up the residue with a drop of dilute hydrochloric acid and add a small lead nitrate crystal, a cobalt nitrate crystal and 1 or 2 drops of saturated sodium nitrite solution. After thorough mixing, black, cubinal crystals of the complex nitrite of lead, cobalt and potassium appear in a short time.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.88}$ ($1 : 7.5 \cdot 10^4$).

The ions of the following alkaline elements do not interfere : Li, Na, Rb and Cs; those of the alkaline-earth elements as well as the ammonium cation interfere.

REAGENTS.

1. Hydrochloric acid 0.1 N.
2. Solid lead nitrate.
3. Solid cobalt nitrate.
4. Saturated solution of sodium nitrite in water.

58. RUBIDIUM

BY

J. GILLIS

AN 37 AW 85.48

A. Rb^{+1}, 13.

12-MOLYBDATOSILICIC ACID, SILICO-12-MOLYBDIC ACID, or AMMONIUM 12-MOLYBDATOSILICATE, AMMONIUM SILICO-12-MOLYBDATE $SiO_2 . 12\ MoO_3 . 2\ H_2O . n\ H_2O$

BIBLIOGRAPHY : 920-922.

MECHANISM OF REACTION.

A crystalline, yellow silicomolybdate of rubidium is formed, probably having the formula :

$$SiO_2 . 12\ MoO_3 . 2\ Rb_2O . n\ H_2O$$

P. E. WENGER and R. DUCKERT.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed and evaporate to dryness. Take up the residue in a drop of the reagent solution.

In the presence of rubidium a lemon-yellow precipitate of octahedral crystals and of spheroids is formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

The Cs^{+1} cation gives an analogous reaction. The NH_4^{+1} cation prevents the detection of rubidium. Ammonium chloride is precipitated in the form of crystals of 8 to 12 micron; rubidium chloride gives crystals of 10 to 20 micron. The ions of Ag, Hg (Hg^{+1}), Tl, Ba, Ca, Mg, Li, Na and K do not interfere.

REAGENTS.

1*a*. Saturated solution of silicomolybdic acid in water, or
b. Saturated solution of ammonium silicomolybdate in water.

Preparation of ammonium silicomolybdate.

Prepare a saturated solution of ammonium molybdate in dilute nitric acid and also a solution of sodium silicate in dilute nitric acid. Mix the two solutions and boil; a yellow crystalline precipitate is formed, the quantity of which can be increased by adding solid ammonium nitrate to the solution. Decant and recrystallize the ammonium silicomolybdate in hot water.

B. Rb^{+1}, 18.

GOLD (III) BROMIDE, AURIC BROMIDE + SILVER BROMIDE (PHOTO 45) $AuBr_3 + AgBr$

BIBLIOGRAPHY : 923-925.

MECHANISM OF REACTION.

The precipitate of red prismatic needles corresponds to a formula of the following type :

$3\,AuI \cdot AuI_3 \cdot AgI \cdot 4\,RbI$ or
$3\,AuI \cdot AuI_3 \cdot 2\,AgI \cdot 3\,RbI$

E. S. BURKSER and S. G. RUBLOV (924).

DETAILS OF TEST.

Under the microscope.

Evaporate on a slide a drop of the solution to be analysed and add to the residue a drop of auric bromide solution and a drop of silver bromide solution. After some moments and in the presence of rubidium a precipitate of red, prismatic needles appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

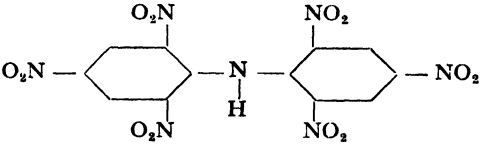
The Na^{+1} cation in a 100 : 1 proportion reduces the sensitivity to $10^{-3.30}$ ($1 : 2 \cdot 10^3$). The K^{+1} cation in a 1,300 : 1 proportion reduces the sensitivity to $10^{-4.30}$ ($1 : 2 \cdot 10^4$). The Cs^{+1} cation reacts in the same way. The ions of the following elements interfere as well : Sb, Sn, Ru, Rh and Pt. Finally, the ions of As, Ba, Ca, Mg, Li, Br and sulphuric acid do not interfere.

REAGENTS.

1. Solution of auric bromide, 4.5 %, in hydrobromic acid 40 % ($d = 1.38$).
2. Solution of silver bromide, 0.8 %, in hydrobromic acid 40 % ($d = 1.38$).

C. Rb^{+1}, 33.

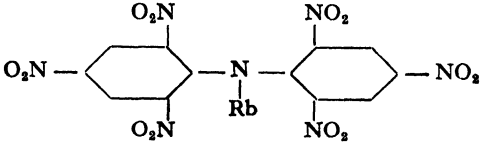
2 : 4 : 6 : 2' : 4' : 6'-HEXANITRODIPHENYLAMINE, DIPICRYLAMINE



BIBLIOGRAPHY : 926-927.

MECHANISM OF REACTION.

The rubidium salt of the following formula is probably formed :



P. E. WENGER and R. DUCKERT.

DETAILS OF TEST.

Under the microscope.

Evaporate on a slide a drop of the solution to be analysed and place a drop of the slightly alkaline reagent solution on the residue. A blood-red precipitate is formed, which appears immediately if the rubidium concentration is high, but which can be observed only after some time for low concentrations of the cation.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

The K^{+1} cation gives crystals analogous to rubidium but much smaller. It is possible to eliminate the greater part of RbCl, treating the mixture of the dry chlorides KCl + RbCl with ethyl alcohol 90%, having the greater part of KCl as residue. The ions of the following elements interfere with the reaction : Hg (Hg^{+2}), Cu, Pb, Bi, V, Al, Fe, Cr, Ti, Zr, Th, Gl, Tl, Co, Ni, Cs and the NH_4^{+1} cation. The Na^{+1} cation does not interfere.

REAGENT.

1. Solution of dipicrylamine, 1 %, in water.

59. CAESIUM

BY

J. GILLIS

AN 55 **AW 132.91**

A. Cs^{+1}, 8.

OCTAHYDROGEN HEXADITUNGSTATOSILICIC ACID, SILICOTUNGSTIC ACID $H_8[Si(W_2O_7)_6]$

BIBLIOGRAPHY : 928.

MECHANISM OF REACTION.

A caesium salt of silicotungstic acid is precipitated.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed and evaporate; after cooling add a drop of a saturated solution of silicotungstic acid. In order to expedite the formation of the precipitate, rub with a glass rod. On examination against a black background a white precipitate is distinguished, which indicates the presence of caesium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ $(1 : 5 \cdot 10^5)$.

The Li^{+1}, Na^{+1} and K^{+1} ions do not interfere; the Rb^{+1} and NH_4^{+1} ions give an analogous reaction.

REAGENT.

1. Saturated solution of silicotungstic acid in water.

B. Cs^{+1}, 20.

12-MOLYBDATOSILICIC ACID, SILICO-12-MOLYBDIC ACID or AMMONIUM 12-MOLYBDATOSILICATE, AMMONIUM SILICO-12-MOLYBDATE $SiO_2 . 12\ MoO_3 . 2\ H_2O . n\ H_2O$

BIBLIOGRAPHY : 929-931.

MECHANISM OF REACTION.

Some crystals of caesium silicomolybdate are formed :

$$Cs_4SiO_4 . 12\ MoO_3 . n\ H_2O$$

BEHRENS-KLEY (930).

DETAILS OF TEST.

Under the microscope.

Evaporate on a slide a drop of the solution to be analysed (caesium in the form of chloride), and take up the residue in a drop of a saturated solution of silicomolybdic acid (or of ammonium silicomolybdate). In the presence of caesium a precipitate of small yellow crystals is formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6.30}$ (1 : $2 \cdot 10^6$).

The ions of Ag, Hg (Hg^{+1}), Ba, Ca, Sr, Mg, Li, Na and K do not interfere. Tl^{+1} and Rb^{+1} ions give an analogous reaction.

REAGENTS.

1*a*. Saturated solution of silicomolybdic acid in water or
b. Saturated solution of ammonium silicomolybdate in water.

C. Cs^{+1}, 22.

MONOPOTASSIUM TETRAIODOBISMUTHATE, POTASSIUM BISMUTHIIODIDE (PHOTO 46) $K[BiI_4]$

BIBLIOGRAPHY : 932-936.

MECHANISM OF REACTION.

An orange-yellow precipitate is formed of the complex :

$$2\ BiI_3 \cdot 3\ CsI$$

H. WELLS and H. W. FOOTE (932).

DETAILS OF TEST.

a. On filter paper.

Place on filter paper a drop of the solution to be analysed and a drop of the reagent solution. In the presence of caesium a yellow or orange-coloured stain is produced. It is necessary to carry out a blank test, as the reagent itself is coloured.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The Rb^{+1} cation does not interfere; the Na^{+1} and K^{+1} cations only interfere with the identification of caesium, if they are present in a proportion higher than 10 : 1. The Tl^{+1} cation gives an identical reaction.

b. Under the microscope.

Evaporate on a slide a drop of the solution to be analysed (caesium in the form of chloride). After cooling take up the residue in a drop

of the reagent solution. In the presence of caesium crystals composed of small, orange-coloured hexagonal plates are formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ ($1 : 5 \cdot 10^5$).

The Na^{+1} cation does not affect the sensitivity, whereas the K^{+1} cation in large proportions reduces it.

REAGENT.

1. Dissolve 1 g bismuth (III) oxide in 10 ml of a saturated solution of potassium iodide (say 5 g potassium iodide), then add 25 ml glacial acetic acid in small portions.

D. Cs^{+1}, 27.

GOLD (III) BROMIDE, AURIC BROMIDE + PLATINUM (IV) BROMIDE, PLATINIC BROMIDE $AuBr_3 + PtBr_4$

BIBLIOGRAPHY : 937-940.

MECHANISM OF REACTION.

Not yet known exactly.

DETAILS OF TEST.

On filter paper.

Place on filter paper a drop of the solution to be analysed and a drop of the reagent solution. A grey or black stain indicates the presence of caesium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.60}$ ($1 : 4 \cdot 10^4$).

The ions of alkaline-earth elements and of lithium do not interfere, the Na^{+1} cation in a 100 : 1 proportion reduces the sensitivity to $10^{-3.70}$ ($1 : 5 \cdot 10^3$), whereas the K^{+1} cation in a 1,000 : 1 proportion reduces it to $10^{-3.78}$ ($1 : 6 \cdot 10^3$). The Rb^{+1} cation gives an analogous reaction and the NH_4^{+1} cation interferes with the detection of caesium.

REAGENT.

1. Dissolve 0.36 g platinum (IV) bromide and 0.86 g gold (III) bromide in 10 ml water.

E. Cs^{+1}, 29.

TRIPOTASSIUM HEXACYANOFERRATE (III), POTASSIUM FERRICYANIDE + LEAD ACETATE $K_3[Fe(CN)_6] + (CH_3CO_2)_2Pb$

BIBLIOGRAPHY : 941-942.

MECHANISM OF REACTION.

An orange-coloured complex is formed according to the equation :

$$[Fe(CN)_6]\,(CH_3CO_2Pb)_2^{-1} + Cs^{+1} \longrightarrow [Fe(CN)_6]\,(CH_3CO_2Pb)_2Cs.$$

P. E. WENGER and G. GUTZEIT (942).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed and add a drop of the reagent solution. In the presence of caesium an orange-coloured crystalline precipitate appears, which is insoluble in alcohol, only slightly soluble in cold water, but soluble in hot water.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.40}$ $(1 : 2.5 \cdot 10^5)$.

No other cation of the alkali elements gives this reaction.

REAGENT.

1. Mixture in equal proportions of a potassium ferricyanide solution (saturated in the cold) and an aqueous solution of lead acetate (saturated in the cold).

F. Cs^{+1}, 35.

SILVER IODIDE + SODIUM IODIDE (PHOTO 47) AgI + NaI

BIBLIOGRAPHY : 943.

MECHANISM OF REACTION.

The yellow crystals which are formed have the formula :

$$2\,AgI \,.\, CsI.$$

H. GRAVESTEIN (943).

DETAILS OF TEST.

Under the microscope.

Evaporate on a slide to dryness, a drop of the solution to be analysed (caesium in the form of chloride), take up the residue with a drop of reagent and dilute with a drop of alcohol. In the presence of caesium fine yellow needles are formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ ($1 : 10^6$).

The Na^{+1} cation in a 100 : 1 proportion reduces the sensitivity to $10^{-3.30}$ ($1 : 2 \cdot 10^3$), whereas the K^{+1} cation in a 10 : 1 proportion reduces it to 10^{-4} ($1 : 10^4$). The Rb^{+1} cation interferes.

REAGENTS.

1. Dissolve 5 g silver nitrate in 20 ml water and add 20 to 21 g sodium iodide, dissolving the silver iodide precipitate by agitation.
2. Ethyl alcohol 96 %.

G. Cs^{+1}, NR.

LEAD ACETATE + POTASSIUM IODIDE (PHOTO 48) $(CH_3CO_2)_2Pb + KI$

BIBLIOGRAPHY : 944.

MECHANISM OF REACTION.

A precipitate (greenish yellow needles) is formed of monocaesium triiodoplumbate (II), $Cs\,[PbI_3]$.

H. JURÁNY (944).

DETAILS OF TEST.

Under the microscope.

Evaporate on a slide a drop of the solution to be analysed; after cooling take up the residue in a drop of reagent. In the presence of caesium greenish yellow needles are formed.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

The ions of Li, Na and Rb in a 10 : 1 proportion reduce the sensitivity to $10^{-4.30}$ ($1 : 2 \cdot 10^4$); the K^{+1} cation, also in a 10 : 1 proportion,

reduces the sensitivity to $10^{-3.30}$ ($1 : 2 \cdot 10^3$). The ammonium cation interferes because it gives the same crystals as caesium.

REAGENT.

1. Dissolve 0.1 g lead acetate in 100 ml water and add 0.5 g potassium iodide; the precipitate which forms at first, gradually dissolves.

60. AMMONIUM

BY

J. GILLIS

IW 18.040

A. NH_4^{+1}, 9.

SILVER NITRATE + METHANAL, FORMALDEHYDE $AgNO_3 + HCHO$

BIBLIOGRAPHY : 945-948.

MECHANISM OF REACTION.

Reduction of the Ag^{+1} cation to the state of metallic silver by the aldehyde; this reduction can affect silver only in the state of the complex ammine, $[Ag(NH_3)_2]^{+1}$.

DETAILS OF TEST.

In a micro gas chamber (See Fig. 2, p. 253 or F. FEIGL [948]).

Place in the test tube a drop of the solution to be analysed and a drop of sodium hydroxide solution, suspend a drop of the reagent from the glass bulb of the little condenser and heat the apparatus in a water-bath to 60°. After five minutes wipe off the drop by means of filter paper when a black stain appears in the presence of ammonium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ ($1 : 10^6$).

None of the cations of the alkali elements interfere. Organic amines interfere, often giving the same reaction.

REAGENTS.

1. Sodium hydroxide 2 N.
2. Add 5 drops of formaldehyde (commercial aqueous solution, 40 %) and a few drops of sodium hydroxide 2 N to 10 ml of silver nitrate solution, 20 %; filter off the metallic silver which is formed.

B. NH_4^{+1}, 16.

MERCURY (I) CHLORIDE, MERCUROUS CHLORIDE Hg_2Cl_2

BIBLIOGRAPHY : 949-952.

MECHANISM OF REACTION.

A mixture is formed of mercury-amine chloride and of black elementary mercury :

$$Hg_2Cl_2 + 2\,NH_4OH \longrightarrow Hg\begin{matrix}NH_2\\Cl\end{matrix} + Hg + NH_4Cl + H_2O.$$

P. E. WENGER and G. GUTZEIT (952).

DETAILS OF TEST.

In a micro gas chamber (See Fig. 2, p. 253 or F. FEIGL [948]).

Place in the test tube a drop of the solution to be analysed and a drop of the sodium hydroxide solution, attach a drop of a suspension of mercurous chloride in water to the glass bulb of the condenser and heat in a water-bath to 60°. In the presence of ammonium the mercurous salt becomes black.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

None of the cations of alkaline elements interfere. Organic amines interfere, often giving the same reaction.

REAGENTS.

1. Sodium hydroxide 2 N.
2. Suspension of mercurous chloride in water.

C. NH_4^{+1}, 17.

DIPOTASSIUM TETRAIODOMERCURATE (II), POTASSIUM MERCURI-IODIDE $K_2[HgI_4]$
(Nessler reagent)

BIBLIOGRAPHY : 953-965.

MECHANISM OF REACTION.

The orange-red compound which is produced, is formed according to the following equation :

$$2\,K_2[HgI_4] + 3\,KOH + NH_4OH \longrightarrow O\begin{matrix}Hg - NH_2\\ \\ HgI\end{matrix} + 7\,KI + 3\,H_2O$$

F. FEIGL (960).

DETAILS OF TEST.

In a micro gas chamber.

Place in the test tube a drop of the solution to be analysed and a drop of sodium hydroxide solution. Hang a strip of filter paper steeped in Nessler's reagent on a glass hook attached to the stopper. Heat in a water-bath to 40°. In the presence of ammonium an orange-red stain appears. A blank test is necessary.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ $(1 : 5 \cdot 10^5)$.

The ions of Li, Na, K, Rb and Cs do not interfere. Metallic mercury, the ions of calcium, magnesium, the SO_4^{-2} and S^{-2} anions and organic amines interfere with the detection of ammonium.

REAGENTS.

1. Sodium hydroxide 2 N.

2. Nessler reagent. Mix in equal volumes the following two solutions :

a. 5 g mercuric iodide + 3.65 g potassium iodide dissolved in 100 ml water.

b. Potassium hydroxide 3 N.

Separately these solutions keep, but their mixture deteriorates.

D. NH_4^{+1}, 20.

DIHYDROGEN HEXACHLOROPLATINIC (IV) ACID, CHLOROPLATINIC ACID (PHOTO 49) $H_2[PtCl_6]$

BIBLIOGRAPHY : 966-971.

MECHANISM OF REACTION.

The following well-known salt is formed : $(NH_4)_2\,[PtCl_6]$.

DETAILS OF TEST.

Under the microscope.

Allow to react for some minutes (maximum 5) a drop of the solution to be analysed with a drop of a sodium hydroxide solution in a micro desiccator (See Fig. 1, p. 253), at 30°. Place a drop of hydrochloric acid in the top part of the apparatus. Around this drop, in the presence of ammonium, ammonium chloride is deposited. Place a drop of the reagent solution on it and examine with the microscope the ammonium hexachloroplatinate crystals, which are coloured yellow.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.70}$ $(1 : 5 \cdot 10^3)$.

The Na^{+1} cation in a 100 : 1 proportion reduces the sensitivity to $10^{-3.30}$ $(1 : 2 \cdot 10^3)$. Volatile amines give an analogous reaction.

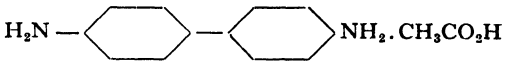
REAGENT.

1. Sodium hydroxide 6 N.
2. Hydrochloric acid 6 N.
3. Solution of hexachloroplatinic acid, 10 %, in water.

E. NH_4^{+1}, 42.

MANGANESE (II) SULPHATE, MANGANOUS SULPHATE + SILVER NITRATE + BENZIDINE ACETATE

$MnSO_4 + AgNO_3 +$



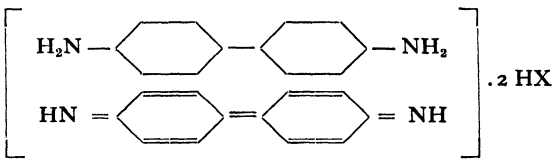
BIBLIOGRAPHY : 972-975.

MECHANISM OF REACTION.

The oxidation reaction of the Mn^{+2} cation, viz.

$$Mn^{+2} + 2\,Ag^{+1} + 4\,OH^{-1} \longrightarrow MnO_2 + 2\,Ag + 2\,H_2O$$

is only possible in the presence of OH^{-1} ions provided by the ammonia. The tetravalent manganese is then detected by its characteristic reaction with benzidine, which is oxidized to the blue meriquinoid dyestuff, having the formula :



F. FEIGL (972) (975), F. FEIGL and R. STERN (973).

DETAILS OF TEST.

In a micro gas chamber (See Fig. 2, p. 253 or F. FEIGL [948]).

Place in the test tube a drop of the solution to be analysed and a drop of sodium hydroxide solution; suspend a drop of the reagent at the extreme end of the condenser and heat the apparatus in a water-bath to 45°. After several minutes place the drop from the condenser on filter paper, when a black stain will indicate the presence of the ammonium cation.

The sensitivity of the reaction is increased, if managanese (IV) is detected in the following manner : moisten the stain with a drop of a solution of benzidine in acetic acid, when a blue stain indicates the precense of ammonium.

SENSITIVITY AND SELECTIVITY. $D = 10^{-7}$ ($1 : 10^7$).

The Na^{+1} cation in a 1,000 : 1 proportion reduces the sensitivity to 10^{-5} ($1 : 10^5$) and the K^{+1} cation diminishes it to $10^{-4.70}$ ($1 : 5 \cdot 10^4$), if it is present in a 100 : 1 proportion. Ions of other alkali elements do not interfere. Volatile organic amines interfere, because they give an analogous reaction.

REAGENTS.

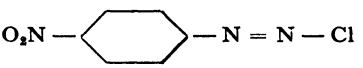
1. Sodium hydroxide 2 N.

2. Dissolve 2.87 g manganous sulphate in 40 ml water and add a solution of 3.55 g silver nitrate in 40 ml water; dilute with water to 100 ml and neutralize with sodium hydroxide 0.1 N until a black precipitate appears, which is eliminated by filtration.

3. Solution of benzidine, 0.05 %, in acetic acid, 10 %.

F. NH_4^{+1}, 47.

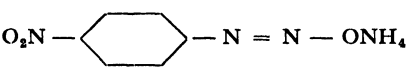
p-NITROBENZENEDIAZONIUM CHLORIDE *(Riegler's reagent)*



BIBLIOGRAPHY : 976-983.

MECHANISM OF REACTION.

The red colour is due to the formation of a salt having the formula :



E. RIEGLER (976).

DETAILS OF TEST.

On a spot plate.

Place in a section of the plate a drop of the solution to be analysed and a drop of the reagent solution. Add a small piece of calcium oxide (of the size of a pea) between the two drops. In the presence of ammonium cations a red colour appears immediately. It is necessary to carry out a blank test.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

The reaction is specific for the NH_4^{+1} cation in the presence of ions of alkali elements.

The K^{+1} and Na^{+1} ions in a 1,000 : 1 proportion reduce the sensitivity to $10^{-5.30}$ (1 : $2 \cdot 10^5$). Organic amines and oxidizing agents (such as molecules of the halogen elements) interfere with the detection of ammonium.

REAGENTS.

1. Solution of *p*-nitrobenzenediazonium chloride obtained in the following manner : dissolve 1 g *p*-nitraniline in 20 ml water and 2 ml dilute hydrochloric acid; dilute with 160 ml water, stirring thoroughly, then add 20 ml of a sodium nitrite solution, 2.5 %. On stirring complete solution is obtained.

The reagent gradually gets cloudy, but it can be used after filtration.

2. Solid calcium oxide.

G. NH_4^{+1}, 49.

LITMUS

BIBLIOGRAPHY : 984-988.

MECHANISM OF REACTION.

Colour change of the indicator under the action of hydroxyl ions, due to the dissociation of ammonium hydroxide.

DETAILS OF TEST.

In a micro gas chamber (See Fig. 1, p. 253, or F. FEIGL [948]).

Place in the test tube a drop of the solution to be analysed and a drop of sodium hydroxide solution, suspend a strip of damp red litmus paper from the book of the apparatus, and heat the apparatus in a water-bath to 40°, when in the presence of ammonium the litmus paper turns blue.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ $(1 : 5 \cdot 10^5)$.

The Na^{+1} cation in a 1,000 : 1 proportion and the K^{+1} cation in a 100 : 1 proportion reduce the sensitivity to $10^{-4.70}$ $(1 : 5 \cdot 10^4)$. The other cations of alkali elements do not interfere. Volatile organic amines give an analogous reaction.

REAGENTS.

1. Sodium hydroxide 2 N.
2. Red litmus paper.

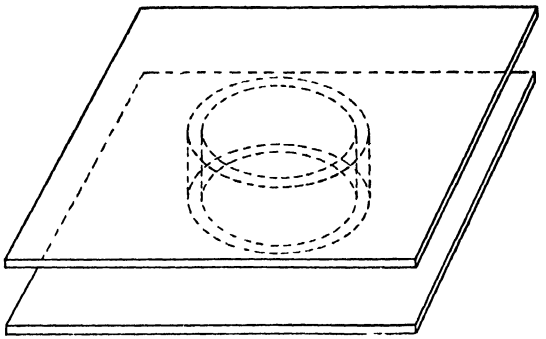


FIG. 1
Micro desiccator
Cf. BEHRENS-KLEY, p. 38, fig. 29

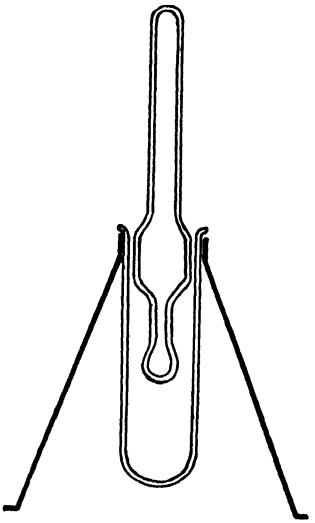


FIG. 2
Micro gas chamber
Cf. F. FEIGL, p. 31, fig. 27.

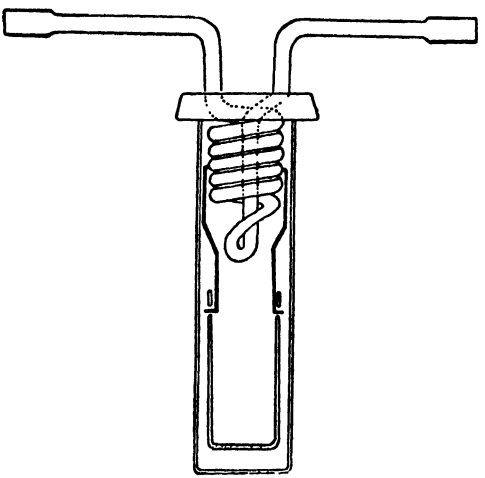


FIG. 3
Extraction apparatus (altered and reduced model) according to HAANEN and BADUM. Cf. Catalogue Schott Cy, Iena, p. 145, fig. 55.

QUALITATIVE SEPARATION OF THE ALKALI ELEMENTS

The best method of identification of alkali metals, if they occur in a mixture, is a spectral analysis. It is also possible to identify them and to make a quantitative estimate by following the method of H. LUNDEGÅRDH (989-994).

The NH_4^{+1} cation can always be identified by the specific *p*-nitrobenzene diazoniumchloride reaction (NH_4, F, p. 250).

Microchemical method of separation of Li, Na, K ions and of the ammonium cation

This method is based on the solubility of lithium chloride in isobutyl alcohol, iso-amyl alcohol, anhydrous acetone or in anhydrous dioxan.

Procedure : evaporate to dryness in a micro-crucible 0.1 ml of the solution containing Li^{+1}, Na^{+1}, K^{+1} and NH_4^{+1} ions, dry the residue for 2 hours at 110° centigrade, then place it in the Jena-glass filter of the extraction apparatus (see Fig. 3, page 253). Lithium chloride is extracted for 2 hours with 3 ml anhydrous dioxan. After cooling, the four elements are identified.

DETECTION OF LITHIUM.

Evaporate the greater part of the dioxan and after cooling add a drop of ammonia 8 N, a drop of sodium biphosphate and a few drops of ethyl alcohol, and boil. The presence of lithium is indicated by the appearance of a white precipitate (see reaction Li, B, p. 226).

DETECTION OF SODIUM, POTASSIUM AND AMMONIUM.

Ths residue from the dioxan extraction is dissolved in as little water as possible. The Na^{+1} cation is identified by means of the reaction with uranyl acetate (Na, A, p. 227). The K^{+1} cation is detected by means of dipicrylamine (K, D, p. 234). Finally, the ammonium cation is identified by means of Riegler's reagent (*p*-nitrobenzene diazoniumchloride : NH_4, F, p. 250).

THE SENSITIVITIES ARE :

For lithium 10^{-3} ($1 : 10^3$) in the presence of the sodium cation in a 100,000 : 1 proportion, of the potassium cation in a 100,000 : 1 proportion and of the ammonium cation in a 1,000,000 : 1 proportion.

The sensitivity changes to 10^{-5} ($1 : 10^5$) in the presence of the same three ions in a 100 : 1 proportion.

See the instructions given by E. M. CHAMOT and C. W. MASON (996) and by A. SINKA (995).

Microchemical separation of the ions of alkali-elements

Generally speaking the analysis becomes very difficult if all three alkali elements are present in the same mixture. However, it is possible to carry out the analysis if the details given by A. A. BENEDETTI-PICHLER and J. T. BRYANT (997) are followed, these being very briefly : first of all detect the Cs^{+1} cation by means of the reaction with tetraiodobismuthic acid (Cs, C, p. 241), provided it is present in a quantity greater than 5 γ or by means of the reaction with potassium ferricyanide + lead acetate (Cs, E, p. 243) provided it is present in a quantity greater than 0.6 γ. The elimination of caesium simplifies the investigation of elements of the potassium sub-group and in particular the separation of potassium and of rubidium, conditioned by the presence of caesium.

The reaction of the triple chloride of gold, silver and the alkali cation, introduced by F. EMICH (see F. EMICH, p. 127), can be used as a control test for rubidium and caesium.

II. ANIONS

61. HYDROFLUORIC ANION

BY

C. J. VAN NIEUWENBURG

IW 19.00

A. F^{-1}, 13.

SILICON DIOXIDE $SiO_2 + H_2SO_4 + NaCl$
+ SULPHURIC ACID
+ SODIUM CHLORIDE (PHOTO 50)

BIBLIOGRAPHY : 998-1000.

MECHANISM OF REACTION.

Hexagonal crystals of sodium hexafluosilicate are formed, $Na_2[SiF_6]$.

BEHRENS-KLEY (998).

DETAILS OF TEST.

Under the microscope.

Evaporate the solution to be analysed in a small platinum or lead crucible until it is dry. After cooling add a few mg quartz (finely pulverized; amorphous silica must not be used) and two drops of concentrated sulphuric acid. Heat over a micro-burner for five minutes, 6-8 cm above the flame, covering the crucible with a piece of cellophane from which a drop of a sodium chloride solution is suspended. In the presence of hydrofluoric anions sodium fluosilicate crystals are formed, which are pale pink and present in very characteristic hexagons.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

Rhe sensitivity is scarcely reduced by the following anions in a 100 : 1 proportion : Cl^{-1}, ClO^{-1}, ClO_3^{-1}, Br^{-1}, BrO^{-1}, BrO_3^{-1}, I^{-1}, IO_3^{-1}, IO_4^{-1}, SO_4^{-2}, PO_4^{-3}. The boric anion, if present in large quantities, interferes because of the formation of boron fluoride.

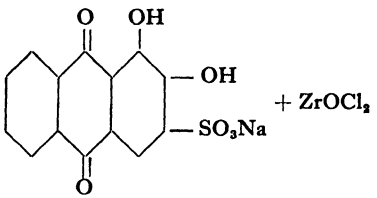
The reaction is good and selective. Still, for a large number of fluosilicates it is advisable to disintegrate beforehand with a fragment of sodium hydroxide.

REAGENTS.

1. Finely powdered quartz.
2. Sulphuric acid 35 N.
3. Solution of sodium chloride, 1 %, in water.
4. Solid sodium hydroxide.

B. F^{-1}, 19.

SODIUM 1 : 2-DIHYDROXY-ANTHRAQUINONE-3-SULPHONATE, SODIUM ALIZARIN-3-SULPHONATE *(alizarin S)* + **ZIRCONIUM OXYDICHLORIDE, ZIRCONYL CHLORIDE**



BIBLIOGRAPHY : 1001-1019.

MECHANISM OF REACTION.

Zirconium salts (in hydrochloric medium) give a dark purplish red colour with alizarin sodium sulphonate. But in the presence of hydrofluoric anions the zirconium cation changes to the form of the complex anion $[ZrF_6]^{-2}$, which no longer reacts with alizarin sodium sulphonate. On that account a solution of the zirconium salt with the dyestuff is decolourized by the addition of hydrofluoric anions.

J. H. De Boer (1001) (1002) and F. Pavelka (1003).

DETAILS OF TEST.

On filter paper or in a micro test tube.

On a reaction paper of the zirconium alizarin sulphonate place a drop of acetic acid and a drop of the solution to be examined. In the presence of hydrofluoric anions a yellow stain is produced against a purple background. The reaction is accelerated by heating in a stream of water vapour.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The reaction effected in a test tube is a little more sensitive, it is doubtful at the limit of 10^{-5} (1 : 10^5).

The sensitivity is not reduced by the following anions in a 100 : 1 proportion : Cl^{-1}, ClO_3^{-1}, Br^{-1}, BrO_3^{-1}, I^{-1}, IO_3^{-1}, IO_4^{-1}.

The following anions interfere with the detection of the hydrofluoric anion : ClO^{-1}, BrO^{-1}, and $[Fe(CN)_6]^{-3}$. The phosphoric and oxalic anions give an analogous reaction. The NO_3^{-1} anion does not interfere, NO_2^{-1} interferes considerably, $S_2O_3^{-2}$ and BO_3^{-3} hardly interfere. The latter in a 100 : 1 proportion does not interfere.

The hydrofluoric anion can be detected in a 1 : 1,000 concentration in the presence of thiosulphuric and sulphuric anions in a 1 : 20 concentration. The nitric anion in a 1 : 100 solution does not interfere.

REAGENTS.

1. Filter paper impregnated in the following manner : steep the clean filter paper in a 0.1 % solution of zirconyl chloride in hydrochloric acid 5 N, to which is added a solution of sodium alizarinsulphonate, 0.2 %, in ethyl alcohol, in such a way that there is a slight excess of dyestuff. This excess can be revealed by treating the solution with ether which is coloured yellow. Heat for 10 minutes in a water bath before introducing the filter paper. Dry the papers in air.

2. Solution of acetic acid, 50 %, in water.

62. HYDROCHLORIC ANION

BY

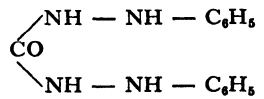
C. J. VAN NIEUWENBURG

IW 35.457

A. Cl^{-1}, 18.

POTASSIUM DICHROMATE + SULPHURIC ACID + *sym*-DIPHENYLCARBAZIDE

$K_2Cr_2O_7 + H_2SO_4 +$



BIBLIOGRAPHY : 1020-1023.

MECHANISM OF REACTION.

Heating potassium dichromate with a chloride in the presence of concentrated sulphuric acid, chromium dioxydichloride is realised according to the equation :

$$K_2Cr_2O_7 + 4\ KCl + 6\ H_2SO_4 \longrightarrow 2\ CrO_2Cl_2 + 6\ KHSO_4 + 3\ H_2O.$$

This gas dissolves in water yielding hydrochloric acid and dichromic acid, the latter being identified by an oxidationreduction reaction, with diphenylcarbazide as indicator.

F. FEIGL (1020).

DETAILS OF TEST.

In a micro test tube and on a spot plate.

Evaporate the solution to be examined to dryness and place the residue in a micro test tube, add a little solid potassium dichromate and a drop of concentrated sulphuric acid. Heat slightly over a micro burner, collecting the brown chromyl chloride vapours in a drop of water, and taking care that the drop does not get into contact with the reagent.

Place the drop of water in a section of the spot plate and identify the chromic anion by addition of a drop of a diphenylcarbazide solution and a drop of dilute sulphuric acid. A red colour indicates the presence of hydrochloric anions in the substance to be analysed.

SENSITIVITY AND SELECTIVITY.

The sensitivity is of the order of 10^{-4} ($1 : 10^4$); it depends on the quantity of solution which is evaporated.

The hydrofluoric anion gives an analogous reaction. NO_2^{-1} and NO_3^{-1} anions interfere on account of the formation of nitrosyl chloride, NOCl. Br^{-1}, BrO^{-1} and BrO_3^{-1} anions effect a release of bromide, which interferes with the reaction, but which can be eliminated by addition of a little phenol and a little sulphuric acid. I^{-1}, IO_3^{-1} and IO_4^{-1} anions release elementary iodine, but only after the formation of chromyl chloride; small quantities of iodine do not colour the reagent. It is possible to detect the hydrochloric anion in the presence of the following ions in a 100 : 1 proportion : ClO_3^{-1}, ClO_4^{-1}, Br^{-1}, BrO_3^{-1}, I^{-1}, IO_3^{-1} and IO_4^{-1}.

Silver chloride and mercurous chloride are not attacked by sulphuric acid.

REAGENTS.

1. Solid potassium dichromate.
2. Sulphuric acid 35 N.
3. Solution of diphenylcarbazide, 1 %, in ethyl alcohol 96 %.
4. Solid phenol.
5. Sulphuric acid 2 N.

B. Cl^{-1}, 1.

THALLIUM (I) NITRATE, $TlNO_3$ [+ $Pt(SO_4)_2$]
THALLOUS NITRATE (PHOTO 51),
if necessary + PLATINUM (IV) SULPHATE,
PLATINIC SULPHATE

BIBLIOGRAPHY : 1024.

MECHANISM OF REACTION.

Cubes of thallous chloride, TlCl, are formed which are highly refractive and colourless; if platinic sulphate is added, crystals are formed of dithallium hexachloroplatinate : $Tl_2[PtCl_6]$.

BEHRENS-KLEY (1024).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed to which is added a grain of thallous nitrate. In the presence of hydrochloric anions colourless cubes are formed, often arranged in cross-shaped rosettes and very refractive.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

As the thallous chloride which is formed, is soluble in inorganic acids the latter must be neutralized beforehand by buffering with sodium acetate.

The following ions give similar crystals : Br^{-1}, I^{-1}, IO_3^{-1}, and $S_2O_3^{-2}$. Crystals of thallous bromide have the same shape as those of the chloride but they are smaller. Those of the iodide are even smaller and yellow. If hydro-halogenic ions are present alone they can be easily recognized, but if there is a mixture of the three, another reagent must be used.

The bromic anion gives very big crystals, which have no characteristic shape. If it is present in a 100 : 1 proportion, it interferes and in a 10 : 1 proportion it reduces the limit of dilution of the hydrochloric anion to 10^{-4} ($1 : 10^4$). The IO_4^{-1} anion gives crystals, which are shaped as needles and often arranged in the shape of a cross. The sensitivity is the same in the presence of this ion as in the presence of the bromic ion.

The following anions do not interfere, even if they are present in a 100 : 1 proportion.

The sensitivity is considerably increased by the addition of a drop of a platinic sulphate solution; it becomes 10^{-7} ($1 : 10^7$). Still, the precipitate of thallous chloroplatinate is so fine, that it is difficult to recognize, so that this variant is of little use.

REAGENTS.

1. Solid thallous nitrate.
2. Solution of sodium acetate, 10 %, in water.
3. Nitric acid N.
4. Solution of platinic (IV) sulphate, 0.5 %, in water.

C. Cl^{-1}.

The two reactions indicated for elementary chlorine (Cl_2, A, p. 269 : aniline + *o*-toluidine; ClO^{-1}, B, p. 270 : aniline + phenol) can also be used for the detection of the hydrochloric anion : for that purpose it is sufficient to oxidize the chlorides by means of manganese dioxide or potassium permanganate in sulphuric acid medium.

63. HYDROBROMIC ANION

BY

C. J. VAN NIEUWENBURG

IW 79.916

A. Br^{-1}.

As bromides are very easily oxidized, releasing elementary bromine, wo do not indicate a reagent for the hydrobromic anion itself, but only for elementary bromine. The reader is therefore referred to the two reactions Br_2, A, p. 271 : *m*-phenylenediamine, and Br_2, B, p. 273: fluorescein, where all the data are supplied for the detection of the hydrobromic anion.

64. HYDRIODIC ANION

BY

C. J. VAN NIEUWENBURG

IW 126.92

A. I^{-1}, 5.

DIMERCURY (II)-AMMONIUM NITRATE, MERCURIC AMMONIUM NITRATE NHg_2NO_3

BIBLIOGRAPHY : 1025-1026.

MECHANISM OF REACTION.

Dimercuriammonium iodide is precipitated according to the following equation :

$$NHg_2NO_3 + I^{-1} \longrightarrow NHg_2I + NO_3^{-1}$$

R. CIUSA and A. TERNI (1025).

DETAILS OF TEST.

In a micro test tube.

Place in the test tube 1 ml of the solution to be examined and add 3 to 5 drops of the reagent solution. In the presence of hydriodic anions a brown precipitate is formed (for 1 % solutions), which is orange coloured to yellow if the solution is more dilute. In the absence of iodide a white precipitate may appear, which is soluble in an excess of reagent.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ ($1 : 10^4$), yellow precipitate. $D = 10^{-5}$ ($1 : 10^5$), yellowish opalescence.

The following anions interfere with the detection of the hydriodic anion : ClO^{-1}, S^{-2}, SiO_3^{-2}, NC^{-1}, HCO_2^{-1}, and $CH_3CO_2^{-1}$. BrO^{-1}, N_3^{-1}, CNS^{-1}, $[Fe(CN)_6]^{-3}$ and $[Fe(CN)_6]^{-4}$ anions give an analogous reaction.

Hydrobromic and iodic anions in a 100 : 1 proportion reduce the sensitivity. It is advisable to carry out a blank test.

REAGENT.

1. Dissolve 10 g mercury(II)nitrate in 50 ml water containing 5 ml concentrated nitric acid, then add 60 ml concentrated ammonia 7.5 N.

B. I^{-1}, 10.

PALLADIUM (II) CHLORIDE, PALLADOUS CHLORIDE $PdCl_2$

BIBLIOGRAPHY : 1027-1030.

MECHANISM OF REACTION.

Dark brown palladous iodide is precipitated.

DETAILS OF TEST.

On filter paper.

Place on a filter paper a drop of the solution to be analysed and a

drop of the reagent solution. In the presence of hydriodic anions a dark brown precipitate is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-1.70}$ ($1 : 5 \cdot 10^4$).

The sensitivity is not reduced by the anions in a 100 : 1 proportion : F^{-1}, Cl^{-1}, ClO_3^{-1}, ClO_4^{-1}, Br^{-1}, BrO_3^{-1}, IO_3^{-1}, and IO_4^{-1}. Hypochloric and hypobromic anions in large proportions interfere, because they liberate iodine. The S^{-2} anion gives a black precipitate and interferes, whereas the $S_2O_3^{-2}$ anion gives a yellow stain and only interferes if present in excessive quantity. The following anions give yellow stains, but they only reduce the sensitivity if present in a 10 : 1 proportion : N_3^{-1}, $[Fe(CN)_6]^{-3}$ and $[Fe(CN)_6]^{-4}$. Hydrocyanic and thiocyanic anions interfere with the detection of the hydriodic anion.

It is not advisable to use palladous nitrate, because it also gives a brownish red precipitate with the hydrobromic anion.

REAGENT.

1. Solution of palladous chloride, 1 %, in water.

C. I^{-1}, 29.

DIAMMONIUM TRISULPHATOCERIATE (IV) + SODIUM ARSENITE $(NH_4)_2[Ce(SO_4)_3] + NaAsO_2$

BIBLIOGRAPHY : 1031-1032.

MECHANISM OF REACTION.

The reaction :

$$As^{+3} + 2\ Ce^{+4} \longrightarrow As^{+5} + 2\ Ce^{+3}$$

is extremely slow and so the yellow colouration of the cerium (IV) salt persist a long time. The hydriodic anion considerably accelerates the reduction of cerium (IV), so that decolourisation occurs very rapidly.

E. B. SANDELL and I. M. KOLTHOFF (1031).

DETAILS OF TEST.

On a spot plate.

Place in a section of the plate a drop of the solution to be analysed and in the next section a drop of water. Add a drop of each of the reagents to the two sections. The yellow colour disappears most quickly in the test section, if hydriodic anions are present.

The decolourisation is produced in one minute for a solution of 10^{-7} ($1 : 10^7$), whereas the control test keeps its colour for 15 minutes.

The sensitivity is not reduced by the following ions in a 100 : 1 proportion : Cl^{-1}, ClO^{-1}, ClO_3^{-1}, ClO_4^{-1}, Br^{-1}, BrO^{-1}, and BrO_3^{-1}, nor by chlorine, bromine nor elementary iodine; it is necessary, however, to add an excess of sodium arsenite in the presence of oxidizing agents. F^{-1}, $S_2O_3^{-2}$, N_3^{-1}, NO_2^{-1}, CNS^{-1} anions as well as osmium salts give the same reaction. The yellow colouration is intensified by the oxalic anion which interferes, as well as by the hexacyanoferrate (III) and (IV) anions (same colour), hydrosulphuric anion (yellow precipitate) and iodic and periodic anions. Coloured cations (Cu^{+2}, Fe^{+3}, UO_2^{+2}, Co^{+2}, Ni^{+2} etc.) interfere also.

REAGENTS.

1. 0.05 Molar solution of diammonium trisulphatoceriate (IV) in sulphuric acid 2 N.

2. 0.05 Molar solution of sodium arsenite in water (neutral or slightly acidified).

D. I^{-1}.

As iodides are easily oxidized (for example by means of sodium nitrite and dilute sulphuric acid) the reaction for elementary iodine I, A, p. 274 : starch, can be used advantageously for the detection of the hydriodic anion.

65. CHLORINE

BY

C. J. VAN NIEUWENBURG

AN 17 AW 35.457

AND

66. HYPOCHLOROUS ANION

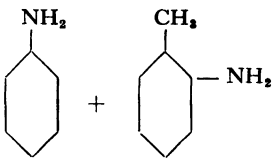
BY

C. J. VAN NIEUWENBURG

IW 51.457

A. Cl_2, 18.

ANILINE + *o*-TOLUIDINE



BIBLIOGRAPHY : 1033-1034.

MECHANISM OF REACTION.

Oxidation products of amines are formed, the structure of wich is not yet known.

A. VILLIERS and M. FAYOLLE (1033).

DETAILS OF TEST.

On filter paper.

Expose a filter paper impregnated with reagent to the vapours which are released from the solution to be analysed, heated in a micro test tube. In the presence of elementary chlorine, or hypochlorous anions, the reagent paper is coloured purplish blue.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The reaction is excellent and selective.

Unfortunately elementary bromine and iodine interfere, even in a 1 : 1 proportion, probably because they retain the chlorine by forming bromine chloride (non volatile) and iodic acid. But neither bromine, iodine nor the other volatile oxidizing agents give a blue colour.

For the detection of the hydrochloric anion after oxidation by manganese dioxide or by potassium permanganate and sulphuric acid

there is no difficulty in the absence of hydrobromic and hydriodic anions. But in their presence a preliminary elimination must be effected, by evaporating the solution to dryness with a mixture of lead dioxide and dilute acetic acid. The evaporation with a few ml of water is repeated, and the dry residue is then placed in a micro test tube in order to carry out the reaction as described above. In this manner the hydriodic anion does not interfere, while the hydrobromic anion does not interfere unless it is present in a proportion larger than 100 : 1.

REAGENTS.

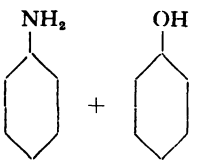
1. Mix 100 ml of a saturated aqueous solution of colourless aniline (3.5 volumes for 100), 20 ml of a saturated aqueous solution of *o*-toluidine 1.5 %, and 30 ml glacial acetic acid. The solution keeps for some months in a brown glass flask.
2. Solid lead dioxide.
3. Acetic acid 2 N.

If required :

4. Solid manganese dioxide or potassium permanganate.
5. Sulphuric acid 4 N.

B. Cl_2, ClO^{-1}, 11.

ANILINE
+ PHENOL



BIBLIOGRAPHY : 1035.

MECHANISM OF REACTION.

The blue colour is due to oxidation products of the reagents.

DETAILS OF TEST.

In a micro test tube.

Place in the test tube 1 ml of the solution to be analysed and add 5 drops of sodium hydroxide solution, 0.5 ml of aniline solution and 5 drops of phenol solution. After heating, in the presence of elementary chlorine or hypochlorous anions a blue colour is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.48}$ (1 : $3 \cdot 10^4$).

The sensitivity is not reduced by the following anions in a 100 : 1 proportion : F^{-1}, Cl^{-1}, ClO_3^{-1}, ClO_4^{-1}, Br^{-1}, BrO^{-1}, I^{-1}, IO_3^{-1} and IO_4^{-1}. The hypobromous anion and elementary bromine give the solution a brown or yellow colour, but they do not interfere. The colour obtained in their presence with chlorine is green and not blue. The following ions interfere: S^{-2}, $S_2O_3^{-2}$, CNS^{-1} and $[Fe(CN)_6]^{-3}$, whereas the peroxydisulphuric anion gives the same reaction.

REAGENTS.

1. Sodium hydroxide N.
2. Saturated solution of aniline in water.
3. Solution of phenol, 5 %, in water.

67. BROMINE

BY

C. J. VAN NIEUWENBURG

AN 35 AW 79.916

AND

68. HYPOBROMOUS ANION

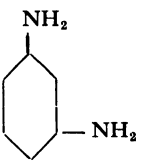
BY

C. J. VAN NIEUWENBURG

IW 95.916

A. Br_2, 6.

m-PHENYLENEDIAMINE (PHOTO 52)



BIBLIOGRAPHY : 1036.

MECHANISM OF REACTION.

The precipitate formed is 2 : 4 : 6-tribromo-1 : 3-diaminobenzene.

C. W. MASON and E. M. CHAMOT (1036).

DETAILS OF TEST.

Under the microscope.

Collect the bromine vapours in a drop of the reagent solution which is then placed on a slide to be examined under the microscope. In the presence of bromine a precipitate is formed of thin colourless needles, only slightly soluble in water, slightly more soluble in dilute sulphuric acid and readily soluble in ethyl alcohol.

If this reaction is to be used for the detection of the hydrobromous anion, place the solution in a micro crucible, adding some potassium permanganate crystals and a drop of nitric acid. Cover the crucible with a slide from which is suspended a drop of the reagent solution and heat gently.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The sensitivity is not reduced by the other halogens, when present in large proportions. Chlorine and iodine do not give any precipitate, but at high concentrations they may form oily drops, which disappear in the air. For the detection of the hydrobromic anion in the presence of large quantities of iodides it is advisable to eliminate the latter beforehand by means of nitrous acid. For that purpose one must heat gently in order to drive off the iodine and nitrogen oxides, since they give a brown colour with the reagent. Small quantities of nitrogen oxides, however, do not interfere with the detection of the hydrobromic anion.

In the presence of reducing anions, such as S^{-2}, $S_2O_3^{-2}$ and CNS^{-1}, an excess of potassium permanganate must be added.

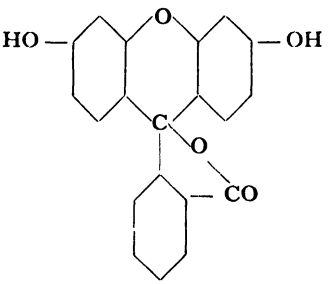
The hydrocyanic anion alone interferes with the detection of bromine.

REAGENTS.

1. Solution of *m*-phenylenediamine, 5 %, in water, slightly acidified with sulphuric acid.
2. Solid potassium permanganate.
3. Nitric acid 6 N (d = 1.2).
4. Solid potassium nitrite.

B. Br_2, 11.

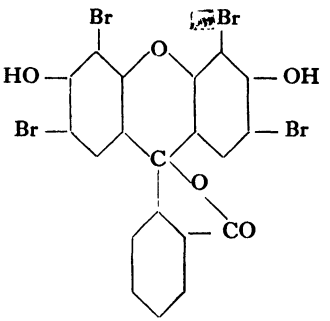
2-(3' : 6' : 9'-TRIHYDROXYXANTHYL)-BENZOLIDE,
3 : 6-DIHYDROXYFLUORAN,
FLUORESCEIN



BIBLIOGRAPHY : 1037-1051.

MECHANISM OF REACTION.

Bromine attaches itself to the fluorescein molecule giving eosin (tetrabromofluorescein), which has a characteristic pink colour.



H. BAUBIGNY (1037).

DETAILS OF TEST.

On filter paper.

Expose a filter paper, steeped in the reagent solution, to the vapours which are given off from a micro test tube, in which 1 ml of the solution to be analysed is heated. In the presence of bromine a pink colour is produced, which is due to the formation of eosin.

If this reaction is used with a view to detecting the hydrobromic anion, the solution to be analysed must be heated in a micro test tube with a little lead dioxide and 5 drops of dilute acetic acid.

It is advisable to use pure filter papers, which do not contain starch, so as to avoid complications with iodine.

SENSITIVITY AND SELECTIVITY. D = 10^{-5} to 10^{-6} (1 : 10^5 to 1 : 10^6).

The sensitivity is not reduced by the following anions in a 100 : 1 proportion : F^{-1}, Cl^{-1}, ClO_3^{-1}, ClO_4^{-1}, BrO_3^{-1}, IO_3^{-1} and IO_4^{-1}. Chlorine or the hypochlorous anion in the same proportion leads to a sensitivity of 10^{-4} (1 : 10^4).

The reducing anions such as S^{-2}, $S_2O_3^{-2}$, CN^{-1} and CNS^{-1} interfere, whereas the other ions including the nitrous anion do not.

The hydrogen sulphide anion can be eliminated, if the solution is heated with acetic acid before the reaction.

In the presence of a very large excess of free chlorine, it is preferable first to reduce the halogens to the chloride, bromide and iodide form and then to oxidize them with lead dioxide and acetic acid. If there is a very large excess of iodide, it is advisable to effect the oxidation by means of potassium permanganate, which converts the greater part of the iodine to the form of the iodic anion.

REAGENTS.

1. Filter paper impregnated with a solution of fluorescein, 0.1 %, in a faintly alkaline mixture of equal quantities of water and ethyl alcohol.

2*a*. Solid lead dioxide, or if required.

b. Solid potassium permanganate.

3. Acetic acid 2 N.

69. IODINE

BY

C. J. VAN NIEUWENBURG

AN 53 **AW 126.92**

A. I_2, NR.

STARCH $(C_6H_{10}O_5)n$

BIBLIOGRAPHY : 1052-1056.

MECHANISM OF REACTION.

It is the classic reaction leading to the formation of a compound of iodine and starch (coloured bleu), the structure of which it has not yet been possible to define.

DETAILS OF TEST.

On a spot plate or in a micro test tube.

Place on the plate or in a micro test tube a drop of the solution to be analysed and add a drop of the starch solution. A blue colour indicates the presence of iodine.

For the detection of the hydriodic anion the solution must be treated with a few drops of a potassium nitrite solution after having added a few drops of dilute hydrochloric acid.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$) in a micro test tube and at a low temperature, the sensitivity being much less in hot solutions.

It should be borne in mind that chlorine and bromine in large proportions interfere with the detection of iodine, because bromine reacts with starch and chlorine oxidizes iodine to the state of non-active iodic acid. It is therefore advisable to isolate the iodine by means of an oxidizing agent such as nitrous acid, which reacts only slightly with chlorides and bromides.

The hydrocyanic anion interferes, because it reacts with iodised starch, but it can be removed by heating the solution with sodium bicarbonate. The thiocyanic anion in large amounts reduces the sensitivity.

This well-known reaction still remains the best that can be recommended for the detection of iodine.

REAGENTS.

1. Solution of soluble starch, 1 %, in water (previously heated).
2. Solution of potassium nitrite, 10 %, in water.
3. Hydrochloric acid N.
4. Solid sodium bicarbonate.

70. CHLORIC ANION

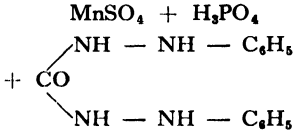
BY

C. J. VAN NIEUWENBURG

IW 83.457

A. ClO_3^{-1}, 19.

MANGANESE (II) SULPHATE
MANGANOUS SULPHATE +
PHOSPHORIC ACID,
if necessary + *sym*-DIPHENYLCARBAZIDE



BIBLIOGRAPHY : 1057-1059.

MECHANISM OF REACTION.

The purple colour which appears in the presence of manganese is due to the formation of a compound of trivalent manganese, trihydrogen diphosphatomanganic (III) acid, because the chlorine anion oxidizes the manganese (II) of the reagent to manganese (III) according to the equation :

$$ClO_3^{-1} + 6\,Mn^{+2} + 12\,PO_4^{-3} + 6\,H^{+1} \longrightarrow 6\,[Mn(PO_4)_2]^{-3} + Cl^{-1} + 3\,H_2O$$

Diphenylcarbazide intervenes only to intensify the colour of the manganese complex.

F. FEIGL (1058).

DETAILS OF TEST.

In a micro-crucible.

Place in a micro-crucible 0.1 ml of the solution to be examined and a drop of the reagent solution, then heat over a micro burner. In the presence of chloric anions a purple colour appears after cooling.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The reaction becomes considerably more sensitive if a drop of an alcoholic solution of diphenylcarbazide is added, but this variant is

not always to be recommended, because it makes the reaction unreliable, as a blank test can often give the characteristic colour of the chloric anion.

The reaction is not at all selective; in fact the following anions react in the same way : ClO^{-1}, BrO_3^{-1}, IO_3^{-1}, IO_4^{-1}, $S_2O_8^{-2}$, and NO_2^{-1}. Hexacyanoferric (II) and (III) anions interfere.

The sensitivity is not reduced by the following ions in a 100 : 1 proportion F^{-1}, Cl^{-1}, ClO_4^{-1}, Br^{-1}, BrO^{-1} and I^{-1}.

REAGENTS.

1. Mixture in equal volumes of a saturated solution of manganous sulphate in water and phosphoric acid (d = 1.7).
2. Solution of diphenylcarbazide, 1 %, in ethyl alcohol 96 %.

71. PERCHLORIC ANION

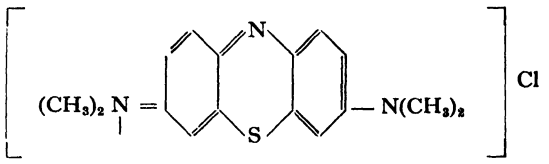
BY

C. J. VAN NIEUWENBURG

IW 99.457

A. ClO_4^{-1}, 10.

2 : 7-BIS-(DIMETHYLAMINO)-PHENOTHIAZONIUM CHLORIDE
(methylene blue)
(PHOTO 53)



BIBLIOGRAPHY : 1060-1063.

MECHANISM OF REACTION.

The perchlorate of the dyestuff is formed, the exact formula of which has not been determined.

K. A. HOFMANN, R. ROTH, K. HÖBOLD and A. METZLER (1060).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be examined, add a drop of saturated solution of sodium acetate, and evaporate to dryness. Take up the residue in a drop of the reagent solution; in certain cases it is necessary to heat until crystallization begins at the edge of the drop.

In the presence of perchloric anions a purplish precipitate is produced, which is partly flocculent and but slightly characteristic and partly formed of thin needles, grouped in bundles which are very characteristic.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

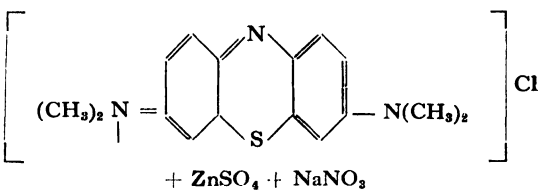
This reaction is fairly sensitive, but it is not selective, because the following anions give similar crystals, which are often blue : ClO^{-1}, ClO_3^{-1}, Br^{-1}, I^{-1}, S^{-2}, $S_2O_8^{-2}$, N_3^{-1}, NO_2^{-1} and NO_3^{-1}. These reactions are generally less sensitive than that with the perchloric anion.

REAGENTS.

1. Saturated solution of sodium acetate in water.
2. Solution of methylene blue, 0.5 %, in water.

B. ClO_4^{-1}, 16.

2 : 7-BIS-(DIMETHYLAMINO)-PHENOTHIAZONIUM CHLORIDE
(methylene bleu)
+ ZINC SULPHATE
+ SODIUM NITRATE



$+ ZnSO_4 + NaNO_3$

BIBLIOGRAPHY : 1064-1065.

MECHANISM OF REACTION.

Not yet known.

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube 1 ml of the solution to be analysed and add 5 drops of zinc sulphate solution, 5 drops of sodium nitrate solution and 1 to 3 drops of methylene blue solution. In the presence of perchloric anions a purplish red colour is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.30}$ $(1 : 2 \cdot 10^3)$.

The reaction is not sensitive, but it has the advantage of being much more selective than the preceding one. Only the peroxydisulfuric anion gives the same reaction. Some oxidizing agents decolourise the reagent. The hexacyanoferric (II) anion renders the reaction less clear.

REAGENTS.

1. Solution of zinc sulphate heptahydrate, 100 %, in water.
2. Solution of sodium nitrate, 20 %, in water.
3. Solution of methylene blue, 0.03 %, in water.

72. BROMIC ANION

BY

C. J. VAN NIEUWENBURG

IW 127.916

A. BrO_3^{-1}.

For the detection of the bromic anion in the presence of the hydrobromic anion it is sufficient to acidify the solution. Bromine is set free and it can be identified by the reaction with fluorescein (Br_2, B, p. 273).

In order to detect the bromic anion in a mixture of chlorate and iodate Schiff's reagent can be used (fuchsin solution, decolourized with sodium hydrogen sulphite and hydrochloric acid, see FEIGL, Spot Tests, 2nd Ed. p. 163). In the presence of a bromic anion a purplish blue colour is produced. This reaction is not selective.

In the same case the reaction with manganese (II) sulphate + sulphuric acid can also be used, see FEIGL, Spot Tests, 2nd Ed. p. 191.

73. IODIC ANION

BY

C. J. VAN NIEUWENBURG

IW 174.92

A. IO_3^{-1}.

Generally speaking the iodic anion is detected taking advantage of the fact that it can be reduced, thereby releasing elementary iodine. The reduction is effected by means of a solution of potassium thiocyanate, 5 %, in water. In acid medium there is no formation of iodide, even with an excess of reagent, but (and this is an advantage) only elementary iodine is obtained, according to the equation :

$$5\ CNS^{-1} + 6\ IO_3^{-1} + 6\ H^{+1} + 2\ H_2O \longrightarrow 5\ HSO_4^{-1} + 5\ HCN + 3\ I_2$$

F. FEIGL (1067).

BILBIOGRAPHY : 1067.

74. PERIODIC ANION

BY

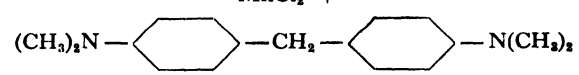
C. J. VAN NIEUWENBURG

IW 190.92

A. IO_4^{-1}, NR.

MANGANESE (II) CHLORIDE, MANGANOUS CHLORIDE + BIS-(*p*-DIMETHYLAMINOPHENYL)-METHANE, *p*-TETRAMETHYLDIAMINO-DIPHENYLMETHANE

$MnCl_2$ +



BIBLIOGRAPHY : 1068.

MECHANISM OF REACTION.

First of all the Mn^{+2} cation is oxidized to the permanganic anion by the periodic anion according to the equation :

$$2\ Mn^{+2} + 5\ IO_4^{-1} + 3\ H_2O \longrightarrow 2\ MnO_4^{-1} + 5\ IO_3^{-1} + 6\ H^{+1}.$$

The sensitivity of the reaction is increased if the permanganic anion is made to react on a base (bis-(*p*-dimethylaminophenyl)-methane) which gives a blue meriquinoid dyestuff by oxidation.

F. FEIGL and H. BALLABAN (1068).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the acid solution to be analysed and add a drop of the manganous chloride solution and a drop of the organic base solution. In the presence of the periodic anion a blue colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

Chloric, bromic and iodic anions do not interfere. The peroxydisulphuric anion gives an analogous reaction, but it can be removed by heating the acid solution with a drop of silver nitrate solution.

The reaction is not selective.

REAGENTS.

1. Solution of manganous chloride, 10 %, in water.
2. Saturated solution of bis-(*p*-dimethylaminophenyl)-methane in acetic acid 2 N.
3. Solution of silver nitrate, 10 %, in water.

75. HYDROSULPHIC ANION

BY

C. J. VAN NIEUWENBURG

IW 32.06

A. S^{-2}, 7.

DISODIUM NITROSOPENTACYANOFERRATE (III)

(sodium nitroprusside) $Na_2[Fe(CN)_5(NO)] . 2 H_2O$

BIBLIOGRAPHY : 1069-1073.

MECHANISM OF REACTION.

The purplish red colour is due to the formation of a complex whose formula is roughly :

$$Na_4[Fe(CN)_5(NO)S]$$

It is probable, but this has not yet been definitely established, that the iron is reduced to the bivalent state.

F. FEIGL (1070).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the solution to be analysed, a drop of ammonia and a drop of the reagent solution. In the presence of hydrogen sulphide anions a purplish red colour is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 5 \cdot 10^4$).

The reaction is good and selective.

The SO_3^{-2}, $S_2O_3^{-2}$ and SO_4^{-2} anions do not interfere, even in a 100 : 1 proportion.

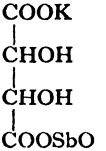
REAGENTS.

1. Ammonia 2 N.

2. Solution of disodium nitrosopentacyanoferrate (III), 1 %, in water.

B. S^{-2}, 9.

POTASSIUM ANTIMONYL TARTRATE



BIBLIOGRAPHY : 1074.

MECHANISM OF REACTION.

The orange-yellow colour is due to the formation of antimony (III) sulphide.

DETAILS OF TEST.

On a paper filter.

Place on a paper filter a drop of the reagent solution and then a drop of the solution to be analysed. In the presence of hydrosulphic anions an orange-yellow stain is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

The sensitivity is not affected by other ions.

The reaction is selective, but not very sensitive.

REAGENT.

1. Solution of potassium antimonyl tartrate, 5 %, in water.

C. S^{-2}, 15.

SODIUM NITRIDE + IODINE $NaN_3 + I_2$

BIBLIOGRAPHY : 1075-1081.

MECHANISM OF REACTION.

The velocity of the reaction

$$2\ NaN_3 + I_2 \longrightarrow 2\ NaI + 3\ N_2$$

is extremely low, but it is catalytically accelerated by compounds which contain negative bivalent sulphur, such as sulphides, thiosulphates, thiocyanates and a large number of organic sulphur compounds in the solid state or in a solution.

The bubbles which can be seen to escape are therefore of nitrogen.

F: RASCHIG (1075).

DETAILS OF TEST.

Under the microscope or on a spot plate.

Place on a spot plate or on a slide a drop of the solution to be analysed and add a drop of the sodium nitride solution and a drop of the iodine solution.

In the presence of hydrosulphic anions some nitrogen bubbles are released; it is advisable to compare the velocity of release in the analysis with that of a blank test.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The reaction is excellent, because the sensitivity is not reduced by other ions; it is specific for the compounds enumerated above and it lends itself particularly well to the detection of sulphur in minerals.

Hydroselenic and hydrotelluric anions give an analogous reaction.

REAGENTS.

1. Solution of sodium nitride, 2.5 %, in water.
2. Solution of iodine, 0.1 N, in potassium iodide, 10 %, in water.

76. SULPHUROUS ANION

BY

C. J. VAN NIEUWENBURG

IW 80.06

AND

77. SULPHUR DIOXIDE

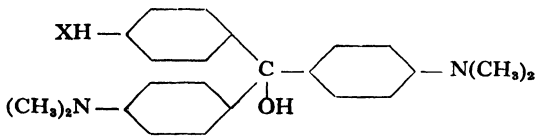
BY

C. J. VAN NIEUWENBURG

MW 64.06

A. SO_3^{-2}, 22.

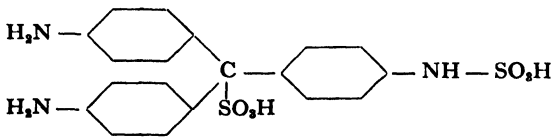
SALT OF BIS-(*p*-DIMETHYLAMINOPHENYL)-PHENYLCARBINOL
(malachite green)



BIBLIOGRAPHY : 1082-1083.

MECHANISM OF REACTION.

Sulphites in aqueous solution (even dilute) immediately decolourize solutions of malachite green. An N-sulphinic acid is probably formed of the following type :



F. FEIGL (1082).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the neutral solution to be analysed and add a drop of the reagent solution. Decolourisation takes place in the presence of sulphurous anions.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.30}$ ($1 : 2 \cdot 10^4$).

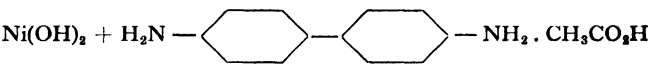
The sensitivity is reduced to 10^{-4} ($1 : 10^4$) by SO_4^{-2} and $S_2O_3^{-2}$ anions in a proportion of 100 : 1. The S^{-2} anion reacts in the same manner as the sulphurous anion, as well as ClO^{-1}, CN^{-1}, CNO^{-1} and $C_2O_4^{-2}$ anions at higher concentration. ClO_4^{-1}, IO_3^{-1}, IO_4^{-1}, CNS^{-1}, formic and tartaric ions interfere.

REAGENT.

1. Solution of malachite green, 0.0025 %, in water.

B. SO_3^{-2}, 12 and 32.

NICKEL (II) HYDROXIDE + BENZIDINE ACETATE



BIBLIOGRAPHY : 1084-1087.

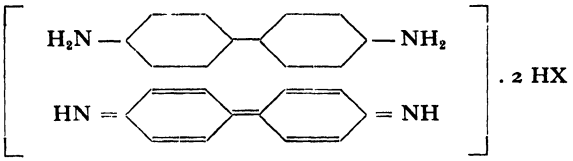
MECHANISM OF REACTION.

The auto-oxidation of the sulphurous anion induces the oxidation of nickel (II) hydroxide to nickel (III) hydroxide, which is remarkable, because this action can only by realized by energetic oxidizing agents. A black precipitate of nickel (III) hydroxide is observed, which is gradually decomposed, restoring the green coloured, bivalent hydroxide.

These reactions can be formulated in the following manner :

$$2\,Ni(OH)_2 + O_2 + H_2O + Na_2SO_3 \longrightarrow 2\,Ni(OH)_3 + Na_2SO_4$$
$$2\,Ni(OH)_3 + Na_2SO_3 \longrightarrow 2\,Ni(OH)_2 + Na_2SO_4 + H_2O.$$

The reaction is continued by making trivalent nickel react on benzidine, which is oxidized to a blue dyestuff of the following formula :



F. HABER and F. BRAN (1085), F. FEIGL (1087).

DETAILS OF TEST.

In a micro test tube and on filter paper.

Heat in a micro test tube the solution to be analysed with a little hydrochloric acid, and expose a filter paper on which a stain of bivalent nickel hydroxide has been made to the gases evolved from the test tube. In the presence of sulphurous anions the sulphur dioxide which is released, blackens the stain. In order to make the reaction more sensitive a drop of a benzidine acetate solution is added on the filter paper. A blue colouration then appears.

It should be noted, however, that the reaction with benzidine is rather unreliable and that care should be taken completely to remove the sodium hydroxide which served to precipitate the nickel (II) hydroxide, otherwise the benzidine assumes a blue colour, even in the absence of sulphur dioxide.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 5 \cdot 10^4$), with benzidine.

The sensitivity is not reduced by sulphuric and peroxydisulphuric anions in a 100 : 1 proportion.

It is obvious that thiosulphates, which also release sulphur dioxide give the same reaction as the sulphurous anion.

The sulphides, which release hydrogen sulphide, interfere because black nickel sulphide is formed.

REAGENTS.

1. Hydrochloric acid 5 N.
2. Filter paper on which nickel (II) hydroxide is deposited, prepared by precipitation from a chloride solution with sodium hydroxide. It is essential that the nickel hydroxide should have been thoroughly washed by centrifuging.
3. Solution of benzidine acetate, 1 %, in acetic acid, 25 %.

78. THIOSULPHURIC ANION

BY

C. J. VAN NIEUWENBURG

IW 112.12

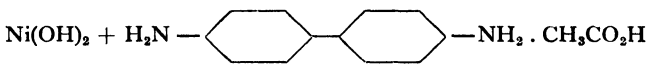
A. $S_2O_3^{-2}$, 18.

SODIUM NITRIDE + IODINE $NaN_3 + I_2$

The reaction is identical with that already described for the hydrogen sulphide anion, see S^{-2}, C, p. 283.

B. $S_2O_3^{-2}$, NR.

NICKEL (II) HYDROXIDE + BENZIDINE ACETATE



The reaction has already been described for the sulphurous anion, see SO_3^{-2}, B, p. 285.

To detect the thiosulphuric anion in the presence of the hydrosulphic anion, the latter must be removed by precipitation with cadmium carbonate. The filtered solution gives a precipitate of sulphur with evolution of sulphur dioxide, when treated with a mineral acid.

The detection of the thiosulphuric anion in the presence of hydrosulphic anions can also be effected by means of a solution of a mercury (II) chloride in a concentrated solution of potassium chloride. In the presence of thiosulphuric anions the solution becomes acid.

This acidity results from the liberation of sulphuric acid according to the equation :

$$S_2O_3^{-2} + Hg^{+2} + H_2O \longrightarrow HgS + SO_4^{-2} + 2\,H^{+1}$$

As mercury (II) chloride gives a certain acidity by hydrolysis, it must be reduced by converting the mercury to the state of a strongly dissociated complex anion, having the formula $[HgCl_4]^{-2}$, which is obtained by means of a concentrated solution of potassium chloride.

A. SANDER (1088), F. FEIGL (1089).

The thiosulphuric anion is distinguished from the sulphurous anion inasmuch as it does not decolourise (in a pH = 8 solution) a solution of fuchsin and malachite green.

E. VOTOČEK (1090).

79. SULPHURIC ANION

BY

C. J. VAN NIEUWENBURG

IW 96.06

A. SO_4^{-2}, NR.

POTASSIUM PERMANGANATE + BARIUM CHLORIDE + HYDROGEN PEROXIDE $KMnO_4 + BaCl_2 + H_2O_2$

BIBLIOGRAPHY : 1091-1092.

MECHANISM OF REACTION.

Barium sulphate precipitated in a solution containing potassium permanganate is coloured pink by adsorption of the manganous salt. Potassium permanganate thus fixed cannot be reduced by its ordinary reducing agents or by hydrogen peroxide. It will therefore be possible to decolourize the solution in which the test will be carried out, whilst retaining on the barium sulphate precipitate its pink colour.

H. E. WOHLERS (1091), F. FEIGL and W. AUFRICHT (1092).

DETAILS OF TEST.

In a micro tube of a centrifuge.

Place in a micro tube of a centrifuge (or better still in a small Emich tube) a drop of the solution to be analysed to which is added a drop of potassium permanganate solution and a drop of barium chloride solution. The precipitation of barium sulphate, which adsorbs the potassium permanganate and turns a deep purple, indicates the presence of sulphuric anions. If some drops of a hydrogen (or oxalic acid) solution are added, the precipitate remains coloured. It is preferable to collect the precipitate by centrifuging, which makes it more visible. The sensitivity of the reaction is increased in this manner; the reaction can also be carried out in a test tube or on a spot plate, but with fewer advantages.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.30}$ ($1 : 2 \cdot 10^4$).

The sensitivity is not reduced by S^{-2}, SO_3^{-2} and $S_2O_3^{-2}$ anions in a proportion of 100 : 1. The fluosilicic anion, which precipitates the barium cation in acidified medium, does not react in the same way as the sulphuric anion.

The following anions interfere with the reaction : ClO^{-1}, CN^{-1}, CNO^{-1}, CNS^{-1}, $[Fe(CN)_6]^{-3}$ and $[Fe(CN)_6]^{-4}$. Ions which give a precipitate with the barium cation in a neutral solution decrease the sensitivity, which changes to the value of $10^{-3.70}$ ($1 : 5 \cdot 10^3$), when these ions are present in a concentration equal to that of the sulphuric anion. It is possible, however, to avoid this complication by carrying out the test in a solution which is acidified with acetic acid, which only produces an imperceptible reduction of the sensitivity.

REAGENTS.

1. Solution of potassium permanganate, 1 %, in water.
2. Solution of barium chloride, 1 %, in water.
3. Acetic acid 4 N.
4. Solution of hydrogen peroxide, 3 %, in water.

80. PEROXIDISULPHURIC ANION

BY

C. J. VAN NIEUWENBURG

IW 192.12

We have not a reaction at our disposal which is really characteristic of the peroxidisulphuric anion. By heating an acid solution, preferably with a drop of a silver nitrate solution, the anion is decomposed with formation of the sulphuric anion.

To distinguish this anion from hydrogen peroxide the reaction with potassium permanganate or with titanous sulphate is used (see p. 144): only hydrogen peroxide reacts. In the case when benzidine is used as a reagent, the peroxidisulphuric anion reacts and peroxiboric and hydrogen peroxide anions do not react.

Methylene blue gives the same precipitate with the peroxidisulphuric anion as with the perchloric anion (see p. 277).

81. HYDRAZOIC ANION

BY

C. J. VAN NIEUWENBURG

IW 42.024

A. N_3^{-1}, 5.

IRON (III) CHLORIDE, FERRIC CHLORIDE $FeCl_3$

BIBLIOGRAPHY : 1093-1094.

MECHANISM OF REACTION.

The red colour is due to the formation of a non-dissociated salt having the formula $Fe(N_3)_3$.

J. F. REITH and J. H. A. BOUWMAN (1093).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube a drop of the solution to be analysed and add a drop of the ferric chloride solution. In the presence of hydrazoic anions a red colour is produced; if the concentration is high, a brown precipitate can be obtained by heating.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ (1 : 10^5).

The thiocyanic anion gives an analogous reaction. The hydriodic anion interferes, because iodine is formed. The hexacyanoferric (II) and (III) anions must be removed by precipitation with cadmium sulphate, because they interfere on account of their own colour.

Moreover the hydrofluoric, phosphoric, oxalic and tartaric anions, which make the Fe^{+3} cation change to the state of a compound, require addition of an excess of reagent. The same is true in the presence of S^{-2} and $S_2O_3^{-2}$ anions, which cause the precipitation of sulphur.

The sensitivity is not reduced by the other ions.

REAGENT.

1. Solution of ferric chloride, 1 %, in water.

82. NITROUS ANION

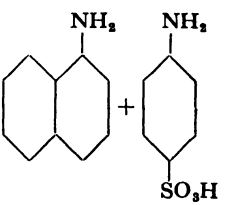
BY

C. J. VAN NIEUWENBURG

IW 46.008

A. NO_2^{-1}, 26.

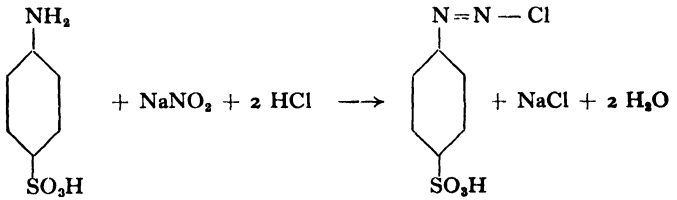
α-NAPHTHYLAMINE + *p*-AMINOBENZENE SULPHONIC ACID
(p-sulphanilic acid)



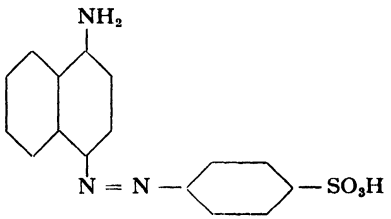
BIBLIOGRAPHY : 1095-1101.

MECHANISM OF REACTION.

The reaction consists in a diazotisation of sulphanilic acid by the nitrous anion, according to the equation :



followed by a coupling of the diazonium salt with α-naphthylamine, which results in the formation of a red azo dyestuff :



P. GRIESS (1095).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the solution to be analysed and a drop of both reagent solutions. In the presence of nitrous anions a pink colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6.70}$ $(1 : 5 \cdot 10^6)$.

The nitric anion does not react and it does not reduce the sensitivity, even in a proportion of 100 : 1.

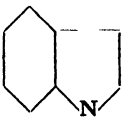
The reaction is excellent and selective. It should be noted that very energetic oxidants can destroy the reagent. The Fe^{+3} cation must be masked by tartaric acid.

REAGENTS.

1. Solution of 1 % sulphanilic acid, 1 %, in acetic acid 30 %.
2. Solution of α-naphthylamine, 0.3 %, in acetic acid 30 %.
3. Solution of tartaric acid, 20 %, in water.

B. NO_2^{-1}, 23.

INDOLE



BIBLIOGRAPHY : 1102.

MECHANISM OF REACTION.

The red coloured nitroso-indole (probably in position 3) is formed.

DANÉ (1102).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube a drop of the solution to be analysed, 10 drops of the reagent solution and 5 drops of sulphuric acid. In the presence of nitrous anions a purplish red colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-6}$ (1 : 10^6).

The reaction is excellent and selective. The sensitivity is not diminished by the nitric anion in a proportion of 100 : 1; it does not react.

Energetic oxidants can destroy the reagent.

REAGENTS.

1. Solution of indole, 0.015 %, in ethyl alcohol 96 %.
2. Sulphuric acid 15 N.

There are still a large number of excellent reactions of the nitrous anion, such as those with chrysene (see FEIGL, Spot Tests, p. 250), and with 1 : 8-diaminonaphthalene (see FEIGL, Spot Tests, p. 249), etc. However, we believe that the two reactions quoted above will suffice in all possible circumstances.

83. NITRIC ANION

BY

C. J. VAN NIEUWENBURG

IW 62.008

A. NO_3^{-1}, 47.

There exists a very large number of reagents for the detection of the nitric anion; some among them are sufficiently sensitive, as for example iron (II) sulphate, concentrated sulphuric acid and diphenylamine, brucine etc. Unfortunately, these reagents are not selective and the nitrous anion as well as a large number of oxidants react in the same way. In our opinion the best method consists in a reduction of the nitric anion to the nitrous anion by means of zinc powder and acetic acid. For that purpose the solution to be analysed is treated with a little pure zinc powder and a few drops of dilute acetic acid. The nitrous anion formed is then identified, by means of the reaction with sulphanilic acid and naphthylamine (see NO_2^{-1}, A, p. 291). As a precaution the zinc powder should be washed in several ml of dilute acetic acid and this operation repeated.

It is evident that this procedure only holds good if nitrites have been previously removed, preferably by means of sodium nitride in acetic acid solution. The excess of hydrazoic acid is removed by prolonged heating.

BIBLIOGRAPHY : 1103-1106.

84. ORTHOPHOSPHORIC ANION

BY

C. J. VAN NIEUWENBURG

IW 94.98

There exists a large number of variants of the classical reaction of the phosphoric anion with molybdic acid (see the First Report of the International Committee on Reagents). Generally speaking the

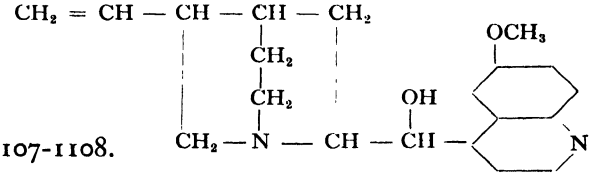
sensitivity of the variants is greater than that of the original reaction, which only attains a limiting dilution of 10^{-5} ($1 : 10^5$).

We restrict ourselves to mentioning one reaction, but in so doing do not claim that it is the only good one.

A. PO_4^{-3}, 34.

AMMONIUM MOLYBDATE + QUININE SULPHATE

$$(NH_4)_2MoO_4 + 2\ C_{20}H_{24}O_2N_2 \cdot H_2SO_4 \cdot n\ H_2O$$



BIBLIOGRAPHY : 1107-1108.

MECHANISM OF REACTION.

The exact structure of the product formed in the course of the reaction is not yet known.

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube a ml of the solution to be analysed and add a ml of the reagent solution. After some minutes, and if necessary after heating slightly, a pale yellow precipitate is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5.70}$ ($1 : 5 \cdot 10^5$).

Reducing ions such as S^{-2} or $S_2O_3^{-2}$ interfere because they reduce molybdenum (blue colour). The ferrocyanide anion interferes, because it gives a red colour.

Arsenic and silicon anions give the same reaction, but with lower sensitivity; it is therefore necessary to remove them, the silicon anion by rendering it insoluble by means of hydrochloric acid, and the arsenic anion by precipitation with hydrogen sulphide.

The sensitivity is not reduced by the other ions.

REAGENT.

1. Solution of 4 g ammonium molybdate + 0.1 g quinine sulphate in 100 ml nitric acid (d = 1.4).

85. BORIC ANION

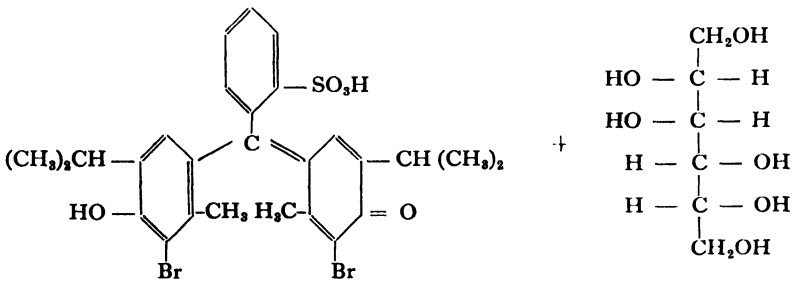
BY

C. J. VAN NIEUWENBURG

IW 58.82

A. BO_3^{-3}, 14.

3 : 3'-DIBROMO-2 : 2'-DIMETHYL-
5 : 5'-DIISOPROPYL-4'-HYDROXY-2''-SULPHOFUCHSONE
(dibromosulphophtalein,
bromothymol blue)
+ *d*-**MANNITOL**



BIBLIOGRAPHY : 1109.

MECHANISM OF REACTION.

Neutralize the solution up to the change-point of the indicator (bromothymol blue), then add mannitol; in the presence of boric anions a compound of mannitol and boric acid is formed, the dissociation of which is very high with respect to that of simple boric acid. Hence a change of colour takes place in the indicator because of the increase in concentration of hydrogen ions.

F. HAHN (1109).

DETAILS OF TEST.

In a micro test tube.

Place in a micro test tube a few drops of the solution to be analysed, which is very accurately neutralized beforehand, using bromothymol blue as indicator; add an equal volume of reagent solution. In the presence of boric anions the colour changes to orange-yellow (" acid " colour of bromothymol blue).

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ (1 : $5 \cdot 10^4$).

The reaction is only interfered with by the periodic and germanic anions which cause the same change of colour, but it is easy to decompose them by heating on charcoal.

REAGENTS.

1. Solution of bromothymol blue, 0.04 %, in ethyl alcohol, 96 %.
2. Solution of mannitol, 10 %, in water, neutralized with potassium hydroxide 0.01 N, using bromothymol blue as indicator.

86. SILICIC ANION

BY

C. J. VAN NIEUWENBURG

IW 76.06

It is always advisable to separate the silicic anion by volatilization as silicon fluoride. For this purpose the solid silicates are mixed with a little solid sodium fluoride and a few drops of concentrated sulphuric acid in a small lead or platinum crucible. Cover the crucible with a small sheet of cellophane from which is suspended either a drop of dilute sodium hydroxide solution for reaction A, or a drop sodium chloride solution for reaction B. Heat for 5 minutes over a micro-burner, the crucible being 6-8 cm over the flame. For certain fluoriferous silicates it is preferable to first of all disintegrate the material by fusion with a small fragment of solid sodium hydroxide. The boric anion in large proportions interferes and must be removed by means of methylic alcohol and sulphuric acid.

A. SiO_3^{-2}, 19.

MOLYBDIC ACID H_2MoO_4 + $SnCl_2$
TIN (II) CHLORIDE, STANNOUS CHLORIDE

BIBLIOGRAPHY : 1110-1113.

MECHANISM OF REACTION.

Stannous chloride cannot reduce simple molybdic acid in basic medium. But when the latter is in the state of a heteropolyacid, it is easily reduced to the blue oxide. In the present case the complex acid derived from silicon and molybdic acid has the following formula :

$$SiO_2 . 12\ MoO_3 . xH_2O.$$

F. PARMENTIER (1110).

DETAILS OF TEST.

In a porcelain micro-crucible.

After having collected the silicon fluoride as indicated above, place the drop of sodium hydroxide in a porcelain micro-crucible, add 2 drops of ammonium molybdate solution and then acetic acid until a feebly acid reaction is obtained. Finally add 3 drops of stannous chloride solution and an excess of sodium hydroxide solution, so that all the stannous hydroxide redissolves. In the presence of silicon a blue colour is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ (1 : 10^4).

Because the silicon has been separated, other ions do not interfere with the exception of the boric anion in large proportions, which is isolated at the same time as silicon owing to the volatility of its fluoride. Phosphoric and arsenic anions, which give the same reaction, therefore do not interfere.

The sodium hydroxide solution must not contain any silicic acid; so a freshly prepared solution must be used.

REAGENTS.

1. Sodium hydroxide 2 N, freshly prepared.
2. Solution of ammonium molybdate, 10 %, in water, freshly prepared.
3. Acetic acid 4 N.
4. Solution of stannous chloride, 5 %, in hydrochloric acid 2.5 N.

B. SiO_3^{-2}, 3.

SODIUM CHLORIDE (PHOTO 54) NaCl

BIBLIOGRAPHY : 1114.

MECHANISM OF REACTION.

Disodium hexafluosilicate, $Na_2[SiF_6]$ is formed.

DETAILS OF TEST.

Under the microscope.

Collect the silicon fluoride vapours in a drop of sodium chloride (vide the general mode of operation, p. 297). After some minutes crystals of sodium fluosilicate are formed, having a slightly pink colour and occurring in characteristic hexagons. Examine these through the microscope.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 5 \cdot 10^4$).

The reaction is excellent and selective. Only the boric anion in large proportions interferes with the detection of the silicic anion.

REAGENT.

1. Solution of sodium chloride, 1 %, in water.

87. CARBONIC ANION

BY

C. J. VAN NIEUWENBURG

IW 60.010

A. CO_3^{-2}, 1.

The detection of soluble carbonates does not offer great difficulties. One of the best reactions is that of BEHRENS-KLEY (1115), viz., strontium acetate + sodium acetate. The spheroids formed are

fairly characteristic. This reaction is of little use for the detection of small quantities of insoluble carbonates in minerals; this is, however, the most general case. In fact, this reaction requires the carbon dioxide to be released by means of an acid so that the gas can be collected in an alkaline solution. Now, alkaline solutions always absorb a little carbon dioxide from the air. Even if the solution is prepared by dissolving a small fragment of sodium in water, it will contain carbonates even before it can be examined under the microscope.

B. CO_3^{-2}, NR.

One of the best methods is described by F. FEIGL (1116): the reagents consist of a solution of sodium carbonate, 0.1 N, with phenolphtalein as indicator; the solution is decolourized under the action of carbon dioxide released by the carbonate.

This reaction, however, is not very sensitive and a blank test is essential.

The release of sulphur dioxide can be prevented by means of a mixture of sulphuric acid and potassium dichromate. In the presence of nitrous anions fixing them by means of aniline hydrochloride is recommended.

88. HYDROCYANIC ANION

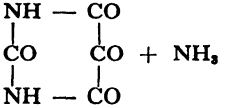
BY

C. J. VAN NIEUWENBURG

IW 26.018

A. CN^{-1}, NR.

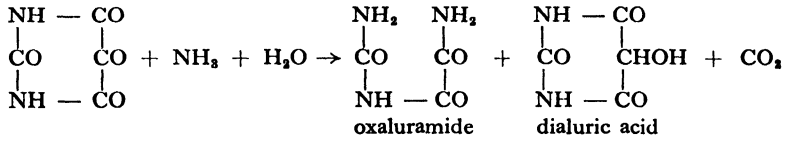
ALLOXAN + AMMONIA (PHOTO 55)



BIBLIOGRAPHY : 1117-1119.

MECHANISM OF REACTION.

Of the two products which are formed in the reaction, catalysed by the CN^{-1} anion :



the oxaluramide has characteristic crystals.

G. DENIGÈS (1117).

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed, to which add some alloxan crystals and a drop of ammonia. In the presence of hydrocyanic anions thin colourless needless are formed, which are often grouped in asterisks.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.70}$ ($1 : 5 \cdot 10^3$).

The boric anion also gives a precipitate and the phosphoric anion interferes with the formation of reaction products of the hydrocyanic anion. Cyanic, thiocyanic, hexacyanoferric (II) and (III) anions in a proportion of 10 : 1 reduce the sensitivity to $10^{-3.30}$ ($1 : 2 \cdot 10^3$).

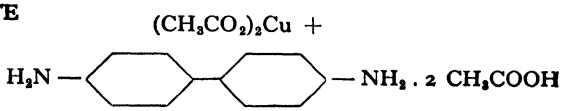
Other ions do not interfere.

REAGENTS.

1. Solid alloxan.
2. Ammonia 2 N.

B. CN^{-1}, 16.

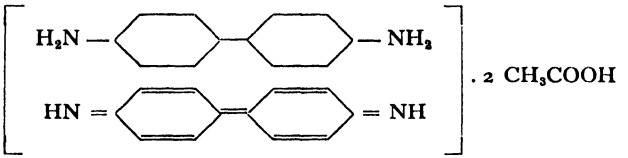
COPPER (II) ACETATE, CUPRIC ACETATE + BENZIDINE ACETATE



BIBLIOGRAPHY : 1120-1124.

MECHANISM OF REACTION.

The blue colour which is observed in the presence of copper and hydrocyanic anions is due to the formation of a benzidine dyestuff, having the formula :



The oxidation of benzidine is effected by the cupric cation, the redox potential of which is increased by the hydrocyanic anion.

F. FEIGL (1124).

DETAILS OF TEST.

On filter paper or in a micro test tube.

The solution to be analysed is slightly heated in a micro test tube with a little sodium bicarbonate in order to liberate hydrocyanic acid. Under these conditions the hexacyanoferric (II) and (III) anions are not decomposed. Collect the vapours on a filter paper which has been impregnated with a drop of cupric acetate solution and a drop of benzidine acetate solution. In the presence of hydrocyanic acid a blue stain appears on the filter paper.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.30}$ ($1 : 2 \cdot 10^4$).

Free chlorine and bromine are liberated from the solution by treatment with sodium bicarbonate and they react in the same way as the hydrocyanic anion. The nitrous anion would also react, but it does not interfere, because nitrites are not decomposed.

Other ions do not interfere.

REAGENTS.

1. Solid sodium bicarbonate.
2. Solution of cupric acetate, 3 %, in water.
3. Solution of benzidine, 1 %, in acetic acid, 10 %.

89. THIOCYANIC ANION

BY

C. J. VAN NIEUWENBURG

IW 58.078

A. CNS^{-1}, NR.

IRON (III) CHLORIDE, FERRIC CHLORIDE + HYDROCHLORIC ACID $FeCl_3 + HCl$

BIBLIOGRAPHY : 1126-1141.

MECHANISM OF REACTION.

Ferric thiocyanate is formed, which is red and soluble in water and has been known for a very long time.

DETAILS OF TEST.

In a micro test-tube.

Place in a micro test tube 0.1 ml of the solution to be analysed, which is acidified with hydrochloric acid; add a drop of a solution of ferric chloride. In the presence of thiocyanic anions a red colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-5}$ ($1 : 10^5$).

The hydriodic anion interferes because of the formation of free iodine. The hydrazoic anion gives the same reaction. Hydrogen sulphide and thiosulphuric anions give a precipitate of sulphur, which does not interfere, but an excess of ferric chloride is required. In the presence of anions which form complexes of iron (III), such as hydrofluoric, phosphoric, oxalic and tartaric anions, an excess of reagent will also be necessary. Hexacyanoferric (II) and (III) anions interfere; but they can be removed by addition of cadmium sulphate, which precipitates them. It should be noted that this operation reduces the sensitivity to $10^{-4.30}$ ($1 : 2 \cdot 10^4$).

Other ions do not interfere.

REAGENTS.

1. Hydrochloric acid 2 N.
2. Solution of ferric chloride, 1 %, in water.
3. Solid cadmium sulphate.

B. CNS^{-1}, 13.

SODIUM NITRITE + IODINE $NaN_3 + I_2$

The reaction is similar in every respect to that of the hydrogen sulphide anion to which we refer the reader (S^{-2}, C, see p. 283).

90. HEXACYANOFERRIC (II) ANION, FERROCYANIDE ANION

BY

C. J. VAN NIEUWENBURG

IW 211.958

A. $[Fe(CN)_6]^{-4}$, NR.

IRON (III) CHLORIDE, FERRIC CHLORIDE $FeCl_3$

BIBLIOGRAPHY : 1142-1158.

MECHANISM OF REACTION.

The well-known iron (III) salt $Fe_4[Fe(CN)_6]_3$, Prussian blue, is precipitated.

DETAILS OF TEST.

In a micro test tube.

Acidify the solution to be analysed with hydrochloric acid in a micro test tube and add a few drops of ferric chloride solution. In the presence of hexacyanoferric (II) anions a blue colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 5 \cdot 10^4$).

The hexacyanoferric (III) anion gives a brown colour which only slightly interferes; in a 100 : 1 proportion it reduces the sensitivity to 10^{-4} ($1 : 10^4$). The thiocyanic anion, which gives the well-known red colour, only interferes if the concentration in ferrocyanide anion is lower than $10^{-3.70}$ ($1 : 5 \cdot 10^3$). The hydrocyanic anion in a 100 : 1 proportion reduces the sensitivity to $10^{-4.30}$ ($1 : 2 \cdot 10^4$). ClO^{-1}, I^{-1} and S^{-2} anions interfere more or less. The iodic anion gives a precipitate which renders the reaction less positive.

Other ions do not interfere.

REAGENTS.

1. Hydrochloric acid 2 N.
2. Solution of ferric chloride, 1 % in water.

B. $[Fe(CN)_6]^{-4}$, NR.

HEXAMMINOCOBALT (III) NITRATE, LUTEOCOBALTIC NITRATE (PHOTO 56) $[Co(NH_3)_6](NO_3)_3$

BIBLIOGRAPHY : 1159.

MECHANISM OF REACTION.

The complex cobaltic salt is formed, the exact formula of which has not yet been discovered.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed and a few crystals of reagent. In the presence of hexacyanoferric (II) anions hexagonal crystals appear, often grouped in asterisks.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ ($1 : 10^4$).

The ferricyanide anion also gives crystals, but of an entirely different shape (see $[Fe(CN)_6]^{-3}$, B, p. 307), it does not reduce the sensitivity. The hydrocyanic anion does not interfere. The thiocyanic anion

in a 50 : 1 proportion reduces the sensitivity to $10^{-3.70}$ ($1 : 5 \cdot 10^3$). F^{-1}, ClO_3^{-1} and IO_4^{-1} anions give rather similar crystals. The hydrogen sulphide anion gives a black precipitate which interferes and the hypochlorous anion causes an amorphous precipitation.

REAGENT.

1. Solid luteocobaltic nitrate.

91. HEXACYANOFERRIC (III) ANION FERRICYANIDE ANION

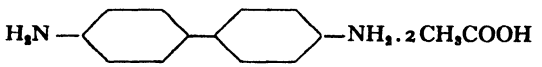
BY

C. J. VAN NIEUWENBURG

IW 211.958

A. $[Fe(CN)_6]^{-3}$, 7.

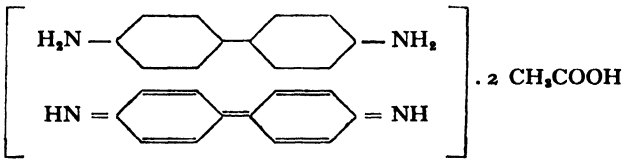
BENZIDINE ACETATE



BIBLIOGRAPHY : 1160-1161.

MECHANISM OF REACTION.

The hexacyanoferric (III) anion easily oxidizes benzidine to a blue meriquinoid dyestuff, having the formula :



F. FEIGL (1161).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the solution to be analysed and a drop of the saturated reagent solution. In the presence of ferricyanide anions, a blue colour is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.30}$ ($1 : 2 \cdot 10^4$).

The hydrocyanic anion in a proportion of 100 : 1 reduces the sensitivity to $10^{-3.70}$ ($1 : 5 \cdot 10^3$). The ferrocyanide anion in a 100 : 1 proportion reduces the sensitivity to 10^{-4} ($1 : 10^4$). A large number of oxidizing agents give the same reaction; consequently the reaction is only useful to detect ferricyanides in the presence of ferrocyanides.

REAGENT.

1. Saturated solution of benzidine acetate in water.

B. $[Fe(CN)_6]^{-3}$, NR.

HEXAMMINOCOBALT (III) NITRATE, LUTEOCOBALTIC NITRATE (PHOTO 57) $[Co(NH_3)_6]\ (NO_3)_3$

BIBLIOGRAPHY : 1162.

MECHANISM OF REACTION.

A cobaltic ammine salt is formed, the exact composition of which is not yet known.

DETAILS OF TEST.

Under the microscope.

Place on a slide a drop of the solution to be analysed and add a few reagent crystals. In the presence of hexacyanoferric (III) anions crystals in the form of bars are produced, the extremity of which has an oblique face; they are sometimes grouped in pairs or in asterisks.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4}$ ($1 : 10^4$).

The ferrocyanide anion also gives a precipitate, but of an altogether different form (see $[Fe(CN)_6]^{-4}$, B, p. 305); it does not reduce the sensitivity. The hydrocyanic anion does not interfere. The thiocyanic anion in a 100 : 1 proportion reduces the sensitivity to $10^{-3.70}$ ($1 : 5 \cdot 10^3$).

The hypochlorous and hydrogen sulphide anions interfere.

REAGENT.

1. Solid luteocobaltic nitrate.

92. FORMIC ANION

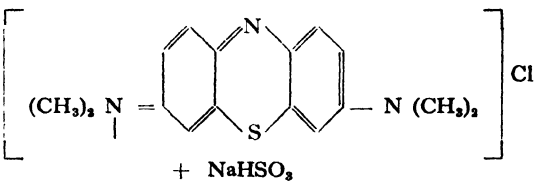
BY

C. J. VAN NIEUWENBURG

IW 45.018

A. HCO_2^{-1}, 17.

2 : 7-BIS-(DIMETHYLAMINO)-PHENOTHIAZONIUM CHLORIDE
(methylene bleu)
+ SODIUM HYDROGEN SULPHITE



BIBLIOGRAPHY : 1163.

MECHANISM OF REACTION.

Methylene blue is reduced and decolourized, but the exact mechanism is not yet known.

DETAILS OF TEST.

In a micro test tube.

Place in the test tube 1 ml of the slightly acidified solution to be analysed, and add a drop of the solution of methylene blue and a little solid sodium hydrogen sulphite. Heat slightly. In the presence of formic anions the blue colour disappears, to reappear after prolonged contact with air.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ ($1 : 5 \cdot 10^4$).

Acetic, oxalic and tartaric anions do not give this reaction; they reduce the sensitivity to 10^{-4} ($1 : 10^4$) and in a 50 : 1 proportion they reduce it to $10^{-3.70}$ ($1 : 5 \cdot 10^3$). The following anions give an analogous reaction : F^{-1}, ClO_3^{-1}, ClO_4^{-1}, BrO_3^{-1}, N_3^{-1}, NO_2^{-1}, S^{-2}

and CN^{-1}. Iodic and periodic anions interfere, because iodine is set free. Hexacyanoferric (II) and (III) anions interfere owing to their own colour.

The SO_3^{-2} anion in large proportions gives the same reaction.

This reaction is useful for the detection of the formic anion in a mixture of other organic anions.

REAGENTS.

1. Solution of methylene blue, 0.01 %, in water.
2. Solid sodium hydrogen sulphite.

93. ACETIC ANION

BY

C. J. VAN NIEUWENBURG

IW 59.044

A. $CH_3CO_2^{-1}$, 13.

LANTHANUM NITRATE + IODINE $La(NO_3)_3 + I_2$

BIBLIOGRAPHY : 1164-1168.

MECHANISM OF REACTION.

The reaction is based on the hot precipitation of a basic lanthanum salt, which has the property of adsorbing elementary iodine to give a blue colour.

D. KRÜGER and E. TSCHIRCH (1165-1166).

DETAILS OF TEST.

On a spot plate.

Place on the plate a drop of the solution to be examined and add a drop of lanthanum nitrate solution, then a drop of a very dilute

solution of iodine in potassium iodide and finally a drop of ammonia. In the presence of acetic anions a blue colour is produced.

SENSITIVITY AND SELECTIVITY. $D = 10^{-3.30}$ (1 : $2 \cdot 10^3$).

A more concentrated iodine solution than the one indicated must not be used in order to avoid the appearance of a more or less blue colour, even in the absence of acetic anions. The propionic anion reacts as the acetic anion. Formic, butyric, valeric and lactic anions do not give this reaction.

The reaction is characteristic, but not at all sensitive.

REAGENTS.

1. Solution of lanthanum nitrate, 5 %, in water.
2. Iodine, 0.01 N, in potassium iodide.
3. Ammonia, N.

94. OXALIC ANION

BY

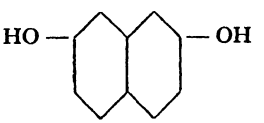
C. J. VAN NIEUWENBURG

IW 88.020

A. $C_2O_4^{-2}$, 18.

MAGNESIUM
+ 2 : 7-DIHYDROXYNAPHTHALENE

Mg +

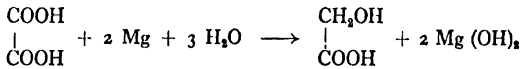


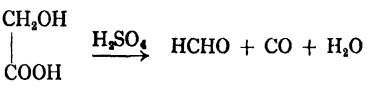
BIBLIOGRAPHY : 1169-1172.

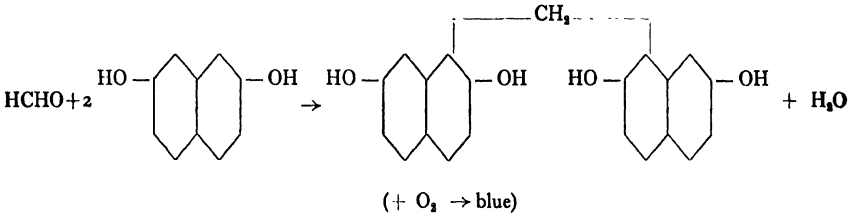
MECHANISM OF REACTION.

First of all a reduction of the oxalic anion to glycollic anion is effected. By the action of sulphuric acid the latter is transformed

to formaldehyde, which, when condensed with dihydroxynaphthalene, gives a product which is coloured purplish blue by oxidation :







E. EEGRIWE (1171).

DETAILS OF TEST.

In a micro test tube.

Separate the oxalic anion from the other ions by precipitation with calcium sulphate from a neutral solution (W. BÖTTGER (1169), filter and wash the precipitate and redissolve it in hot sulphuric acid. Place a few drops of this solution in a micro test-tube and effect reduction by means of magnesium shavings. Then add 2 ml of the dihydroxynaphthalene solution and heat in a water-bath for 20 minutes. A purplish colour appears.

SENSITIVITY AND SELECTIVITY. $D = 10^{-4.70}$ (1 : $5 \cdot 10^4$).

The formic anion also reacts, but less intensely, giving a colour which is rather pinkish. The acetic anion (pure) does not give this reaction, whereas the tartaric anion gives a slight brown colour.

It is always advisable to use the reagent when it is freshly prepared and also to compare results with those of a blank test, because the reagent is often coloured a pale pink.

The reaction is excellent, but not very selective; hence it is advisable to separate the oxalic anion first as calcium oxalate.

REAGENTS.

1. Saturated solution of calcium sulphate in water.
2. Sulphuric acid, 2 N.
3. Magnesium in chips.
4. Solution of 0.01 g 2 : 7-dihydroxynaphthalene in 100 ml sulphuric acid, 35 N.

QUALITATIVE SEPARATION OF ANIONS

The separation of anions is summarized in the following table, which does not require any further explanation.

ANIONS TO BE IDENTIFIED	ANIONS PRESENT (IN LARGE PROPORTIONS)	REAGENTS USED AND OPERATIONS TO BE CARRIED OUT
F^{-1}	BO_3^{-3}	Sodium alizarin sulphonate + $ZrOCl_2$.
F^{-1}	PO_4^{-3} and $C_2O_4^{-2}$	Separate as SiF_4; reaction with NaCl.
Cl^{-1}	F^{-1}	Thallium (I) nitrate.
Cl^{-1}	Br^{-1} and I^{-1}	$K_2Cr_2O_7 + H_2SO_4$, 35 N.
Cl^{-1}	ClO^{-1}, ClO_3^{-1}, ClO_4^{-1}	Thallium (I) nitrate.
ClO^{-1} and Cl_2	IO^{-1} and I_2	Aniline + phenol.
ClO^{-1} and Cl_2	BrO^{-1}, Br_2, IO^{-1}, I_2	Evaporate to dryness with PbO_2 + dilute acetic acid; reaction with aniline + *o*-toluidine.
ClO_3^{-1}	BrO_3^{-1} and IO_3^{-1}	Reduce to the state of hydrogen halide anion by means of SO_2.
ClO_3^{-1}	Cl^{-1} and ClO_4^{-1}	$MnSO_4 + H_3PO_4$.
ClO_4^{-1}	ClO_3^{-1} and IO_4^{-1}	Methylene blue + $ZnSO_4$ + $NaNO_3$.
BrO_3^{-1}	ClO_3^{-1} and IO_3^{-1}	Fuchsin + $NaHSO_3$.
Br^{-1}	Cl^{-1}, I^{-1}, BrO_3^{-1}	*m*-Phenylenediamine or fluorescein.
I^{-1}	Cl^{-1} and Br^{-1}	$PdCl_2$ or starch (after oxidation).
IO_3^{-1}	ClO_3^{-1} and BrO_3^{-1}	Starch after reduction with the aid of CNS^{-1}.
IO_4^{-1}	ClO_3^{-1}, ClO_4^{-1}, IO_3^{-1}	$MnCl_2$ + tetramethyldiaminodiphenylmethane.
S^{-2}	SO_3^{-2} and $S_2O_3^{-2}$	Sodium nitrosopentacyanoferrate or antimonyl tartrate.
SO_3^{-2}	$S_2O_3^{-2}$	Malachite green.
$S_2O_3^{-2}$	S^{-2} and SO_3^{-2}	Eliminate the S^{-2} anion by means of $CdCO_3$; reaction with HCl (precipitate of sulphur).
$S_2O_3^{-2}$	S^{-2}	$K_2[HgCl_4]$
$S_2O_3^{-2}$	SO_3^{-2}	Sodium nitride + iodine.
SO_4^{-2}	$[SiF_6]^{-2}$	$KMnO_4 + BaCl_2 + H_2O_2$.
$S_2O_6^{-2}$	BO_2^{-1} and H_2O_2	Benzidine.

ANIONS TO BE IDENTIFIED	ANIONS PRESENT (IN LARGE PROPORTIONS)	REAGENTS USED AND OPERATIONS TO BE CARRIED OUT
PO_4^{-3}	AsO_4^{-3} and SiO_3^{-2}	Eliminate SiO_3^{-2} by evaporation with HCl, and AsO_4^{-3} by precipitation with H_2S; reaction with $(NH_4)_2MoO_4$ + HNO_3 + quinine sulphate.
NO_2^{-1}	NO_3^{-1}	α-Naphthylamine + sulphanilic acid or indole.
NO_3^{-1}	NO_2^{-1}	Decompose the NO_2^{-1} anion by means of NH_3; remove the excess, reduce with Zn + acetic acid; carry out the reaction of NO_2^{-1}.
BO_3^{-3}	IO_4^{-1}	Ignite on charcoal, then reaction of bromothymol blue + mannitol.
CO_3^{-2}	SO_3^{-2}	Liberate CO_2 by means of chromic acid.
CO_3^{-2}	NO_2^{-1}	Liberate CO_2 in the presence of aniline hydrochloride.
SiO_3^{-2}	PO_4^{-3} and AsO_4^{-3}	Isolate SiO_3^{-2} in the form of SiF_4, then reaction with molybdic acid or with sodium chloride.
SiO_3^{-2}	BO_3^{-3}	Eliminate BO_3^{-3} by means of methyl alcohol, then convert SiO_3^{-2} into SiF_4, etc.
CN^{-1}	CNS^{-1} and $[Fe(CN)_6]^{-4}$	Alloxan + ammonia.
CN^{-1}	Cl^{-1}, Br^{-1}, I^{-1}	Liberate HCN by means of $NaHCO_3$; then reaction with copper acetate + benzidine acetate.
CNS^{-1}	CN^{-1}	Sodium nitride + iodine.
$[Fe(CN)_6]^{-4}$	$[Fe(CN)_6]^{-3}$	Luteocobaltic nitrate.
$[Fe(CN)_6]^{-3}$	$[Fe(CN)_6]^{-4}$	Benzidine acetate.
HCO_2^{-1}	$CH_3CO_2^{-1}$	Methylene blue + $NaHSO_3$.
$CH_3CO_2^{-1}$	HCO_2^{-1}	Lanthanum nitrate + iodine.
$C_2O_4^{-2}$	$CH_3CO_2^{-1}$	Mg + 2 : 7-dihydroxynaphthalene.

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TABULAR SUMMARY

TABULAR SUMMARY

No.	Substance identified	Reagents or test reactions	Page
1	Ag^{+1}	A. KBr + metol	3
		B. $(NH_4)_2[Ce(SO_4)_3]$ + HCl or $(NH_4)_2[Ce(NO_3)_6]$ + HNO_3	4
		C. $MnSO_4$ + $KMnO_4$ + HCl	5
		D. RbCl	6
		E. Dimethylaminobenzylidenerhodanine	7
2	Hg^{+1}, Hg^{+2}	A. Diphenylcarbazide + HNO_3	8
		B. $SnCl_2$ + aniline	10
		C. $NaNO_2$ + $AgNO_3$	11
		D. Iodine derivative of methylene blue	12
3	Cu^{+2}	A. $ZnSO_4$ + $(NH_4)_2[Hg(CNS)_4]$	13
		B. $Fe(CNS)_3$ + $Na_2S_2O_3$	15
		C. Rubeanic acid	16
		D. Na-salicylate + NH_3 + benzidine acetate + KCN	17
4	Pb^{+2}	A. Thiourea + HNO_3	19
		B. Dithizone + KCN	20
		C. Tetramethyldiaminodiphenylmethane + H_2O_2 + KOH	22
5	Bi^{+3}	A. $SnCl_2$ + KOH	23
		B. $SnCl_2$ + KOH + $(CH_3COO)_2Pb$	24
		C. Cinchonine + KI	26
		D. KCNS	27
		E. Thiourea	28
6	Cd^{+2}	A. Brucine acetate + NaBr	29
		B. Cadion + KOH	30
		C. Dinitrodiphenylcarbazide + KCN + NaOH + HCHO	32
		D. Na-oxalate	33
7	As^{+3}	A. Zn + HCl + $HgCl_2$	34
		B. Al + KOH + $HgCl_2$	35
	As^{+5}	C. $FeMoO_4$	37
8	Sb^{+3}	A. Rhodamine B	38
		B. $H_7[P(Mo_2O_7)_6]$	39
	Sb^{+3}, Sb^{+5}	C. Gallocyanine	40
9	Sn^{+2}	A. Zn + HCl	41
	Sn^{+2}, Sn^{+4}	B. Dimethylglyoxime + tartaric acid + $FeCl_3$	42
	Sn^{+2}	C. Cacotheline	44
10	Au^{+3}	A. Tetramethyldiaminodiphenylmethane	45
		B. Aniline sulphate	47
		C. Pyridine + HBr	48
11	Ru^{+3}	A. Thiourea	49
		B. Rubeanic acid	49

No.	Substance identified	Reagents or test reactions	Page
12	Rh^{+3}	A. $SnCl_2$	50
13	Pd^{+2}	A. Dimethylglyoxime	51
		B. Dimethylaminobenzylidenerhodanine	52
		C. Hg_2Cl_2	53
		D. Anthranilic acid	53
14	Os^{+4}, Os^{+8}	A. Thiourea	54
	Os^{+8}	B. KCNS	55
	Os^{+4}, Os^{+6}	C. β-Naphthylamine hydrochloride	55
15	Ir^{+4}	A. Malachite green (leucobase)	56
		B. H_2SO_4 with HNO_3 or $AgNO_3$ or NH_4NO_3	57
		C. Benzidine acetate	58
16	Pt^{+4}	A. KCl	59
		B. Narcotine + $SnCl_2$ + $FeSO_4$	59
		C. NaI + NH_3	60
		D. Rubeanic acid	61
17	Se^{+4}, Se^{+6}	A. SO_2 (gaseous) or Na-metabisulphite (solid)	62
	Se^{+4}	B. HI	63
		C. Pyrocatechol	64
		D. Pyrrole + $FeCl_3$ + H_3PO_4	64
		E. NH_4CNS + HCl	65
		F. Diphenylhydrazine (asymmetric)	66
18	Te^{+6}	A. $(NH_4)_2S_n$ + Na_2SO_3	67
	Te^{+4}, Te^{+6}	B. H_3PO_2	68
	Te^{+4}	C. $SnCl_2$ + NaOH	69
	Te^{+6}	D. $CuSO_4 \cdot 5\,H_2O$ + NaOH + $K_2S_2O_8$	70
		E. $MnSO_4$ + Cu^{+2} + NaOBr	71
19	Ge^{+4}	A. $(NH_4)_2MoO_4$	72
		B. $(NH_4)_2MoO_4$ + benzidine	73
		C. *d*-Mannitol + phenolphtalein	74
		D. Quinalizarin	75
		E. $(NH_4)_2MoO_4$ + Na_2SnO_2	76
20	Mo^{+6}	A. $TlNO_3$	77
		B. KCNS + $SnCl_2$	78
		C. Phenylhydrazine	79
		D. K-xanthogenate	80
		E. Ethyl acetate + $Na_2S_2O_3$	81
		F. αα′-Dipyridyl + $SnCl_2$	82
21	W^{+6}	$TlNO_3$	83
		B. $SnCl_2$	84
22	V^{+5}	A. Hydroxyquinoline	85
		B. H_2O_2	87
		C. Dimethylglyoxime + $FeCl_3$ + NH_3	88
		D. Benzidine acetate	89
		E. Hydroxyquinoline + isoamylalcohol	90

No.	Substance identified	Reagents or test reactions	Page
23	Nb^{+5}	A. NaOH + Na-acetate	91
		B. *m*-Digallic acid	92
		C. KCNS + Zn + HCl	93
		D. Zn	93
		E. Pyrocatechol	94
		F. Na_2SO_3 + pyrogallol	95
24	Ta^{+5}	A. KF	96
		B. *m*-Digallic acid	97
		C. Rhodamine B	97
		D. Methylene blue	98
25	Al^{+3}	A. Cs_2SO_4	108
		B. Alizarine S	109
		C. Alizarine red PS	110
		D. Morin	111
26	Fe^{+2}	A. $\alpha\alpha'$-Dipyridyl	112
		B. *o*-Phenanthroline	114
		C. Dimethylglyoxime	115
	Fe^{+3}	D. Hydroxy-sulphonic-benzoïc acid	116
		E. $K_4[Fe(CN)_6]$	117
		F. Pyramidon + NH_4CNS + Co^{+2}	119
27	CrO_4^{-2}	A. Chromotropic acid	120
		B. H_2O_2	122
		C. Guaiacum resin	123
		D. Strychnine	124
	Cr^{+3}	E. Cs_2SO_4 or CsCl + $KHSO_4$	125
28	UO_2^{+2}	A. 8-Hydroxyquinoline	127
		B. $K_4[Fe(CN)_6]$	128
		C. Quercetin	129
		D. Na-salicylate	130
		E. Anthranilic acid	131
29	$R.E.^{+3}$	A. Oxalic acid	134
30	$C.E.^{+3}$	A. NH_4-succinate	135
31	$Y.E.^{+3}$	A. Lactic acid	136
32	La^{+3}	A. I_2	137
33	Ce^{+4}	A. Anthranilic acid	138
		B. *o*-Tolidine	140
		C. *p*-Phenetidine	141
34	Eu^{+2}	A. Cacotheline + Zn	142
35	Y	———	144
36	Ti^{+4}	A. H_2O_2 + H_2SO_4	144
		B. H_3AsO_4 + $ZrOCl_2$	145
		C. Chromotropic acid	147
37	Zr^{+4}	A. *p*-Dimethylamino-4-azophenylarsonic acid	148
		B. RbCl + NH_4F	149

No.	Substance identified	Reagents or test reactions	Page
		C. Carminic acid	150
		D. Alizarin S	151
38	Hf	———	152
39	Th^{+4}	A. $(NH_4)_2CO_3$ + $TlNO_3$	153
		B. KJO_3	154
		C. Alizarin	155
40	Gl^{+2}, Be^{+2}	A. Acetylacetone	156
		B. *p*-Nitrobenzene-azo-orcinol	157
		C. Ethylenediamine + quinalizarin	158
41	Tl^{+1}	A. $H_7[P(Mo_2O_7)_6]$ + HBr	159
		B. $Bi(NO_3)_3$ + NaI	160
	Tl^{+3}	C. Martius yellow	161
		D. *o*-Tolidine	162
42	Sc^{+3}	A. Cochineal	163
		B. Luteocobaltic nitrate + NaF	164
43	Ga^{+3}	A. CsCl + $KHSO_4$	165
		B. $MnCl_2$ + $KBrO_3$ + $K_4[Fe(CN)_6]$	166
44	In^{+3}	A. Urotropine + NH_4CNS	168
		B. Alizarin	169
45	Zn^{+2}	A. $(NH_4)_2[Hg(CNS)_4]$ + $CuSO_4$	171
		B. $(NH_4)_2[Hg(CNS)_4]$ + $CoCl_2$	172
		C. *p*-Nitrobenzene-azo-orcinol	174
		D. $K_3[Fe(CN)_6]$ + *p*-phenetidine	175
46	Mn^{+2}	A. $K_2S_2O_8$ + $AgNO_3$	177
		B. KIO_4 + *p*-tetramethyldiaminodiphenylmethane	178
		C. KNO_3 + Na_2CO_3	180
		D. Cyanuric acid	181
		E. Acetylsalicylic acid + H_2O_2	181
	MnO_4^{-1}	F. $RbNO_3$ + $KClO_4$	182
		G. *o*-Tolidine	183
47	Re^{+3}	A. $SnCl_2$ + Na_2TeO_4	184
	Re^{+3}, ReO_4^{-1}	B. $SnCl_2$ + dimethylglyoxime	186
	ReO_4^{-1}	C. Acridine hydrochloride	187
48	Co^{+2}	A. $(NH_4)_2[Hg(CNS)_4]$ + Zn^{+2}	188
		B. Rubeanic acid	190
		C. Nitroso-naphthol	191
		D. Nitroso-naphthol-sulphonic acid	193
		E. KCNO	194
		F. KCNS	195
49	Ni^{+2}	A. *o*-Cyclohexanedionedioxime	196
		B. Dimethylglyoxime	197
		C. Diphenylglyoxime	199
		D. Diacetylmonoxime	200
		E. Rubeanic acid	201

No.	Substance identified	Reagents or test reactions	Page
		F. $(NH_4)_2MoO_4$	202
50	Ra^{+2}	A. $(NH_4)_2CO_3$ + K_2CrO_4	210
51	Ba^{+2}	A. K_2CrO_4	210
		B. $KMnO_4$ + H_2SO_4	211
		C. $(NH_4)_2[SiF_6]$	212
52	Sr^{+2}	A. $Cu(NO_3)_2$ + KNO_2	213
		B. HNO_3	214
53	Ca^{+2}	A. H_2SO_4	215
		B. Loretine	217
54	Mg^{+2}	A. Magneson	218
		B. Titan yellow	219
		C. KIO	220
55	Li^{+1}	A. $(NH_4)_2CO_3$	225
		B. Na_2HPO_4	226
		C. KIO_4 + $FeCl_3$ + KOH	227
56	Na^{+1}	A. $(CH_3COO)_2UO_2$	227
		B. $(CH_3COO)_2UO_2 . (CH_3COO)_2Mg$	228
		C. $(CH_3COO)_2UO_2 . (CH_3COO)_2Zn$	229
		D. $Bi(NO_3)_3$ + KNO_2 + $CsNO_3$	230
57	K^{+1}	A. $Na_3[Co(NO_2)_6]$	231
		B. $H_2[PtCl_6]$	232
		C. $(CH_3COO)_2Pb$ + $(CH_3COO)_2Cu$ + $NaNO_2$	233
		D. Dipicrylamine	234
		E. $Na_2Pb[Co(NO_2)_6]$	235
58	Rb^{+1}	A. $SiO_2 . 12\ MoO_2 . 2\ H_2O . nH_2O$	236
		B. $AuBr_3$ + AgBr	237
		C. Dipicrylamine	238
59	Cs^{+1}	A. $H_8[Si(W_2O_7)_6]$	239
		B. $SiO_2 . 12\ MoO_2 . 2\ H_2O . nH_2O$	240
		C. $K[BiI_4]$	241
		D. $AuBr_3$ + $PtBr_4$	242
		E. $K_3[Fe(CN)_6]$ + $(CH_3COO)_2Pb$	243
		F. AgI + NaI	243
		G. $(CH_3COO)_2Pb$ + KI	244
60	NH_4^{+1}	A. $AgNO_3$ + HCHO	245
		B. Hg_2Cl_2	246
		C. $K_2[HgI_4]$	247
		D. $H_2[PtCl_6]$	248
		E. $MnSO_4$ + $AgNO_3$ + benzidine	249
		F. *p*-Nitrobenzene diazoniumchloride	250
		G. Litmus	251
61	F^{-1}	A. SiO_2 + H_2SO_4 + NaCl	259
		B. Alizarin S + zirconylchloride	260
62	Cl^{-1}	A. $K_2Cr_2O_7$ + H_2SO_4 + diphenylcarbazide	261

No.	Substance identified	Reagents or test reactions	Page
		B. $TlNO_3$ + if necessary $Pt(SO_4)_2$	263
		C. Aniline + *o*-tolidine or aniline + phenol	264
63	Br^{-1}	A. *m*-Phenylenediamine or fluorescein	265
64	I^{-1}	A. NHg_2NO_3	265
		B. $PdCl_2$	266
		C. $(NH_4)_2[Ce(SO_4)_3]$ + $NaAsO_2$	267
		D. Starch	268
65-66	Cl_2, ClO^{-1}	A. Aniline + *o*-tolidine	269
		B. Aniline + phenol	270
67-68	Br_2	A. *m*-Phenylenediamine	271
		B. Fluorescein	273
69	I_2	A. Starch	274
70	ClO_3^{-1}	A. $MnSO_4$ + H_3PO_4 + if necessary *sym*-diphenylcarbazide	276
71	ClO_4^{-1}	A. Methylene blue	277
		B. Methylene blue + $ZnSO_4$ + $NaNO_3$	278
72	BrO_3^{-1}	A. Fluorescein or Schiff's reagent	279
73	IO_3^{-1}	A. KCNS	280
74	IO_4^{-1}	A. $MnCl_2$ + *p*-tetramethyldiaminodiphenylmethane	280
75	S^{-2}	A. $Na_2[Fe(CN)_5(NO)] \cdot 2\ H_2O$	281
		B. Potassium antimonyl tartrate	282
		C. NaN_3 + I_2	283
76-77	SO_3^{-2}	A. Malachite green	284
		B. $Ni(OH)_2$ + benzidine	285
78	$S_2O_3^{-2}$	A. NaN_3 + I_2	287
		B. $Ni(OH)_2$ + benzidine	287
79	SO_4^{-2}	A. $KMnO_4$ + $BaCl_2$ + H_2O_2	288
80	$S_2O_8^{-2}$	———	290
81	N_3^{-1}	A. $FeCl_3$	290
82	NO_2^{-1}	A. α-Naphtylamine + *p*-sulphanilic acid	291
		B. Indole	293
83	NO_3^{-1}	A. α-Naphtylamine + *p*-sulphanilic acid	294
84	PO_4^{-3}	A. $(NH_4)_2MoO_4$ + quinine sulphate	295
85	BO_3^{-3}	A. Bromothymol blue + *d*-mannitol	296
86	SiO_3^{-2}	A. H_2MoO_4 + $SnCl_2$	297
		B. NaCl	299
87	CO_3^{-2}	A. $(CH_3COO)_2Sr$ + $(CH_3COO)Na$	299
		B. Na_2CO_3 + phenolphtalein	300
88	CN^{-1}	A. Alloxan + NH_3	300
		B. $(CH_3COO)_2Cu$ + benzidine acetate	301
89	CNS^{-1}	A. $FeCl_3$ + HCl	303
		B. NaN_3 + I_2	304
90	$[Fe(CN)_6]^{-4}$	A. $FeCl_3$	304
		B. $[Co(NH_3)_6](NO_3)_3$	305

No.	Substance identified	Reagents or test reactions	Page
91	$[Fe(CN)_6]^{-3}$	A. Benzidine acetate	306
		B. $[Co(NH_3)_6](NO_3)_3$	307
92	HCO_2^{-1}	A. Methylene blue	308
93	$CH_3CO_2^{-1}$	A. $La(NO_3)_3 + I_2$	309
94	$C_2O_4^{-2}$	A. Mg + 2 : 7-dihydroxynaphthalene	310

TABLE OF REAGENTS

TABLE OF REAGENTS

A

Acetylacetone, Gl, Be, 156.
Acetylsalicylic acid, Mn, 181.
Acridine hydrochloride, Re, 187.
Alizarin, Th, 155; In, 169.
Alizarin Bordeaux, Ge, 75; Gl, Be, 158.
— Red PS, Al, 110.
— S, Al, 109; Zr, 151; F^{-1}, 260.
Alloxan, CN^{-1}, 300.
Aluminium, As, 35.
p-Aminobenzene sulphonic acid, NO_2^{-1}, 291; NO_3^{-1}, 294.
o-Aminobenzoic acid, Pd, 53; UO_2^{+2}, 131; Cc, 138.
Ammonia, Cu, 17; Sn, 42; Pt, 60; V, 88; CN^{-1}, 300.
Ammonium carbonate, Th, 153; Ra, 210; Li, 225.
— ethane - 1 : 2 - dicarboxylate, C. E., 135.
— fluoride, Zr, 149.
— hydroxide, Cu, 17; Sn, 42; Pt, 60; V, 88; CN^{-1}, 300.
— mercurithiocyanate, Cu, 13; Zn, 171; Zn, 172; Co, 188.
— molybdate, Ge, 72; Ge, 73; Ge, 76; Ni, 202; PO_4^{-3}, 295.
— 12 - molybdatosilicate, Rb, 236; Cs, 240.
— nitrate, Ir, 56.
— polysulphide, Te, 67.
— silicofluoride, Ba, 212.
— silico - 12 - molybdate, Rb, 236; Cs, 240.
— succinate, C. E., 135.
— thiocyanate, Se, 65 ; Fe, 119; In, 168.
Aniline, Hg, 10; Cl^{-1}, 264; Cl_2, 269; ClO^{-1}, 270.
— sulphate, Au, 47.
Anthranilic acid, Pd, 53; UO_2^{+2}, 131; Ce, 138.
Arsenic acid, Ti, 145.
Aspirin, Mn, 181.
Auric bromide, Rb, 237; Cs, 242.
1 - (1′ - Azo - 2′ : 4′ - dihydroxyphenyl) - 4 - nitrobenzene, Mg, 218.
1 - (1′ - Azo - 2′ - methyl - 4′ : 6′ - dihydroxyphenyl) - 4 - nitrobenzene, Gl, Be, 157; Zn, 174.

B

Barium chloride, SO_4^{-2}, 288.
Benzidine acetate, Cu, 17; Ir, 58; Ge, 73; V, 89; NH_4^{+1}, 249; SO_3^{-2}, 285; $S_2O_3^{-2}$, 287; CN^{-1}, 247; $[Fe(CN)_6]^{-3}$, 250.
α-Benzil dioxime, Ni, 199.
3 : 6 - Bis-diethylamino - 9 - (2′ - carboxyphenyl) - xanthonium chloride, Sb, 38; Ta, 97.
2 : 7 - Bis - (dimethylamino) - phenothiazonium chloride, Ta, 98; ClO_4^{-1}, 277; ClO_4^{-1}, 278; HCO_2^{-1}, 308.
— — — di-iodo-iodide, Hg, 12.
Bis - (*p* - dimethylaminophenyl) - methane, Pb, 22; Au, 45; Mn, 178; IO_4^{-1}, 280.
Bis - (*p* - dimethylaminophenyl) - phenylmethane, Ir, 56.
Sym - Bis - (*p* - nitrophenyl) carbazide, Cd, 32.
Bismuth nitrate, Tl, 160; Na, 230.
Bromothymol blue, BO_3^{-3}, 296.
Brucine acetate, Cd, 29.
2 : 3 - Butane dioxime, Sn, 42; Pd, 51; V, 88; Fe, 115; Re, 186; Ni, 197.
2 : 3 - Butanone monoxime, Ni, 200.

C

Cacotheline, Sn, 44; Eu, 142.
Cadion, Cd, 30.
Caesium chloride, Cr, 125; Ga, 165.
— nitrate, Na, 230.
— sulphate, Al, 108; Cr, 125.
Carminic acid, Zr, 150.
Chloroplatinic acid, K, 232; NH_4^{+1}, 248.
Chromotropic acid, CrO_4^{-2}, 120; Ti, 147.
Cinchonine, Bi, 26.
Cobalt, triple nitrite lead-sodium, K, 235.
Cobalt (II) cation, Fe, 119.
— chloride Zn, 172.
Cochineal, Sc, 163.
Complex periodate of iron (III), Li, 226.
Copper (II) acetate, K, 233; CN^{-1}, 301.
— cation, Te, 71.
— nitrate, Sr, 213.
— sulphate, Te, 70; Te, 71; Zn, 171.

Cupric acetate, K, 233; CN^{-1}, 301.
— cation, Te, 71.
— nitrate, Sr, 213.
— sulphate, Te, 70; Te, 71; Zn, 171.
Cyanuric acid, Mn, 181.
o - Cyclohexanedione dioxime Ni, 196.

D

Diacetyl monoxime, Ni, 200.
4 : 4′ - Diamino - 3 : 3′ - dimethyldiphenyl, Ce, 140; Tl, 162; MnO_4^{-1}, 183.
1 : 2 - Diamino-ethane, Gl, 158.
Diammonium hexafluosilicate, Ba, 212.
— hexanitratoceriate(IV)Ag, 4.
— tetrathiocyanatomercurate (II), Cu, 13; Zn, 171; Zn, 172; Co, 188.
— trisulphato ceriate (IV), Ag, 4; I^{-1}, 267.
3 : 3′-Dibromo - 2 : 2′ - dimethyl- 5 : 5′ - diisopropyl - 4′ - hydroxy - 2″ - sulphofuchsone, BO_3^{-3}, 296.
Dibromosulphophtalein, BO_3^{-3}, 296.
m-Digallic acid, Nb, 92; Ta, 97.
Dihydrogen hexachloroplatinic (IV) acid, K, 232; NH_4^{+1}, 248.
1 : 2 - Dihydroxyanthraquinone, Th, 155; In, 169.
1 : 2 - Dihydroxybenzene, Se, 64; Nb, 94.
3 : 6 - Dihydroxyfluoran, Br^{-1}, 265; Br_2, 273; BrO_3^{-1}, 279.
2 : 7 - Dihydroxynaphthalene, $C_2O_4^{-2}$, 310.
1 : 8 - Dihydroxynaphthalene - 3 : 6 - disulphonic acid, CrO_4^{-2}, 120; Ti, 147.
Dimercuri-ammonium nitrate, I^{-1}, 265.
4 - Dimethylamino-antipyrine, Fe, 119.
p - Dimethylamino - 4 - azophenylarsonic acid, Zr, 148.
p - Dimethylaminobenzylidenerhodanine, Ag, 7; Pd 52.
4 - Dimethylamino - 1 - phenyl - 2 : 3 - dimethyl - 5 - pyrazolone, Fe, 119.
4 - (*p* - Dimethylaminophenylmethylene) - 2 - thione - 5 - thiazolidone, Ag, 7; Pd, 52.
5 - (4′ - Dimethylamino) - rhodanine, Ag, 7; Pd, 52.
Dimethylglyoxime, Sn, 42; Pd, 51; V, 88; Fe, 115; Re, 186; Ni, 197.
Sym - Di - *p* - nitrodiphenylcarbazide, Cd, 32.
2 : 4 - Dinitro - 1 - naphtol, Tl, 161.
Sym - Diphenylcarbazide, Hg, 8; Cl^{-1}, 261; ClO_3^{-1}, 276.
α : β - Diphenylethane - α : β - dioxime, Ni, 199.
Diphenylglyoxime, Ni, 199.
as - Diphenylhydrazine, Se, 66.
Diphenylthiocarbazone, Pb, 20.
Dipicrylamine, K, 234; Rb, 238.
Dipotassium tetraiodomercurate (II), NH_4^{+1}, 247.
2 : 2′ - Dipyridyl, Mo, 82; Fe, 112.
α : α′ - Dipyridyl, Mo, 82; Fe, 112.
Disodium hydrogen phosphate, Li, 226.
— nitrosopentacyanoferrate (III), S^{-2}, 281.
Dithiooxamide, Cu, 16; Ru, 49; Pt, 61; Co, 190; Ni, 201.
Dithizone, Pb, 20.
Dodecamolybdophosphoric acid dihydrate, Sb, 39; Tl, 159.

E

1 : 2 - Ethanedithiamide, Cu, 16; Ru, 49; Pt, 61; Co, 190; Ni, 201.
4 - Ethoxy-aminobenzene, Ce, 141; Zn, 175.
Ethyl acetate, Mo, 81.
Ethylenediamine, Gl, Be, 158.

F

Ferric chloride, Sn, 42; Se, 64; V, 88; N_3^{-1}, 290; CNS^{-1}, 303; $[Fe(CN)_6]^{-4}$, 304.
— thiocyanate, Cu, 15.
Ferrous molybdate, As, 37.
— sulphate, Pt, 59.
Fluorescein, Br^{-1}, 265; Br_2, 273; BrO_3^{-1}, 279.
Formaldehyde, NH_4^{+1}, 245.
Fuchsin, BrO_3^{-1}, 279.

G

Gallocyanine, Sb, 40.
Gold (III) bromide, Rb, 237; Cs, 242.
Guaiacum resin, CrO_4^{-2}, 123.

H

Heptahydrogen hexadimolybdatophosphoric acid, Sb, 39; Tl, 159.
Hexamethylenetetramine, In, 168.
Hexamminocobalt (III) nitrate, Sc, 164; $[Fe(CN)_6]^{-4}$, 305; $[Fe(CN)_6]^{-3}$, 307.
2 : 4 : 6 : 2′ : 4′ : 6′ - Hexanitrodiphenylamine, K, 234; Rb, 238.
Hydriodic acid, Se, 63.
Hydrobromic acid, Au, 48; Tl, 159.

Hydrochloric acid, Ag, 4; Ag, 5; As, 34; Sn, 41; Se, 65; Nb, 93; CNS^{-1}, 303.
Hydrogen peroxide, Pb, 22; V, 87; CrO_4^{-2}, 122; Ti, 144; Mn, 181, SO_4^{-2}, 288.
1 - Hydroxy - 2 - oxy - 4 - carboxy - 7 - dimethylamino - oxazine, Sb, 40.
α - Hydroxy-propionic acid, Y. E., 136.
8 - Hydroxyquinoline, V, 85; V, 90; UO_2^{+2}, 127.
2 - Hydroxy - 5 - sulphonic benzoic acid, Fe, 116.
Hypophosphorous acid, Te, 68.

I

Indole, NO_2^{-1}, 293.
Iodine, La, 137; S^{-2}, 283; $S_2O_3^{-2}$, 287; CNS^{-1}, 304; $CH_3CO_2^{-1}$, 309.
7 - Iodo - 8 - hydroxyquinoline - 5 - sulphonic acid, Ca, 217.
Iron (II) molybdate, As, 37.
— (II) sulphate, Pt, 59.
— (III) chloride, Sn, 42; Se, 64; V, 88; N_3^{-1}, 290; CNS^{-1}, 303; $[Fe(CN)_6]^{-4}$, 304.
— (III) thiocyanate, Cu, 15.
Isoamyl alcohol, V, 90.

L

Lactic acid, Y. E., 136.
Lanthanum nitrate, $CH_3CO_2^{-1}$, 309.
Lead acetate, Bi, 24; K, 233; Cs, 243; Cs, 244.
— triple nitrite cobalt-sodium, K, 235.
Leucobase of malachite green, Ir, 56.
Litmus, NH_4^{+1}, 251.
Loretine, Ca, 217.
Luteocobaltic nitrate, Sc, 164; $[Fe(CN)_6]^{-4}$, 305; $[Fe(CN)_6]^{-3}$, 307.

M

Magnesium, $C_2O_4^{-2}$, 310.
— uranyl acetate, Na, 228.
Magneson, Mg, 218.
Malachite green, SO_3^{-2}, 284.
— — (leucobase of —), Ir, 56.
Manganese (II) chloride, Ga, 166; IO_4^{-1}, 280.
— sulphate, Ag, 5; Fe, 71; NH_4^{+1}, 249; ClO_3^{-1}, 276; BrO_3^{-1}, 279.
Manganous chloride, Ga, 166; IO_4^{-1}, 280.
— sulphate, Ag, 5; Te, 71; NH_4^{+1}, 249; ClO_3^{-1}, 276; BrO_3^{-1}, 279.
α - Mannitol, Ge, 74; BO_3^{-3}, 296.
Martius yellow, Tl, 161.
Mercuric chloride, As, 34; As, 35.
Mercurous chloride, Pd, 53; NH_4^{+1}, 246.
Mercury (I) chloride, Pd, 53; NH_4^{+1}, 246.
Mercury (II) chloride, As, 34; As, 35.
Methanal, NH_4^{+1}, 245.
Methylamino - 4 - phenol sulphate, Ag, 3.
Methylene blue, Ta, 98; ClO_4^{-1}, 277; ClO_4^{-1}, 278; HCO_3^{-1}, 308.
— — iodine derivative, Hg, 12.
Metol, Ag, 3.
12 - Molybdatosilicic acid, Rb, 236; Cs, 240.
Molybdic acid, SiO_3^{-2}, 297.
Monopotassium tetraiodobismuthate, Cs, 241.
Morin, Al, 111.
α - Naphthylamine, NO_2^{-1}, 291; NO_3^{-1}, 294.
β - Naphthylamine hydrochloride, Os, 55.

N

Narcotine, Pt, 59.
Nessler reagent, NH_4^{+1}, 247.
Nickel (II) hydroxide, SO_3^{-2}, 285; $S_2O_3^{-2}$, 287.
Nitric acid, Pb, 19; Ir, 57; Sr, 214.
p - Nitrobenzene-azo-orcinol, Gl, Be, 157; Zn, 174.
p - Nitrobenzene-azo-resorcinol, Mg, 218.
p - Nitrobenzene diazoniumchloride, NH_4^{+1}, 250.
p - Nitrophenyldiazoaminobenzene - p - azobenzene, Cd, 30.
α - Nitroso-β-naphthol, Co, 191.
β - Nitroso-α-naphthol, Co, 191.
1 - Nitroso-2-naphthol, Co, 191.
2 - Nitroso-1-naphthol, Co, 191.
2 - Nitroso-4-sulpho-1-naphthol, Co, 193.

O

Octahydrogen hexaditungstatosilicic acid, Cs, 239.
Oxalic acid, R. E., 134.

P

Palladium (II) chloride, I^{-1}, 266.
Palladous chloride, I^{-1}, 266.
3 : 5 : 7 : 2′ : 4′ - Pentahydroxyflavone, Al, 111.
3 : 5 : 7 : 3′ : 4′ - Pentahydroxyflavone, UO_2^{+2}, 129.
2 : 4 - Pentanedione, Gl, Be, 156.

o - Phenanthroline, Fe, 114.
p - Phenetidine, Ce, 141; Zn, 175.
Phenol, Cl^{-1}, 264; ClO^{-1}, 270.
Phenolphthalein, Ge, 74; CO_3^{-2}, 300.
m - Phenylenediamine, Br^{-1}, 265; Br_2, 271.
Phenylhydrazine, Mo, 79.
Phosphomolybdic acid, Sb, 39; Tl, 159.
Phosphoric acid, Se, 64; ClO_3^{-1}, 276.
Platinic bromide, Cs, 242.
— sulphate, Cl^{-1}, 263.
Platinum (IV) bromide, Cs, 242.
— sulphate, Cl^{-1}, 263.
Potassium antimonyl tartrate, S^{-2}, 282.
— bismuthiiodide, Cs, 241.
— bromate, Ga, 166.
— bromide, Ag, 3.
— chloride, Pt, 59.
— chromate, Ra, 210; Ba, 210.
— cyanate, Co, 194.
— cyanide, Cu, 17; Pb, 20.
— dichromate, Cl^{-1}, 261.
— ethylxanthate, Mo, 80.
— ferricyanide, Zn, 175; Cs, 243.
— ferrocyanide, Fe, 117; UO_2^{+2}, 128; Ga, 166.
— fluoride, Ta, 96.
— hydrogen sulphate, Cr, 125; Ga, 165.
— hydroxide, Pb, 22; Bi, 23; Bi, 24; As, 35.
— hypoiodite, Mg, 220.
— iodate, Th, 154.
— iodide, Bi, 26; Cs, 244.
— mercuri-iodide, NH_4^{+1}, 247.
— nitrate, Mn, 180.
— nitrite, Sr, 213; Na, 230.
— perchlorate, MnO_4^{-1}, 182.
— periodate, Mn, 178.
— permanganate, Ag, 5; Ba, 211; SO_4^{-2}, 288.
— peroxydisulphate, Te, 70; Mn, 177.
— persulphate, Te, 70; Mn, 177.
— thiocyanate, Bi, 27; Os, 55; Mo, 78; Nb, 93; Co, 195; IO_3^{-1}, 280.
— xanthogenate, Mo, 80.
Pyramidon, Fe, 119.
Pyridine, Au, 48.
Pyrocatechol, Se, 64; Nb, 94.
Pyrogallol, Nb, 95.
Pyrrole, Se, 64.

Q

Quercetin, UO_2^{+2}, 129.
Quinalizarin, Ge, 75; Gl, Be, 158.
Quinine sulphate, PO_4^{-3}, 295.

R

Rhodamine B, Sb, 38; Ta, 97.
Riegler's reagent, NH_4^{+1}, 250.
Rubeanic acid, Cu, 16; Ru, 49; Pt, 61; Co, 190; Ni, 201.
Rubidium chloride, Ag, 6; Zr, 149.
— nitrate, MnO_4^{-1}, 182.

S

Salt of bis - (*p* - dimethylaminophenyl) - phenylcarbinol, SO_3^{-2}, 284.
Schiff's reagent, BrO_3^{-1}, 279.
Silico - 12 - molybdic acid, Rb, 236; Cs, 240.
Silicon dioxide, F^{-1}, 259.
Silicotungstic acid, Cs, 239.
Silver bromide, Rb, 237.
— iodide, Cs, 243.
— nitrate, Hg, 11; Ir, 57; Mn, 177; NH_4^{+1}, 245; NH_4^{+1}, 249.
Sodium acetate, Nb, 91; CO_3^{-2}, 299.
— alizarin - 3 - sulphonate, Al, 109; Zr, 151; F^{-1}, 260.
— arsenite, I^{-1}, 267.
— bromide, Cd, 29.
— cobaltinitrite, K, 231.
— dehydrothio - *p* - toluidine-sulpho - *p* - diazoaminodehydrothio - toluidine sulphonate, Mg, 219.
— 1 : 2 - dihydroxy - anthraquinone - 3 - sulphonate, Al, 109; Zr, 151; F^{-1}, 260.
— fluoride, Se, 164.
— hydrogen sulphite, HCO_3^{-1}, 308.
— hydroxide, Cd, 45; Te, 69; Te, 70; Nb, 91.
— biphosphate, Li, 226.
— bromide, Cd, 29.
— carbonate, Mn, 180; CO_3^{-2}, 300.
— chloride, F^{-1}, 259; SiO_3^{-2}, 299.
— 2 - hydroxybenzoate, Cu, 17; UO_2^{+2}, 130.
— hypobromite, Te, 71.
— iodide, Pt, 60; Tl, 160; Cs, 243.
— metabisulphite, Se^{+4}, Se^{+6}, 62.
— nitrate, ClO_4^{-1}, 278.
— nitride, S^{-2}, 283; $S_2O_3^{-2}$, 287; CNS^{-1}, 304.
— nitrite, Hg, 11; K, 233.
— nitroprusside, S^{-2}, 281.
— oxalate, Cd, 33.
— purpurin - 3 - sulphonate, Al, 110.
— salicylate, Cu, 17; UO_2^{+2}, 130.
— stannite, Ge, 76.
— sulphite, Te, 67; Nb, 95.
— tellurate, Re, 184.

— thiosulphate, Cu, 15; Mo, 81.
— 1 : 2 : 4 - trihydroxyanthraquinone - 3 - sulphonate, Al, 110.
— triple nitrite lead-cobalt, K, 235.
Stannous chloride, Hg, 10; Bi, 23; Bi, 24; Rh, 50; Pt, 59; Te, 69; Mo, 78; Mo, 82; W, 84; Re, 184; Re, 186; SiO_3^{-2}, 297.
Starch, I^{-1}, 268; I_2, 274; IO_3^{-1}, 280.
Strontium acetate, CO_3^{-2}, 299.
Strychnine, CrO_4^{-2}, 124.
p - Sulfanilic acid, NO_2^{-1}, 291; NO_3^{-1}, 294.
Sulphur dioxide, Se, 62.
Sulphuric acid, Ir, 57; Ti, 144; Ba, 211; Ca, 215; F^{-1}, 259; Cl^{-1}, 261; BrO_3^{-1}, 279.

T

Tartaric acid, Sn, 42.
Tetraethylrhodamine, Sb, 38; Ta, 97.
1 : 2 : 5 : 8 - Tetrahydroxyanthraquinone, Ge, 75; Gl, Be, 158.
p - Tetramethyldiamino - diphenylmethane, Pb, 22; Au, 45; Mn, 178; IO_4^{-1}, 280.
Tetrapotassium hexacyanoferrate (II), Fe, 117; UO_2^{+2}, 128; Ga, 166.
Thallium (I) nitrate, Mo, 77; W, 83; Th, 153; Cl^{-1}, 263.
Thallous nitrate, Mo, 77; W, 83; Th, 153; Cl^{-1}, 263.
Thiazole yellow, Mg, 219.
Thiocarbamide, Pb, 19; Bi, 28; Ru, 49; Os, 54.
Thiourea, Pb, 19; Bi, 28; Ru, 49; Os, 54.
Tin (II) chloride, Hg, 10; Bi, 23; Bi, 24; Rh, 50; Pt, 59; Te, 69; Mo, 78; Mo, 82; W, 84; Re, 184; Re, 186; SiO_3^{-2}, 297.
Titan yellow, Mg, 219.
Titan yellow G, Mg, 219.
o - Tolidine, Ce, 140; Tl, 162; MnO_4^{-1}, 183.
o - Toluidine, Cl^{-1}, 264; Cl_2, 269.
1 : 2 : 3 - Trihydroxybenzene, Nb, 95.
2 (3′ : 6′ : 9′ - Trihydroxyxanthyl) - benzolide, Br^{-1}, 265; Br_2, 273; BrO_3^{-1}, 279.
Triple nitrite of lead, cobalt and sodium, K, 235.
Tripotassium hexacyanoferrate (III), Zn, 175; Cs, 243.
Trisodium hexanitritocobaltate (III), K, 231.

U

Uranyl acetate, Na, 227.
Urotropine, In, 168.

Z

Zinc, As, 34; Sn, 41; Nb, 93; Eu, 142.
— cation, Co, 188.
— sulphate, Cu, 13; ClO_4^{-1}, 278.
— uranyl acetate, Na, 229.
Zirconium oxydichloride, Ti, 145; F^{-1}, 260.
Zirconyl chloride, Ti, 145; F^{-1}, 260.

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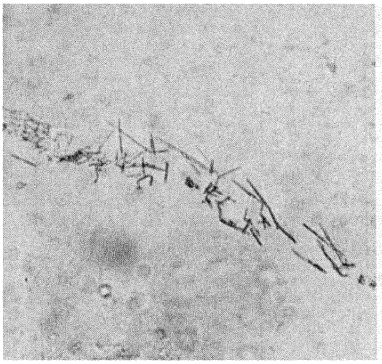


Photo 1.

Reaction of Ag^{+1}
with RbCl (1 D, p. 6) × 75

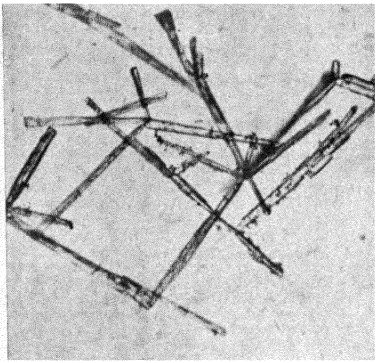


Photo 2.

Reaction of Pb^{+2}
with thiourea (4 A, p. 19) × 75

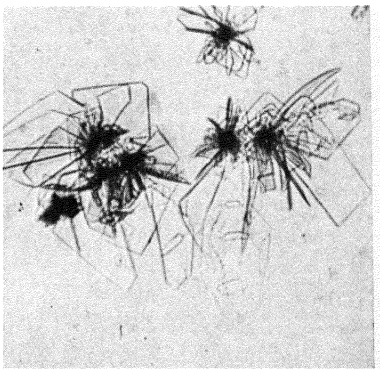


Photo 3.

Reaction of Cd^{+2}
with brucine acetate and NaBr
(6 A, p. 29) × 75

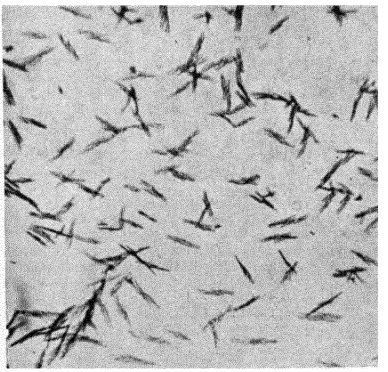


Photo 4.

Reaction of Au^{+3}
with pyridine and HBr
(10 C, p. 48) 75

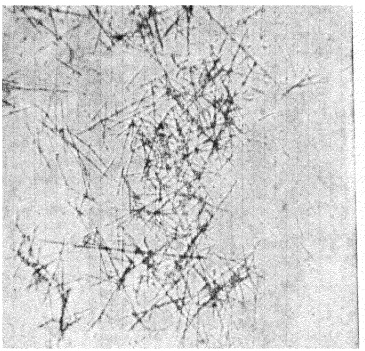


Photo 5.

Reaction of Pd^{+2}
with dimethylglyoxime
(13 A, p. 51) × 75

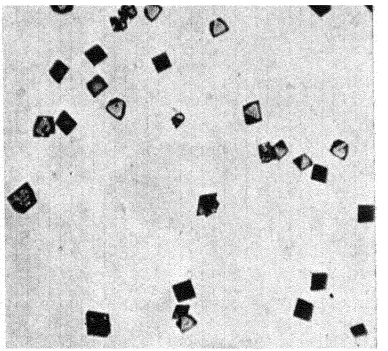


Photo 6.

Reaction of Pt^{+4}
with KCl (16 A, p. 59) × 225

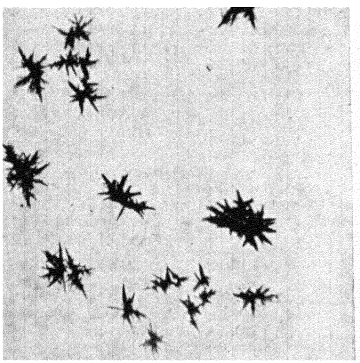


Photo 7.

Reaction of Pt^{+4}
with NaI and NH_4OH
(16 C, p. 60) × 75

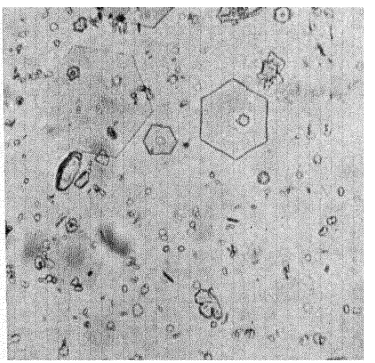


Photo 8.

Reaction of Mo^{+6} with $TlNO_3$
(20 A, p. 77) × 75

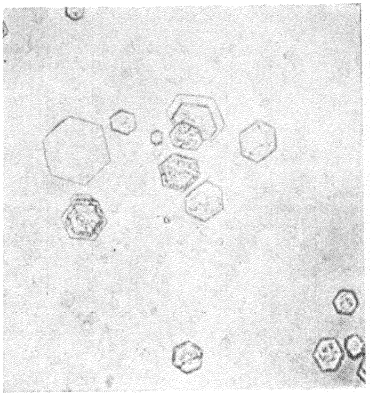


Photo 9.

Reaction of W^{+6} with $TlNO_3$
(21 A, p. 83) × 75

Photo 10.

Reaction of Nb^{+5} with NaOH
and CH_3CO_2Na (23 A, p. 91) × 75

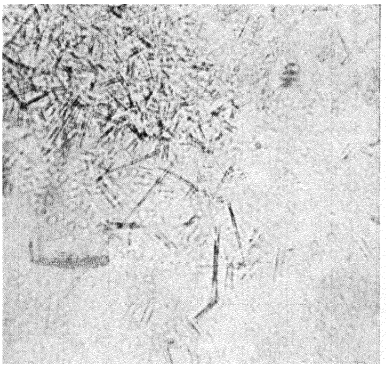


Photo 11.

Reaction of Ta^{+5} with KF
(24 A, p. 96) × 75

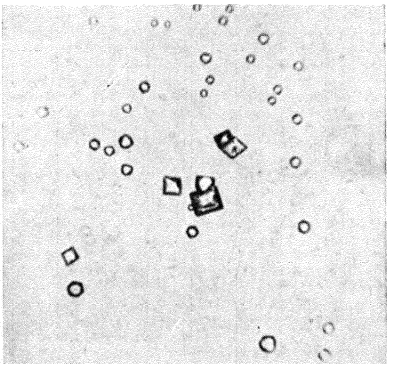


Photo 12.

Reaction of Al^{+3} with Cs_2SO_4
(25 A, p. 108) × 75

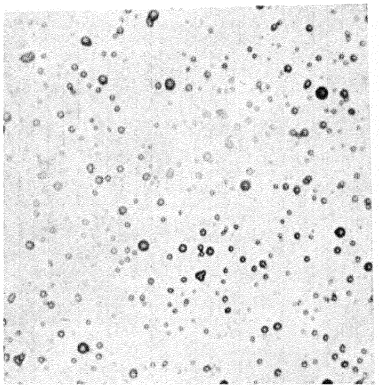


Photo 13.

Reaction of Fe^{+3} with pyramidon, NH_4CNS and Co^{+2} (26 F, p. 119) × 75

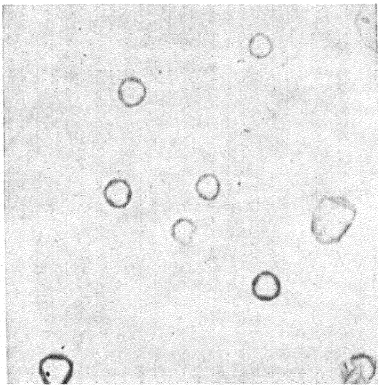


Photo 14.

Reaction of Cr^{+3} with Cs_2SO_4 (27 E, p. 125) × 75

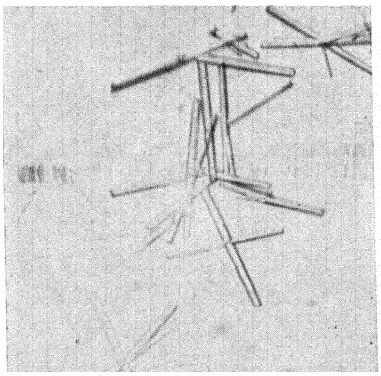


Photo 15.

Reaction of UO_2^{+2} with anthranilic acid (28 E, p. 131) × 225

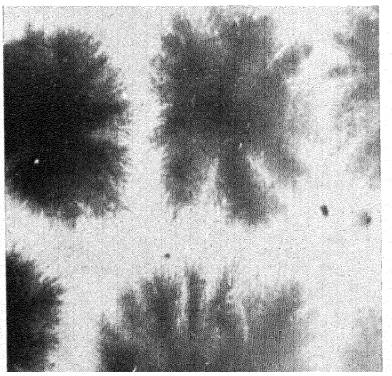


Photo 16.

Reaction of Cerium earths with ammonium succinate (30 A, p. 135) × 75

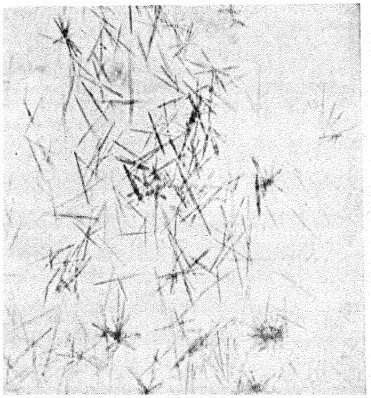
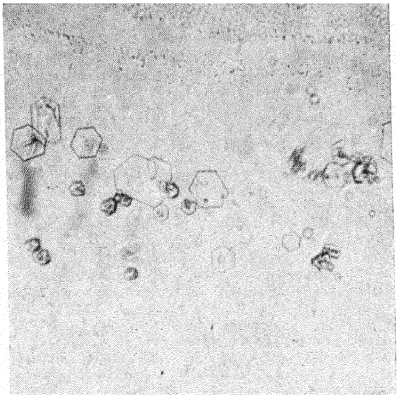


Photo 17.

Reaction of Yttrium earths with lactic acid (31 A, p. 136) × 75



Reaction of Zr^{+4} with RbCl and NH_4F (37 B, p. 149) × 75

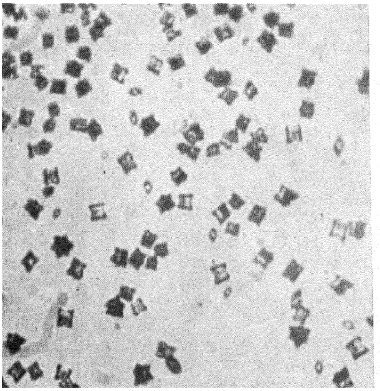


Photo 19.

Reaction of Th^{+4} with $(NH_4)_2CO_3$ and $TlNO_3$ (39 A, p. 153) × 75

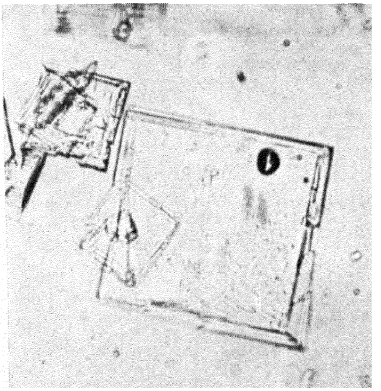


Photo 20.

Reaction of Be^{+2} with acetylacetone (40 A, p. 156) × 75

Photo 21.

Reaction of Tl^{+3} with Martius yellow (41 C, p. 161) × 75

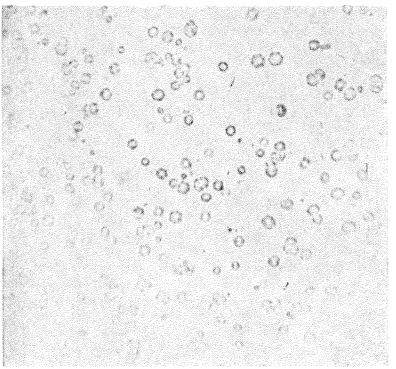


Photo 22.

Reaction of Sc^{+3} with luteocobaltic nitrate and NaF (42 B, p. 164) 75

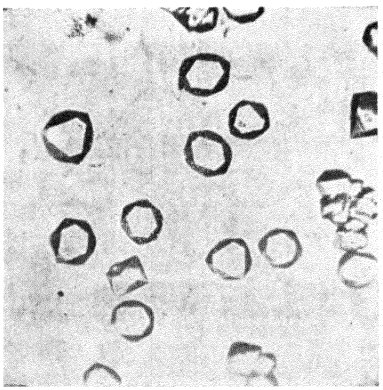


Photo 23.

Reaction of Ga^{+3} with CsCl and $KHSO_4$ (43 A, p. 165) × 75

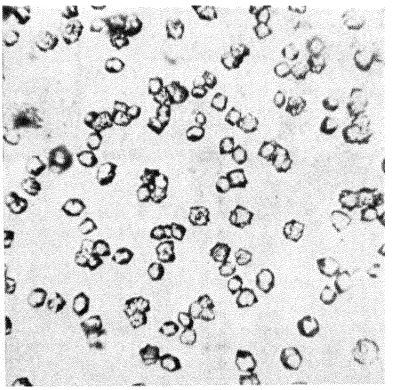


Photo 24.

Reaction of In^{+3} with hexamethylenetetramine and NH_4CNS (44 A, p. 168) × 75

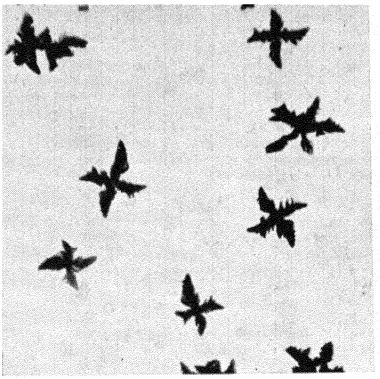


Photo 25.

Reaction of Zn^{+2} with $(NH_4)_2Hg(CNS)_4$ and $CuSO_4$ (45 A, p. 171) × 75

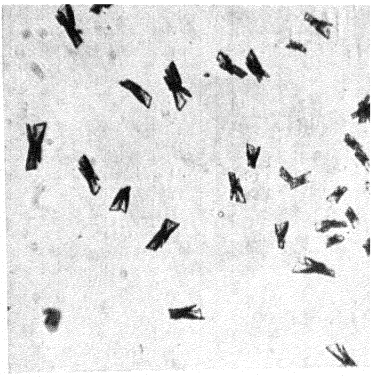


Photo 26.

Reaction of Zn^{+2} with $(NH_4)_2Hg(CNS)_4$ and Co^{+2} (45 B, p. 172) × 75

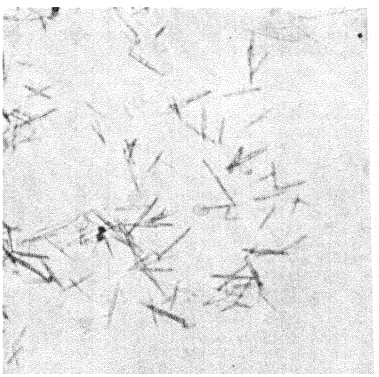


Photo 27.

Reaction of Mn^{+2} with cyanuric acid in NH_4OH (46 D, p. 181) · 75

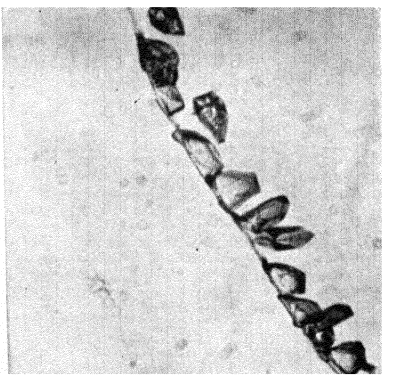


Photo 28.

Reaction of MnO_4^{-1} with $RbNO_3$ and $KClO_4$ (46 F, p. 182) × 75

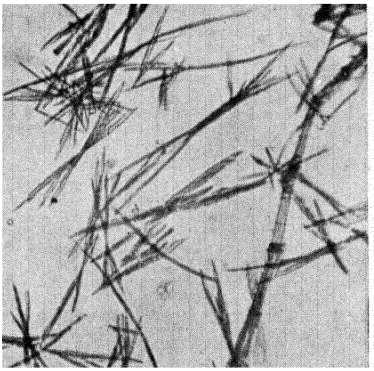


Photo 29.

Reaction of ReO_4^{-1} with acridine hydrochloride (47 C, p. 187) × 75

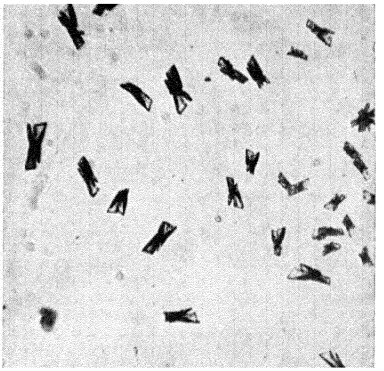


Photo 30.

Reaction of Co^{+2} with $(NH_4)_2Hg(CNS)_4$ + Zn^{+2} (48 A, p. 188) × 75

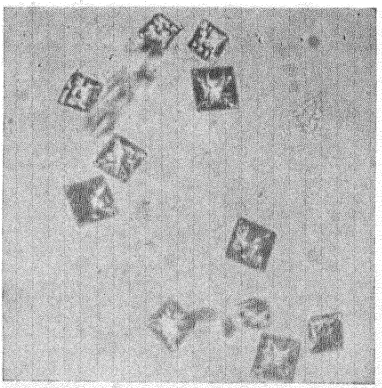


Photo 31.

Reaction of Ni^{+2} with $(NH_4)_2MoO_4$ (49 F, p. 202) × 75

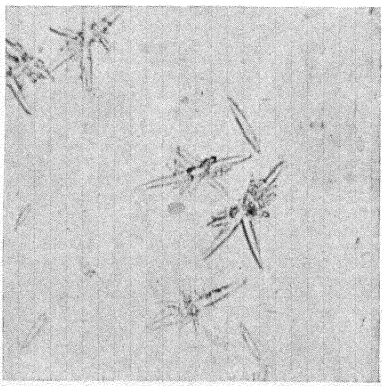


Photo 32.

Reaction of Ba^{+2} with $(NH_4)_2SiF_6$ (51 C, p. 212) × 75

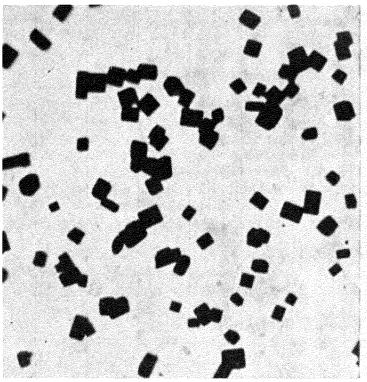


Photo 33.

Reaction of Sr^{+2} with $Cu(NO_3)_2$ and KNO_2 (52 A, p. 213) · 225

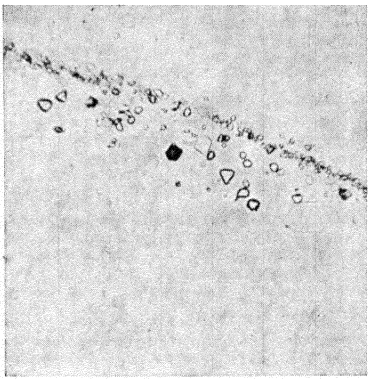


Photo 34.

Reaction of Sr^{+2} with HNO_3 (52 B, p. 214) × 75

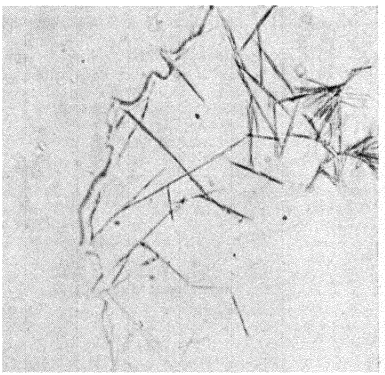


Photo 35.

Reaction of Ca^{+2} with H_2SO_4 (53 A, p. 215) × 75

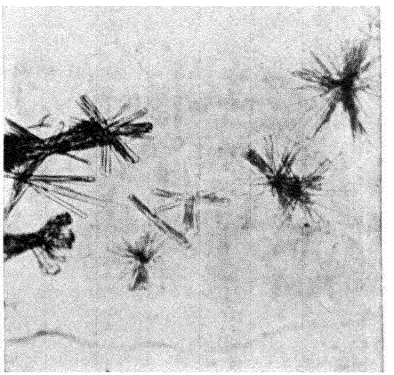


Photo 36.

Reaction of Ca^{+2} with loretine (53 B, p. 217) × 225

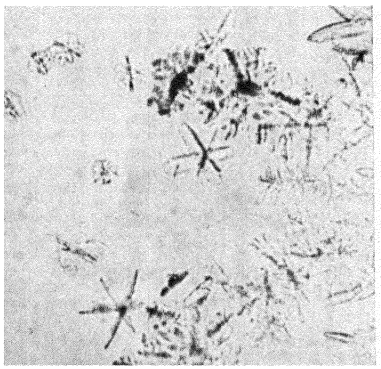


Photo 37.
Reaction of Li^{+1} with $(NH_4)_2CO_3$
(55 A, p. 225) × 225

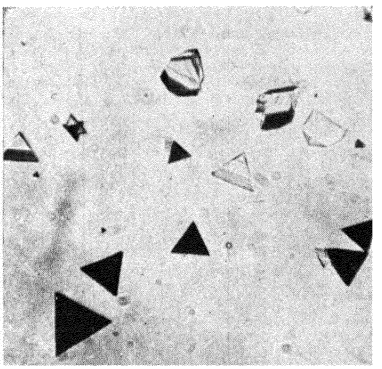


Photo 38.
Reaction of Na^{+1} with uranyl acetate
(56 A, p. 227) × 75

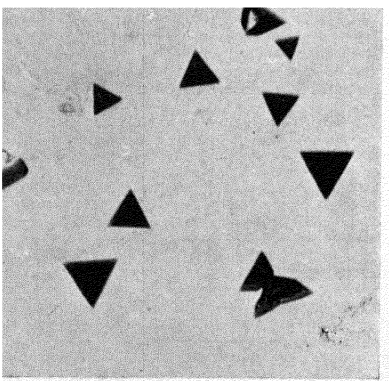


Photo 39.
Reaction of Na^{+1} withMg-uranyl acetate
(56 B, p. 228) × 75

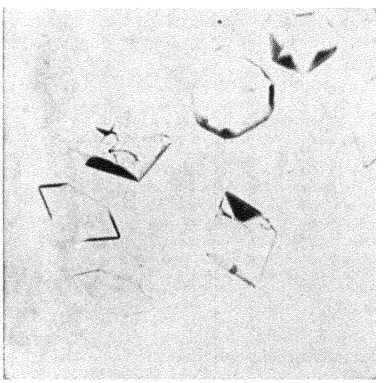


Photo 40.
Reaction of Na^{+1} with Zn-uranyl acetate
(56 C, p. 229) × 75

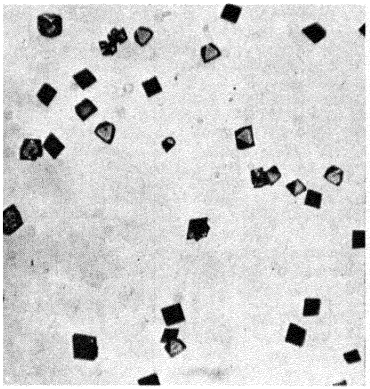


Photo 41.

Reaction of K^{+1} with H_2PtCl_6
(57 B, p. 232) × 75

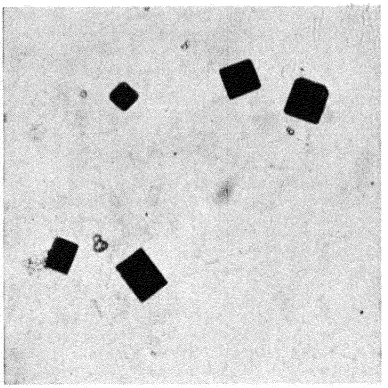


Photo 42.

Reaction of K^{+1} with $(CH_3CO_2)_2$ Pb, $(CH_3CO_2)_2$ Cu and $NaNO_2$
(57 C, p. 233) × 75

Photo 43.

Reaction of K^{+1} with dipicrylamine
(57 D, p. 234) × 75

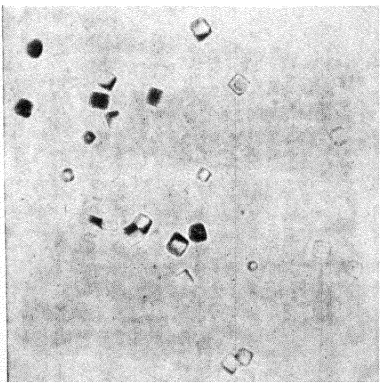


Photo 44.

Reaction of K^{+1} with $Na_2PbCo(NO_2)_6$
(57 E, p. 235) × 75

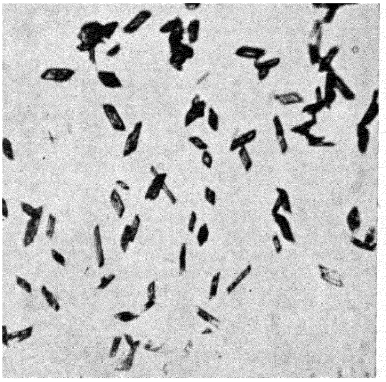


Photo 45.
Reaction of Rb^{+1} with $AuBr_3$ and AgBr
(58 B, p. 237) × 75

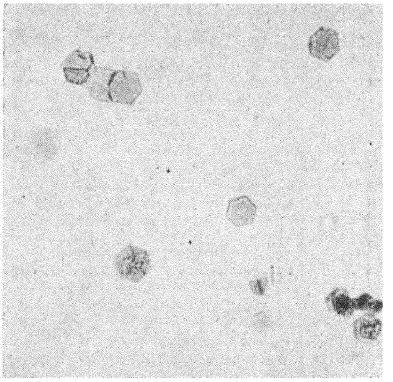


Photo 46.
Reaction of Cs^{+1} with $KBiI_4$
(59 C, p. 241) 75

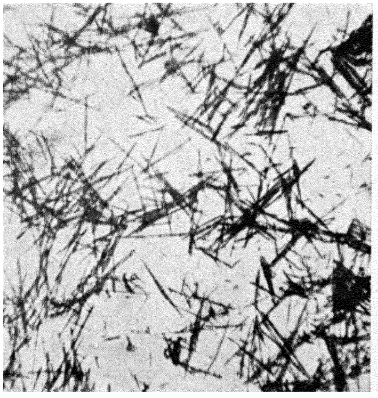


Photo 47.
Reaction of Cs^{+1} with AgI and NaI
(59 F, p. 243) × 75

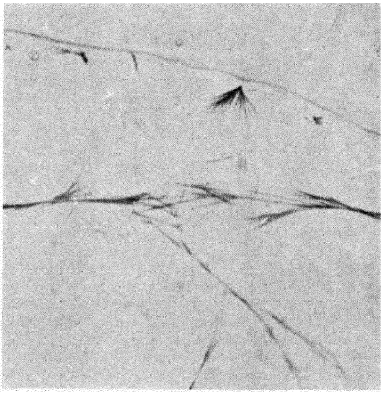


Photo 48.
Reaction of Cs^{+1} with $(CH_3CO_2)_2Pb$ + KI (59 G, p. 244) × 75

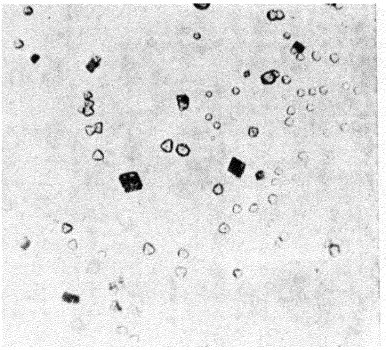


Photo 49.

Reaction of NH_4^{+1} with H_2PtCl_6
(60 D, p. 248) × 75

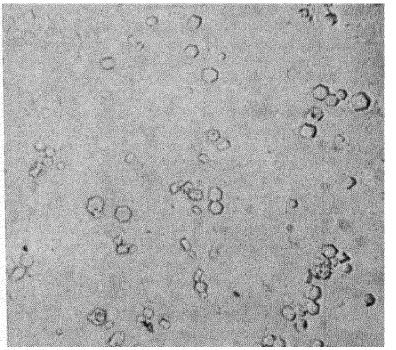


Photo 50.

Reaction of F^{-1} with SiO_2, H_2SO_4
and NaCl (61 A, p. 259) × 75

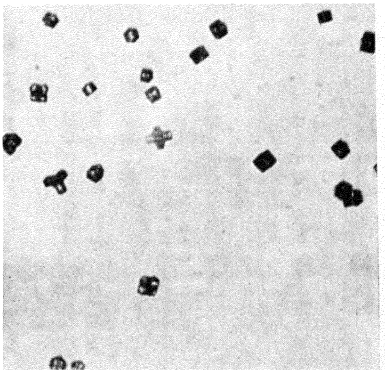


Photo 51.

Reaction of Cl^{-1} with $TlNO_3$
(62 B, p. 263) × 75

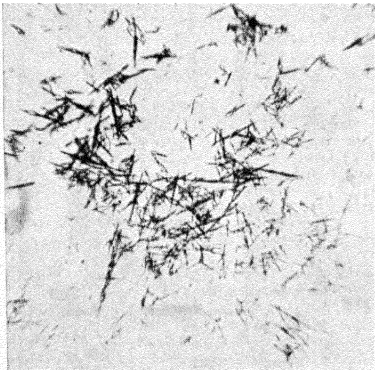


Photo 52.

Reaction of Br^{-1}
with m-phenylenediamine
(67 A, p. 271) × 75

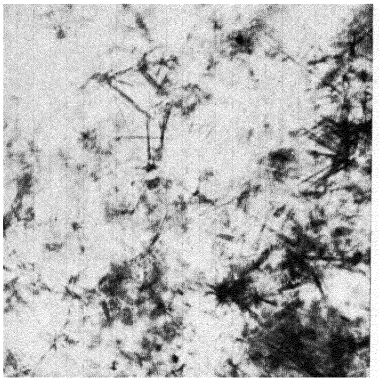


Photo 53.

Reaction of ClO_4^{-1} with methylene blue (71 A, p. 277) × 75

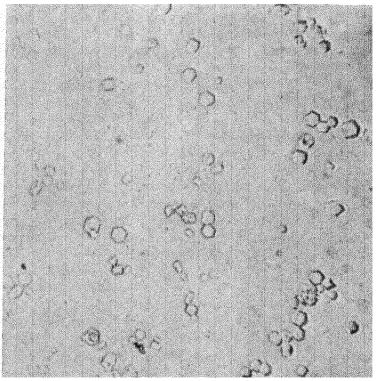


Photo 54.

Reaction of SiO_2 with F^{-1}, NaCl and H_2SO_4 (86 B, p. 299) × 75

Photo 55.

Reaction of CN^{-1} with alloxan and NH_3 (88 A, p. 300) × 75

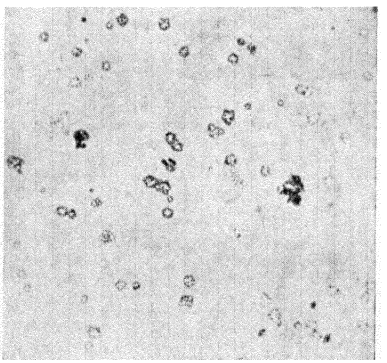


Photo 56.

Reaction of $Fe(CN)_6^{-4}$ with $Co(NH_3)_6(NO_3)_3$ (90 B, p. 305) · 225

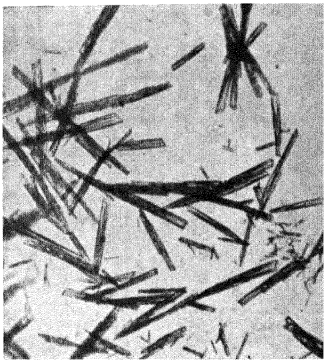


Photo 57.
Reaction of $Fe(CN)_6^{-3}$ with
$Co(NH_3)_6(NO_3)_3$ (91 B, p. 307) × 75