STUDIES IN THE QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES ON A SEMI-MICRO SCALE

By

ARTHUR J. LOWE, B.Sc.

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University of Edinburgh.

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INTRODUCTION.

In recent years the importance of making provision in a scheme of analysis for the "rare" or, better, "uncommon" elements has been emphasised. Many of these elements are finding an ever-increasing industrial application, and the exclusion of certain of them, such as titanium, tungsten and molybdenum, is no longer excusable. In 1927 Noyes and Bray published their book, "A System of Qualitative Analysis for the Rare Elements", which gives a comprehensive and precise scheme of separations for nearly all of the elements that occur in analyses for cations, and allows for the detection of small as well as large proportions of each.

This book will, no doubt, remain standard for some time to come, but, since its publication, inorganic analytical chemistry has seen two major developments in method, first, a great extension of the use of sensitive organic and unusual inorganic reagents as selective testing agents for single ions or several related ions, and as precipitating agents for groups of ions; and secondly, the growth of techniques pertaining to semi-micro or micro-analysis. In practice, the new methods are frequently employed most successfully in combination; for instance, in qualitative/

qualitative work, the use of a sensitive testing reagent facilitates the detection of a very small amount of an element, while the reduction in the scale of operations renders it economically possible to use an expensive reagent.

The main source of information regarding sensitive organic reagents is Feigl's well-known book, "Qualitative Analyse mit Hilfe von Tüpfel-reaktionen", which states how small an amount of an ion is detectable with a given reagent, how it is affected by the presence of other ions, and whether or not interfering effects may be eliminated or reduced. Of value also, as a catalogue of tests using both inorganic and organic reagents, is "Tables of Reagents for Inorganic Analysis", collected by the International Committee on new Analytical Reactions and Reagents.

Many books and papers have been published dealing with the application of the micro-technique to qualitative analysis for inorganic cations. In their book, "Introduction to the Microtechnique of Inorganic Qualitative Analysis", (1935), Benedetti-Pichler and Spikes give a scheme of analysis for very varied proportions of the common metals in 1 mg. of material, and confirm the presence of most by means of crystal tests/

tests under the microscope. Within recent years, numerous books, covering the same ground, but applicable to the semi-micro scale, have been published, particularly in America. A typical example is "Semi-micro Qualitative Analysis" (1936), by Engelder, Dunkelberger and Schiller. In the cation scheme, which is applicable to 20 mg. of material, the groups are formed in the traditional manner, and separated to a considerable extent into their components. A great variety of tests is then given, some of which employ organic reagents, but there is a lack of critical information with respect to interference, and the detection of small proportions.

An interesting paper on semi-micro analysis is that of Winkley, Yanowski and Hynes, (Ref. 1). The elements are separated into groups and then drop reactions are applied directly wherever possible. The tests are well chosen and sensitive, and conditions are adjusted so that interference does not take place. The maximum amount of any cation present in the solution is stated to be 2 mg. but the minimum amount detectable by the methods adopted is not given.

The extension of these methods to include uncommon cations is steadily progressing. In 1934, Nieuwenburg and Dulfer published their "Short Manual of Systematic Qualitative /

Qualitative Analysis", in which a scheme of analysis, based on the classical separation into groups, is applied, after a partial separation of the group components, to the detection with organic and inorganic reagents of about 45 cations in 100 mg. of material. Extremes of quantities are not considered. Benedetti-Pichler and his co-workers, on the other hand, in the gradual extension of their work on the micro scale to all the cations, have utilised the more precise scheme of separations of Noyes and Bray, and have already examined, wholly or in part, all except the osmium, tungsten, tantalum and gold groups. (Ref. 2(a-j)). New procedures have been introduced where necessary, and organic reagents, such as Cupferron and dimethylglyoxime, used for separations. Final confirmation has usually been obtained by methods similar to those in the Noyes and Bray scheme, though crystal tests under the micro-:scope have also been employed. The limits of identification are clearly stated, and the papers are critical in outlook.

So far there has been no comparable development on the semi-micro scale, despite the fact that semi-micro methods, being applicable to quantities of, say, 20-100 mg. (Benedetti-Pichler and Spikes suggest an upper limit of 50 mg.), necessitate no important changes /

changes in method, and are therefore much more easily applied than the true micro methods with their specialised technique. The only important paper is that of Fischer, Dietz, Brünger and Grieneisen (Ref. 3.), who made a comprehensive study of the ammonium sulphide group of Noyes and Bray, separating most of the components completely, and testing for them by modern methods. The authors were aware of the difficulties encountered when small quantities have to be detected in the presence of large, and allowance is made for this eventuality. A maximum of 0.2 g. of material was used, which is rather in excess of the semi-micro limit.

It is evident that there is a wide field of research for further developments on the semi-micro scale. Following the example of Benedetti-Pichler, the author therefore proposed to select for study certain groups of the Noyes and Bray scheme, and by means of the judicious application of modern reagents and tests, to reduce the scale of operations to one tenth of that used in the original. This meant that the maximum amount of material under consideration would be 100 mg., 50 mg. referring to the cations, and that 10 mg. would be the maximum amount of any less common cation present.

In /

In general, the detection of 0.5% of one ion in the presence of 100% of any other common ion or 20% of any less common ion was aimed at, these proportions being similar to those adopted by Noyes and Bray. It was also proposed to make provision for the estimation of the quantities of the components of a mixture.

Since no work has so far been published dealing, either on the micro or the semi-micro scale, with the tungsten, tantalum and gold groups of Noyes and Bray's scheme, these were selected for analysis.

As far as possible it was intended to utilise for confirmatory purposes sensitive organic reagents, giving characteristic coloured solutions or precipitates, in preference to the crystal tests of Behrens and Kley and others, which are more difficult to carry out with certainty (cf. Annual Reports on the Progress of Chemistry, 1935-37).

It was not anticipated that the employment of selective reagents would obviate the necessity for at least a partial separation of the components of the groups, but it was hoped to simplify these separations wherever possible.

The results of the investigations are given in the following pages.

EXPERIMENTAL

APPARATUS.

Centrifuge:- The main item was an electrically driven "International Clinical Centrifuge", provided with two heads, one carrying buckets for 15 ml. conical tubes, the other with buckets for 5-½ ml. tubes. Although the less expensive hand-driven machines were quite suitable, it was a great convenience to have a mechanically operated model.

Hot-Plate:- A hot-plate was constructed from the iron bases of two retort stands joined together by a short length (8") of the original column. When heated by gas at one end, this afforded a very useful gradation of temperature.

Water-bath:- For heating the various sizes of centrifuge tubes, a 600 ml. beaker filled with water was kept on the hot-plate. The beaker was fitted with an aluminium cover in which holes of appropriate size were punched.

Gas-burners:- Micro-Bunsen burners were regularly used. For high temperature fusions a small hand blowpipe was available.

Reagent Bottles:- The solutions of the salts of the elements to be tested and the reagents used were, for the most part, contained in bottles of 60 ml. capacity fitted with cork or rubber stoppers through which pipettes of 3-4 mm. bore, and about 15 cm./

15 cm. long, had been inserted. Hydrofluoric acid solutions were kept in ceresin or guttapercha bottles, and Cellophane drinking straws were used as pipettes, until some made of transparent bakelite became available. When contact with the air was deleterious, the ends of the pipettes were covered with small rubber caps. The concentrated acids and ammonium hydroxide were kept in stoppered bottles of about the same capacity, and reagents which were made up in small quantities, owing to their impermanence or cost, were contained in stoppered bottles of about 20 ml. capacity. Solid reagents in frequent use were kept in little vials. These bottles were for the most part arranged on a long wooden tray.

Platinum Ware:- A few tall 6 ml. crucibles were required for the evaporation of solutions containing hydrofluoric acid, and for various fusions.

Porcelain and Silica Ware:- Porcelain crucibles of various sizes from 2-15 ml. capacity, and shallow basins of 35 mm. diameter were frequently used for the evaporation of solutions. Evaporations were often expedited by arranging an air stream so as to impinge upon the surface of the liquid, (Ref. 4, p. 137). For some fusions, tall, 12 ml. silica crucibles were required. Spotting tiles with twelve cavities were utilised in making many of the tests.

Glassware:- The great majority of the separations required by the scheme of analysis were performed in centrifuge/

centrifuge tubes of size ranging from 15 ml. to 0.5 ml. These were used in conjunction with the centrifuge described above. The tubes were of the standard pattern, but the smallest sizes had very fine points. The separation of solutions from precipitates in centrifuge cones was performed by means of small ordinary pipettes, or pipettes drawn out to a point of 0.2 mm. bore, (Ref. 4, pp. 128-9). When a precipitate was to be washed, it was stirred up with the wash liquid by means of a thin glass rod, drawn out to a thread at one end, and having a bead at the end of the thread. When it was necessary to separate two liquid layers in a tube, e.g. ester from water, a pipette was used which had been made from 10 mm. glass tubing by drawing one end out straight to form a mouthpiece, and drawing out the other end to a capillary, which was bent at 120°. This was placed in the centrifuge tube, which was then held at such an angle that it was possible to see the two layers clearly. When a gas had to be passed into a centrifuge tube, a glass tube drawn out at one end to form a capillary was used.

Test-tubes, 3" x $\frac{3}{8}$", and 2" x $\frac{1}{4}$", were frequently used. A short burette, small graduated cylinders, and graduated pipettes were needed, also small beakers, conical flasks, and other items, all about one-tenth of/

of the usual size.

Spot Test Paper:- Schleicher and Schüll's No. 601 was used when required. The No. 589 "Black-Band" filter papers of the same manufacture were also used upon occasion.

CHEMICALS

Test Solutions

The test solutions of elements studied were made up, in general, in concentrations of 10%, 1% and 0.05%, W/V, calculated with respect to the weight of the element concerned, or in the case of phosphate, with respect to the phosphate ion ($PO_4^{\prime\prime\prime}$). The most concentrated solution used in the case of the gold group elements was of 5%. In certain cases where a 10% solution could not be attained for reasons of solubility, a saturated solution of known strength was used. The concentrated solutions were convenient for testing the effect of a large excess of one radical on a small amount of another.

The following is a list of the chemicals used in the preparation of the solutions, with notes as to their purity.

Antimony. Antimony Trichloride, $SbCl_3$.

Bismuth. Bismuth Nitrate, $BiONO_3.H_2O$

Gold. Gold Chloride, $HAuCl_4$, xH_2O. (51% Au).

Iridium. Iridium Chloride, $IrCl_4$.

Mercury. Mercuric Chloride, $HgCl_2$.

Molybdenum. Ammonium Molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$.

Niobium. x from the element.

Palladium. † Palladium Chloride, $PdCl_2$.

Phosphate. Ammonium Phosphate, $(NH_4)_2HPO_4$.

Platinum. † Platinic Chloride, $H_2PtCl_6.xH_2O$ & HCl(40% Pt).

Rhodium. /

Rhodium.	Rhodium Chloride, $RhCl_3, 4H_2O$.
Tantalum.	* from the element.
Tellurium.	Sodium Tellurite, Na_2TeO_3.
Tin.	Stannous Chloride, $SnCl_2, 2H_2O$ oxidised by perhydrol in hydrochloric acid solution.
Titanium.	Titanous Chloride, $TiCl_3$, oxidised by chlorine gas in hydrochloric acid solution.
Tungsten.	Sodium Tungstate, $Na_2WO_4.2H_2O$.
Vanadium.	Ammonium Metavanadate, NH_4VO_3, converted to the more soluble sodium salt by boiling with an equivalent of sodium hydroxide.
Zirconium.	Zirconium Oxychloride, $ZrOCl_2$.

* "Specpure", supplied by Adam Hilger Ltd. The tantalum solution was made up from 99.5% pure tantalum metal, the niobium, from exceptionally pure niobium metal, containing only a trace of tin. Both were supplied in a 1% solution containing 2%-3% of free hydrofluoric acid.

† Supplied by Johnson, Matthey and Co. Ltd., and stated to contain no base metal impurities, and only very small traces of other metals of the platinum group.

The titanous chloride used was British Drug Houses Ltd, "iron-free" solution in hydrochloric acid.

All the other chemicals used for the test solutions were of analytical grade, and were supplied by British Drug Houses, Ltd., Messrs. Hopkin and Williams, Ltd., and Schering-Kahlbaum, A.G.

Reagents.

The acids, alkalies and other inorganic reagents used were of "AnalaR" standard or of analytical grade.

The special organic reagents employed were obtained from Messrs. Hopkin and Williams, Ltd., or from British Drug Houses, Ltd.

Organic solvents were redistilled before use. The ethyl acetate used for the extraction of gold and mercury in the analysis of the gold group was refluxed over phosphorus pentoxide for a day and then fractionated. The fraction boiling between 76.5° and 77.5° was used.

The Composition of the Tungsten, Tantalum and Gold Groups with Reference to Noyes and Bray's Scheme

The Isolation of the Groups

In the scheme of analysis of Noyes and Bray the material to be analysed is treated first with hydrobromic acid, during which treatment the elements of the selenium group are removed by distillation, and then with nitric and perchloric acids, when the elements of the osmium group are distilled off. All of the material is at this stage held in solution, except possibly, a small amount of unattacked material. The perchloric acid solution is then diluted and boiled with formic acid, which results in the precipitation of the constituents of the tungsten and tantalum group as oxides or phosphates, and the members of the gold group as metals. There may also be thrown out of solution silver as bromide, and lead, chromium and the alkaline earths as sulphates. From this precipitate, the members of the tungsten and tantalum groups are dissolved by means of hydrofluoric acid, and, following removal by carbonate and perchloric acid of the lead, chromium and alkaline earth metals, the/

the constituents of the gold group are dissolved out by means of nitric and hydrochloric acids.

The Constitution of the Groups

The elements which may be present in the hydrofluoric acid solution are tin, antimony, tungsten, molybdenum, tellurium, vanadium, titanium, tantalum, niobium, zirconium and bismuth, as well as phosphate. Lead may be present in small quantity (not more than 1.5 mg.), but need not be tested for in this solution. The gold group may contain mercury, gold, platinum, palladium, rhodium and iridium.

As stated in the Introduction, the maximum amount of material to be allowed for in the scheme to be described was 100 mg., 50 mg. referring to the metallic elements. The latter might be represented by one common element alone. Tin, antimony, phosphate, or mercury might therefore be present in any quantity up to 50 mg. Not more than 0.5 mg. of bismuth was allowed for, this being a reduction to one-tenth of the maximum amount which Noyes and Bray state may come into the hydrofluoric acid solution (Ref. 5, p. 50). 10 mg. was the upper limit for any one of the other elements, except vanadium, rhodium or iridium, for which it was 2 mg., in approximate accordance with Noyes and Bray's findings (Ref. 5, pp. 47 & 48). The minimum amount of/

of any ion considered was 0.25 mg.

Certain of the possible constituents of the groups are only found when certain other elements are also present. Thus the occurrence of zirconium, tellurium or bismuth is dependent upon the presence of phosphate, tin or antimony, respectively. The presence of iridium and rhodium depends mainly on contact catalytic effects.

It was proposed to examine methods of analysis for the tungsten and tantalum groups initially in conjunction, and then for the gold group.

The Separation of the Tungsten and Tantalum Groups

With the exception of the vanadium, which is in the tetravalent form, the elements present in the hydrofluoric acid extract are in their highest state of oxidation. In the scheme of analysis set forth by Noyes and Bray, the solution is evaporated with sulphuric acid to expel the hydrofluoric acid, then made alkaline with ammonium hydroxide, and digested with ammonium sulphide in a pressure bottle. This results in the separation of bismuth, titanium, tantalum, niobium, zirconium, and part of the phosphate and vanadium, constituting the tantalum group, from tin, antimony, tungsten, molybdenum, tellurium and the remainder of the phosphate and vanadium, which form/

form the tungsten group.

Instead of adopting this procedure, it was thought that it would be of interest to investigate the possibility of applying to the combined groups some of the methods proposed by Schoeller (Ref. 6), for solutions containing tantalum and niobium.

Two methods were considered, both applicable to the residue left after expelling hydrofluoric acid by means of sulphuric acid. Synthetic residues of variable composition were prepared by mixing small amounts (usually equivalent to 2-5 mg. of a cation) of the standard solutions of the metals and a few drops of concentrated sulphuric acid, and evaporating them just to dryness in a 6 ml. platinum crucible placed on a hot-plate.

In the first method, corresponding to that used by Schoeller (Ref, 6, p. 69) for separating tantalum, niobium, zirconium and titanium from tin and lead, etc. the residue was fused with a little potassium bisulphate and the cold melt extracted with 3-4 ml. of a 10% solution of tartaric acid. The liquid was transferred to a centrifuge tube, saturated with hydrogen sulphide, and the precipitate and solution separated. The components of the latter, in the absence of phosphate, were expected to be:

Precipitate - Sb, Sn, Mo; Te, and Bi.

Solution - Ta, Nb, Zr, Ti, W and V.

This/

This result was substantially confirmed by applying various distinctive tests that are described in greater detail later. In the presence of phosphate the components of the precipitate and the solution varied so much, owing to the complications caused by phosphate carrying metals like zirconium into the precipitate, and molybdenum into the solution, that the method was abandoned in favour of one that would apply whether or not phosphate was present.

The second method adopted was based on that of Schoeller (Ref. 6, pp. 90-92), for separating tungsten from tantalum, niobium, titanium or zirconium. The synthetic residue (see p.17) was scraped from the bottom of the platinum crucible and thoroughly mixed, and then fused, with 0.5 g. of sodium carbonate. The cooled mass was digested with 2 N sodium hydroxide, and transferred to a centrifuge tube for the separation of the soluble and insoluble portions, which were examined for the following components:

<u>Precipitate</u> - Ta, Nb, Ti, Zr and Bi.

<u>Solution</u> - Sb, Sn, Mo, Te, V, W and P.

Schoeller shows that the precipitation of zirconium is not quite complete, but it was thought that the amount escaping could be ignored in qualitative work./

work. Titanium and niobium in association also pass partly into the solution. This might, however, constitute a special case, if the separation was otherwise reasonably satisfactory. Although ignited or natural stannic oxide is not completely dissolved, following fusion with sodium carbonate, it was supposed that tin in the unignited synthetic residue would be rendered wholly soluble.

Both the precipitate and the solution contained, in general, the elements listed, but the tests for tin, antimony, phosphorus, and occasionally molybdenum were feebler than was to have been expected from the quantities originally added, and small amounts sometimes escaped detection. Presumably they were retained in the precipitate. A more strongly alkaline decomposing reagent was evidently required. Fusion with caustic soda was undesirable because of its attack on metal crucibles, and was probably unnecessary for unignited residues. Instead, the use of a concentrated solution of sodium hydroxide was examined. By this means Noyes and Bray (Ref. 5, pp. 352-353) satisfactorily separated zirconium and titanium from phosphate, and titanium from vanadium. Synthetic residues were prepared as formerly (p.17), but the evaporation with sulphuric acid was stopped just before absolute dryness was attained. 1 ml. of 7 N sodium hydroxide was then added to such a residue, and the mixture boiled and stirred for a few minutes. It/

It was transferred to a centrifuge tube and the precipitate was washed with 2 N sodium hydroxide. Analyses were made in the same manner as after a fusion with sodium carbonate; except that antimony was also sought in the precipitate as it was thought that it might divide.

The experiments showed that the method was superior to that employing sodium carbonate, but antimony was generally found in the precipitate and the solution. With several synthetic residues, usually containing phosphate and vanadium or molybdenum, the mixture became dark in colour when sodium hydroxide was added, showing that there was a tendency for some component, thought to be antimony, to be reduced to the elementary state. However, slight darkening was also subsequently observed in a mixture containing only tin, molybdenum, tellurium, vanadium , and phosphate, and tellurium was found to be responsible. This reduction did not appear to constitute a major problem, nor to warrant the rejection of the sodium hydroxide treatment, which was therefore adopted for the fundamental separation of the constituents of the hydrofluoric acid solution. Any irregularities were to be examined later when more detailed methods had been evolved for the examination of the separate groups.

The two groups thus obtained were designated the Tantalum and Tungsten groups, and were considered to have the following composition:

Tantalum Group - Ta, Nb, Zr, Ti, Bi, Sb (part) and perhaps Te.

Tungsten Group - Sb(part), Sn, Mo, Te, W, V and P.

The former differs from Noyes and Bray's corresponding group in containing antimony and no phosphate or vanadium. The latter contains the same elements as Noyes and Bray's tungsten group.

ANALYSIS OF THE TANTALUM GROUP.

(Ta, Nb, Zr, Ti, Bi and Sb).

This group represented the residue of the sodium hydroxide treatment of the combined tungsten and tantalum groups. It was anticipated that a scheme of separations would be required in order to confirm and estimate the proportions of its components. First of all, however, the conditions under which a number of important cation tests may be applied were examined. The data are given below:-

Titanium.- (a) With hydrogen peroxide a solution of titanium in dilute sulphuric acid forms yellow pertitanic acid. Tantalum, niobium, zirconium, antimony and bismuth do not interfere. It was found that 20 γ of titanium in a volume of 0.2 ml. gave a yellow colour which was only slightly bleached by 0.05 g. of potassium bisulphate or tartaric acid. 0.05 g. of oxalic/

oxalic acid halved the sensitivity.

(b) Chromotropic acid (Ref. 7, p. 246) added in the solid form could be similarly applied, giving a dark red-brown solution. Tartaric acid reduced the sensitivity considerably, but oxalic acid had little influence.

Since with both tests even less than 20% of titanium could easily be detected, and the minimum amount of any cation to be considered in the tantalum group was 250%, the above tests could presumably be applied to a small portion of the tantalum group if it were, for example, fused with bisulphate and taken up in dilute sulphuric acid, with or without an organic acid. The coloured solutions produced with both tests could be compared with standard colours for the assessment of quantity.

Zirconium. - A well-known reagent for zirconium is alizarin - S, but its use is precluded in solutions containing sulphate and large amounts of titanium. Since zirconium in the mixed precipitate above could probably be obtained in solution only after a fusion with bisulphate, the application of another reagent p-dimethylaminobenzene-azo-phenylarsonic acid (Ref. 7, p. 248) was studied. Test papers, impregnated with a 0.3% solution of the reagent in alcohol containing /

containing 5% of hydrochloric acid, were spotted with small drops of solutions containing zirconium,and immersed in 2N hydrochloric acid at 60° for several seconds. It was found that 10% of Zirconium gave a distinct brown spot. Dilute sulphuric acid, potassium bisulphate, antimony and bismuth produced red colours which did not interfere. Perhydrol lowered the sensitivity of the test by bleaching the reagent to a small extent. Niobium and titanium gave strong red colours,but quite large excesses could be masked by perhydrol. Tantalum behaved like zirconium, perhydrol only slightly impairing its reaction(Ref.8). Moderately good assessments of the quantity of zirconium in a test solution could be made by comparison with standard stains.

Bismuth.- For this metal an interesting reagent was found in 4-methyl-1:2-dimercapto-benzene ("dithiol"), which was prepared as a 0.2% solution in 0.25N sodium hydroxide containing 0.3% of thioglycollic acid (cf. P. 46). A drop of the reagent solution was added to a drop of a solution containing bismuth on a spotting tile. On the addition of hydrochloric acid a distinctive brown precipitate was produced with 10% of Bismuth. No other element of the tantalum group gave a brown precipitate. Antimony gave a yellow /

yellow precipitate, which was preferentially formed in mixtures of antimony and bismuth, but an excess of the reagent brought up the brown colour, if the excess of antimony was less than five-fold.

Hydrochloric acid up to 4N did not interfere. It was thought that part of the tantalum group residue might be fused with potassium bisulphate, taken up in concentrated hydrochloric acid and a test applied directly for bismuth. As the amount of bismuth would never be large (see p. 15) an estimation of the amount of bismuth could be made on the spotting tile. The precipitate was also soluble in butyl acetate, giving a brown solution, which could be compared with a standard, if desired.

Antimony. - Presumably antimony could be detected directly with rhodamine - B (see p. 44) in the hydrochloric acid extract of a bisulphate melt. Neither tantalum nor niobium reacted with the reagent.

Tantalum and Niobium. - It seemed unlikely that characteristic tests would be found for tantalum and niobium in association with the other members of the tantalum group. A few tests were made on tantalum - niobium mixtures, e.g. the crystal test for tantalum with potassium fluoride, (Ref. 9), which may be applied in the presence of niobium, and the zinc reduction test /

test (Ref. 10) for niobium, which is unaffected by tantalum. The test for tantalum was satisfactory for about 1 mg. in a drop, and that for niobium was unsuccessful. No other suitable individual test was found.

From the foregoing results it was apparent that the confirmation of all the tantalum group components would have to be preceded by some separations within the group.

The First Scheme of Analysis for the Tantalum Group.

Noyes and Bray's preliminary step in the analysis of the tantalum group, viz., the removal of titanium, as a soluble salicylate complex, was not considered, as it has been adversely criticised by Schoeller (Ref. 6, p. 109). For the rapid approximate separation of earth acids from titanium and zirconium, Schoeller (ibid., p. 118) has recommended fusion with potassium bisulphate and treatment with tannin in dilute sulphuric acid. This method was adapted in the following manner.

The precipitate left from the treatment of a synthetic residue (p. 17) with 7N sodium hydroxide was transferred to, and fused with a ten to twenty-fold excess of potassium bisulphate in a 12 ml. tall, silica crucible, which was manipulated during the cooling so that/

that the melt solidified in a thin film round the walls of the crucible. The latter was then filled with a 1% solution of tannin containing 5% sulphuric acid, and gently heated on the hot plate until the liquid boiled. The tantalic and niobic acids were coagulated by the tannin sol to form a coloured precipitate, which was separated by centrifuging, and washed with 2N sulphuric acid. When tantalum was present alone, the colour of the precipitate was a very light yellow; niobium gave a rich red-brown, and mixtures were intermediate in colour. The bulk of the precipitate could be used to estimate the combined amounts of tantalum and niobium, and the colour, in the absence of interference (see below), to estimate the proportions roughly. A more accurate method of estimation is described on pp. 34 to 39 . Quantities of tantalum and niobium down to 100 γ gave distinct precipitates by the tannin-bisulphate treatment. Zirconium, bismuth and antimony did not interfere, but, if titanium were present, earth acid precipitates, consisting mainly of tantalum, derived a red colour denoting contamination with titanium. According to the results of Schoeller (Ref. 6, p. 112), such contamination might take place to the extent of over 50% of the weight of the precipitate, if a twenty-fold excess of titanium were present, and be /

be reduced to 5% on repetition of the treatment. The red colour due to titanium prevented the estimation of the relative amounts of tantalum and niobium. The bisulphate-tannin procedure was accordingly used at this stage mainly as a means of determining the presence of earth acid, without further separation, and the formation of a precipitate from the tannin solution was found to be characteristic for the earth acids. If the tannin solution was deficient in sulphuric acid, or if insufficient bisulphate had been used in the fusion, titanium might give a red precipitate in the absence of any earth acid. In order to obviate any danger of misinterpretation arising from this effect, the strength of the sulphuric acid was increased, in later experiments, from 5% to 10%.

It was indicated on pp. 21-24 that direct tests might be applied for titanium, antimony and bismuth, in small portions of the tantalum group. If these were adopted then only zirconium remained to be tested for in a tantalum free solution, the filtrate from the bisulphate tannin precipitate being presumably appropriate for this purpose. Before testing for zirconium it was necessary to destroy the tannin by evaporating the solution with sulphuric acid and oxidising with nitric acid. The nitric acid was then driven off, 0.1 gm. of potassium bisulphate added, and the fusion repeated. The cooled melt was taken up in 2N hydrochloric acid and a portion tested for zirconium by means of p-dimethylaminobenzene-azo-phenylarsonic acid test-paper (p.22)

TANTALUM GROUP Scheme of Analysis I

RESIDUE containing Ta, Nb, Zr, Ti, Bi, and perhaps Sb, mainly as oxides or hydroxides. Transfer to a silica crucible, fuse with 0.2-0.3 g. of $KHSO_4$, dissolve in 1 ml. of 5N HCl. Divide into four portions.	
(1) Take 5%. Test with dithiol as on p.23. A brown precipitate shows Bi.	
(2) Take 5%. Test with H_2O_2 or chromotropic acid as on p.21. A yellow or red-brown colour, respectively, shows Ti.	
(3) Take 5% Test with rhodamine-B as on p. 24. A purple precipitate or blue colour in transmitted light shows Sb.	
(4) Take 85%. Evaporate to expel HCl. Precipitate Ta and Nb with tannin in H_2SO_4 as on p. 26. If much Ti is present repeat the treatment.	
PPT. Ta and Nb	FILTRATE -- Destroy tannin as on p. 27. Fuse the residue with $KHSO_4$, take up in a minimum amount of dilute H_2SO_4, and test for Zr with p-dimethylamino-benzene-azo-phenylarsonic acid, as on p. 22.

The simple scheme of analysis (I) shown on p. 28 was put to the test in the analysis of a number of mixtures of composition unknown to the operator, containing members of the tungsten and tantalum groups. The groups were separated as described on p. 19 and the analysis of the tantalum group proceeded with as outlined. Quantities were only roughly assessed, +++, ++ and +, representing large, moderate, and small amounts, respectively, in the table of results shown.

Composition of the Mixtures in Mg.

No.	Ta	Nb	Ti	Zr	Bi	Sb	Sn	Mo	Te	V	W	PO_4
1. Present	2	-	-	-	-	0.25	0.25	-	5	0.25	-	2
Found	+		o	+	o	-						
2. Present	-	-	2	-	-	-	0.5	10	0.25	-	5	-
Found	o		++	o	o	-						
3. Present	0.25	-	-	5	-	5	-	-	0.25	-	-	0.25
Found	++		o	+++	o	-						
4. Present	0.5	-	-	0.25	0.25	0.25	-	-	-	5	0.25	-
Found	+		o	+	+	o						
5. Present	-	0.25	5	-	-	5	-	-	0.25	-	-	0.25
Found	+		+++	o	o	++						

The conclusions reached as a result of these analyses were that the procedure adopted for the joint detection of the earth acids was satisfactory, although the/

the reporting of a moderate amount in No. 3, probably implied the deposition of zirconium (or tannin); the method for the detection of titanium seemed to be adequate, and bismuth, in minimum quantity, had been successfully detected in the one case in which it was present. Zirconium was reported erroniously in No. 1, because of interference from tantalum. Antimony was not tested for in the tantalum section of the analyses of Nos. 1-3, was tested for but was not present in No. 4, and was found in moderate quantity in No. 5. As antimony was partly in the tungsten group, there was no adequate check on the results.

The Second Scheme of Analysis for the Tantalum Group.

The Detection of Zirconium. -Attention was first of all paid to the detection of zirconium. Under the most favourable conditions, the precipitation of tantalum and niobium with bisulphate and tannin is not quite complete, and the negative error is greater after two treatments. (Ref. 6, p. 112). Enough tantalum was escaping in the present experiments to invalidate the test for zirconium with p-dimethylaminobenzene-azo-phenylarsonic acid. Either a better method of separating zirconium from tantalum had to be adopted, or /

or a superior test found.

The separation of zirconium from the earth acids, in particular, by fusion with potassium carbonate was examined.(Ref. 6, pp. 107 and 32). This method, which leaves zirconium undissolved, would be better than that previously adopted, for separating a small amount of zirconium from an excess of earth acids, but the zirconium would still be slightly contaminated with tantalum. As tantalum and niobium are held in solution as their potassium salts, it was important to wash free of sodium salts the precipitate composing the tantalum group. For this purpose a 1% solution of ammonium nitrate was employed, instead of water, in order to repress any tendency of the earth acids to dissolve.The precipitate was placed in a small platinum crucible, dried and fused over a blowpipe with 0.2g. of potassium carbonate. The cooled mass was extracted with 1 ml. of hot 2N potassium hydroxide, and the whole treatment repeated on the residue. Potassium bisulphate was added to the second residue, a fusion effected and the cold melt taken up in a minimum amount, of 4N sulphuric acid. With reference to the whole of the tantalum group, the solution was expected to contain zirconium, some or all of the titanium, bismuth and antimony, and not more than traces of tantalum and perhaps /

perhaps niobium.

About this time an important reagent became available for testing for zirconium viz., p-hydroxyphenylarsonic acid (Ref. 11). It had been proposed primarily as a precipitant for titanium in a solution 3N in sulphuric acid, but this precipitation could be prevented by hydrogen peroxide. A 4% aqueous solution was applied to solutions in 3N sulphuric acid of all the tantalum group metals. 0.1 Ml. of a solution containing 40γ of zirconium gave a precipitate immediately when 1-3 drops of the reagent solution were added and the mixture was boiled. For the assessment of quantity the bulk of the precipitate could be compared with a standard. Towards tantalum the reagent was much less sensitive, 400γ of tantalum giving the same result as 40γ of zirconium; hydrogen peroxide had no appreciable influence. Titanium and niobium gave no precipitates in the presence of a drop of perhydrol. Bismuth and antimony gave precitates which, even if formed from 3 mg. of the cations, dissolved immediately on the addition of a drop of 2N hydrochloric acid. The reagent could therefore be applied directly to the solution from the tantalum group, obtained as described on page 31, if to it a drop of 2N hydrochloric acid and a drop of perhydrol were added. The method was successfully/

successfully applied to various mixtures containing maximum amounts of the group components, with and without the minimum amount of zirconium. A large amount of tantalum might lead to the formation of a very small precipitate, which could not be confused with that referring to the minimum amount of zirconium under consideration.

As this method for zirconium was so satisfactory, and the precipitate did not appear to contain much tantalum, it was thought that the potassium carbonate-hydroxide extracts, which may contain tantalum and niobium, and titanium if niobium is present, might be utilised for testing for the earth acids. A separation from titanium had to be effected, and two methods were tried to achieve this.

The first of these was the formation of the sodium salts, by saturating the solution with sodium chloride (Ref. 6, p. 33); the second, the precipitation of the oxides by saturating the boiling solution with sulphur dioxide gas (Ref. 5, p. 104). Precipitation by the first method was found to be slow and incomplete, but by the second method precipitates were obtained which, when tested by the bisulphate-tannin procedure, showed a high degree of purity, as judged by the colour. Owing to the retention of small amounts of the earth acids /

acids in the zirconium precipitate, however, minimal amounts were lost when an excess of zirconium was present.

It was therefore decided to retain, for the joint detection of tantalum and niobium, the bisulphate-tannin method (p.25), and for the detection of zirconium, the fusion with potassium carbonate (p.31), portions of the tantalum group precipitate being taken for each.

The Separate Identification of Tantalum and Niobium.---- No attempt had so far been made to assess with certainty the relative amounts of tantalum and niobium in their joint precipitate. As no suitable tests had been found for one in the presence of the other, the standardised quantitative separation process utilising tannin, described by Schoeller (Ref. 6, p. 123 et seq.), and stated to be suitable for milligram analyses (ibid., p. 45), was adopted in a simplified form. This method is based on the differential stability of oxalotantalic and oxaloniobic acids in presence of tannin in slightly acid solutions.

A mixture containing 2-3 mg. of tantalum plus niobium, with 5%, 50% or 95% of tantalum was fused with 0.1 g. of potassium bisulphate in a silica crucible and the melt made to solidify in a thin film round the walls of the crucible. It was dissolved in 10 ml. of a hot saturated solution of ammonium oxalate and transferred/

transferred to a 30 ml. beaker. A 2% solution of tannin was then added dropwise from a burette in 0.5 ml. portions at a time.

The first addition of tannin produced a yellow colour, and, on boiling, a yellow precipitate was obtained, which consisted almost solely of tantalum. The contents of the beaker were transferred to a centrifuge tube and the precipitate removed, and retained in the tube for reference. The solution was returned to the beaker, the next portion of tannin solution added, and the solution boiled again. At this stage, or at some subsequent repetition of the cycle, it was found necessary to add a few drops of 2N ammonium hydroxide and a little solid ammonium chloride before a precipitate was obtained. This addition of ammonium hydroxide caused the solution to take on a darker hue, and the precipitate derived therefrom was redder in colour and contained niobium in greater or less amount. The precipitates obtained after each addition of tannin were removed by centrifuging and retained as before.

After about 2.5 ml. of tannin solution had been added, further additions did not produce any precipitate. The results obtained for three mixtures are tabulated below.

Colour of the Precipitate obtained on the Addition of Successive Portions of Tannin Solution.

Mixture	% Ta	(1)	(2)	(3)	(4)	(5)
A	5	small yellow	*orange	*red	*red	* no precipitate
B	50	yellow	very small yellow	*orange	*orange-red	*red
C	95	yellow	yellow	yellow	very small yellow	*orange

* After addition of ammonium hydroxide and chloride.

The intermediate portions, designated above as "orange", could be treated further, by dissolving by dropwise addition of dilute sulphuric acid, and then retreating with tannin and ammonium hydroxide, whereby a separation into tantalum, mixed, and niobium fractions could be obtained (Ref. 12). It was found, however, that by inspection of the colour and relative bulk of the precipitates originally formed, a sufficiently accurate estimate of the proportions of tantalum and niobium could be made after a little practice.

In a mixture like those mentioned above, less than 5%/

5% (i.e. 0.125 g.) of tantalum and niobium could not be detected with certainty on a first treatment. In the actual analysis of the tantalum group, this separation of tantalum from niobium would follow after a bisulphate-tannin precipitation of the earth acids.

When the experiments mentioned on p.34 were repeated, after the earth acids had been subjected to this treatment, and the tannin precipitate produced from the sulphate solution destroyed by nitric acid and re-fused, the results obtained were generally similar to those set forth in the table, with the exception that the 5% quantities were not so distinctly detected. The orange precipitate in a mixture corresponding to C was very small, while in a mixture containing 5% of tantalum (A), the pale yellow solution, formed when the first portion of tannin solution was run in, did not yield a precipitate when boiled, unless ammonium hydroxide was added, in which case a mixed precipitate was produced. These effects were presumably due to loss sustained during the bisulphate-tannin treatment.

As noted on p.26, when titanium is present, contamination of the bisulphate tannin precipitate takes place, and when the ratio of titanium to the metals of the earth acids is 20:1, two treatments by the bisulphate tannin method would still leave 5% of titanium in the precipitate. When mixtures of 2-3 mg. of earth acid elements, containing 5%, 50% and 95%/

95% of tantalum, as before, and 10 mg. of titanium, were treated twice by the bisulphate tannin procedure, the destruction of the tannin precipitate between the treatments, and before the oxalate treatment, being accomplished by evaporation with a few drops of nitric acid, and then dealt with according to the separation precedure, the following results were obtained.

In mixture A, the first precipitate was as dark as the subsequent precipitates.

In mixtures B and C, the first precipitate was darker than the second (and third in the case of C), indicating that the titanium was precipitated more readily than the tantalum.

When two further mixtures similar to the above, but containing (D) no tantalum and (E) no niobium were treated by the procedure, it was found that D gave a small red precipitate immediately on the addition of the tannin, but that the main niobiumiferous precipitate did not appear till after ammonium hydroxide and chloride had been added, while E gave, first, a titanium contaminated precipitate, followed by several pure tantalum yellow precipitates. On the addition of ammonium hydroxide and ammonium chloride to E, no further precipitate was produced.

From a consideration of these results it will be seen that there was no possibility of titanium contamination of the precipitate being mistaken for niobium, because the/

the true criterion of the presence of the latter was not the colour of the precipitate, but the fact that ammonium hydroxide was necessary to produce it.

In the converse case, (cf. A & D) it might be impossible to say whether a first formed red precipitate contained tantalum or not. In this case, it was necessary to destroy the precipitate by means of nitric acid, and attempt to re-form the tannin precipitate by the bisulphate-tannin procedure before final confirmation was obtained.

The Detection of Antimony, Bismuth, Tellurium and Titanium.— On p.20 the possibility of tellurium appearing in the tantalum group was mentioned. Further experiments showed that it was necessary to allow for its detection in this group, as well as in the tungsten group. As three elements precipitable by hydrogen sulphide, antimony, bismuth and tellurium, were now under consideration, it was decided to abandon the direct testing for antimony, bismuth and titanium in separate 5% portions of the aqueous suspension of the tantalum group (cf. p.27), and instead fuse one larger portion with ten times its bulk of potassium bisulphate, extract with a 10% solution of tartaric acid, and saturate with hydrogen sulphide gas as described on p. 17. Thereby a precipitate containing the sulphides of bismuth, antimony and tellurium was separated from/

from tantalum, niobium, zirconium and titanium. The filtrate, after the expulsion of hydrogen sulphide, was tested for titanium with hydrogen peroxide, which is less affected by tartaric acid than chromotropic acid, and compared with a standard containing potassium bisulphate and tartaric acid (cf. p.21). The precipitate was digested with 1:1 hydrochloric acid to dissolve the sulphides of bismuth and antimony. If a residue of tellurium sulphide remained it could be compared in bulk with a standard, and confirmed by dissolving in nitric acid, expelling the latter with hydrochloric acid, and testing with calcium hypophosphite in a solution 2N in hydrochloric acid (p.46).

The solution containing bismuth and antimony was evaporated to a small volume and divided into equal parts, one for the detection and estimation of bismuth with dithiol (p.23), the other for the detection and estimation of antimony with rhodamine-B (p.44). If the amount of antimony, as judged by the appearance of the sulphide precipitate, was large, and likely to interfere with the detection of bismuth, or be inadequately assessed, the sulphides of bismuth and antimony were reprecipitated in the hydrochloric acid solution by diluting with water and resaturating with hydrogen sulphide, and the antimony sulphide extracted/

extracted with a solution of ammonium sulphide. The bismuth sulphide was dissolved in a drop of hydrochloric acid and tested with dithiol, and the antimony sulphide, reprecipitated by acidifying, assessed on the bulk of the precipitate, and, if desired, redissolved in concentrated hydrochloric acid, and confirmed with rhodamine-B. These operations, although apparently complicated, were carried out very quickly on the drop scale.

The final scheme of analysis for the tantalum group was drawn up as shown on p. 42.-43. The suspension of the residue from the sodium hydroxide treatment of the combined tungsten and tantalum groups was divided into three equal portions, which were analysed in the order given. If titanium was absent in the first part, then one precipitation with bisulphate and tannin sufficed for the second portion. If earth acids were found, then the third portion required two fusions with potassium carbonate to eliminate them. Otherwise these could be omitted and zirconium tested for simply after a fusion with potassium bisulphate.

This scheme was put into operation in association with that finally developed for the tungsten group (p.62-63). The results for the analyses of six mixtures of composition unknown to the operator are given on p. 64.

TANTALUM GROUP Scheme of Analysis II

RESIDUE - Ta, Nb, Zr, Ti, Bi and perhaps Sb and Te, mainly as oxides or hydroxides. Wash twice with 1% NH_4NO_3 to remove Na salts, suspend in water. Divide into three equal parts.

(1) Evaporate to dryness, fuse with 10 times the bulk of $KHSO_4$, extract with tartaric acid, and pass H_2S (p. 39)

PRECIPITATE - Sulphides of Sb, Bi and Te. Digest in 1:1 HCl.

FILTRATE -

Boil out H_2S. Test with H_2O_2. A yellow colour shows Ti. (p.40). Assess.

PRECIPITATE - Te. Compare with standard. To confirm, dissolve in a little HNO_3. Evaporate with HCl and test with Ca hypophosphite as on p. 46. Black ppt. shows Te.

FILTRATE - If the sulphide ppt. was small, evaporate to 0.1 ml. Test part with rhodamine-B. A purple ppt. shows Sb; assess (p.40). Test the remainder with dithiol (p.23). A brown ppt. shows Bi; assess. If the sulphide ppt. was large, and contained much Sb, reprecipitate the sulphides in a diluted solution and extract with $(NH_4)_2S$.

PRECIPITATE - Dissolve in 1:1 HCl. Test for Bi with dithiol and assess.

FILTRATE - Reprecipitate Sb_2S_3. Assess the amount. If desired, dissolve in 1:1 HCl and confirm Sb with rhodamine-B.

(2) Fuse with $KHSO_4$ as in (1). Take up in 1% tannin in 10% H_2SO_4. Should a ppt. form, dissolve it in HNO_3 and evaporate to dryness. If more than 0.5 mg. of Ti has been found, repeat the procedure. Assess the combined amount of Ta and Nb on the bulk of the tannin ppt. Finally fuse with $KHSO_4$, take up in saturated $(NH_4)_2C_2O_4$, and test for and apportion Ta and Nb (pp. 34-39).

(3) If Ta and Nb are absent, evaporate just to dryness and fuse with $KHSO_4$. Take up in 4N H_2SO_4 and test with p-hydroxyphenylarsonic acid. A white ppt., the bulk of which is estimated, shows Zr (p. 32).
If Ta and Nb are present, evaporate, fuse in a blowpipe with 0.2 g. of K_2CO_3, and take up in 2N KOH. Separate and wash the ppt. and repeat the fusion. Proceed as in the absence of Ta and Nb.

ANALYSIS OF THE TUNGSTEN GROUP.

(Sb, Sn, Te, Mo, V, W, P as phosphate).

The elements of this group were extracted from the combined tantalum and tungsten groups by means of a 7N solution of sodium hydroxide (see p. 19); and represented the same combination as was obtained by Noyes and Bray. Before proceeding to separate them, many of the newer reagents proposed for these elements were critically tested, and the most important results are recorded below.

Antimony.— As a test for antimony, oxidised to the pentavalent form by means of sodium nitrite, Wegriwe (Ref. 13) used a twenty-fold excess of a 0.01% aqueous solution of rhodamine-B, which gave a violet colour in transmitted light. C.C. Miller (unpublished research) found that a 0.1N solution of sodium vanadate was superior as an oxidising agent, and that the test was much more selective if made with a small amount of a 1% solution of the reagent in 8N hydrochloric acid. The latter method was adopted. To one drop of a hydrochloric acid solution containing antimony, in a 1" test-tube, one drop of the reagent and one drop of the vanadate solution were added; the mixture was stirred. 10γ of antimony gave a strong blue colour. Larger amounts gave purple precipitates, and/

and the blue colour, which was very characteristic, might also be seen. Large excesses of tin (stannic), bismuth, titanium (titanic), zirconium, tellurite, vanadate and phosphate did not interfere. Molybdate gave a very red solution. Tungstate, from which tungstic acid was precipitated, interfered by adsorbing the reagent, but tartaric acid dissolved the precipitate, giving a red solution, and did not vitiate the test for antimony. 10 γ of antimony was found in the presence of 400 γ of tungsten or molybdenum. The assessment of the quantity of antimony from the bulk of the centrifuged precipitate was quite satisfactory for small amounts (<1 mg.) of antimony, but not for large.

Vanadium (as vanadate). — The most generally useful reagent for vanadium was tannin. A solution of tannin gave a strong inky black colour with vanadium near the neutral point. The test was performed on the tile, by adding to a drop of the acid solution containing vanadate one drop of a 5% aqueous solution of tannin, and, either dilute ammonium hydroxide solution, or ammonium acetate, to reduce the acidity. If the concentration of salts in the solution was high, the tannin was precipitated, and the vanadium complex was adsorbed on its surface, giving a blue-grey colour.

The/

The sensitivity of the test was very great, 10γ of vanadium giving a deep blue colour, even when the solution was diluted to one ml. The reaction was too sensitive for the assessment of a large amount of vanadium but excellent for a small quantity. The only members of the group that gave a reaction with tannin, under the same conditions, were tungstate and molybdate, which, in great excess, formed brown compounds. The addition of a little tartrate solution eliminated their interference. Phosphate also prevented the interference of tungstate.

Tellurium (as tellurite). — In hydrochloric acid solution, tellurites are reduced by hypophosphoric acid to black elementary tellurium (Ref. 7, p. 337). To one drop of a 2N hydrochloric acid solution containing 50γ of tellurium, 0.1 g. of calcium hypophosphite was added, and the mixture heated. The black precipitate that immediately separated could be centrifuged, if desired, and compared with a standard for the assessment of the quantity of tellurium present. 4 mg. of antimony or bismuth did not interfere. Molybdate gave a blue colour which was partly suppressed by tartaric acid.

Tin. — For the detection of tin 4-methyl-1:2-dimercaptobenzene ("dithiol") (Ref. 14) proved to be excellent. A 0.02% solution was made up in 0.25N sodium hydroxide containing 0.3% of thioglycollic acid. This solution, stated to be stable for a few days, was found to remain/

remain fully sensitive for tin for not more than twelve hours. A drop or two of the reagent solution was added to a drop of the hydrochloric acid solution of tin in a small test-tube, the final normality of acid being less than four. An opaque red precipitate, the production of which was accelerated by heating in a water-bath, indicated tin. No other element tested gave a red precipitate, which was therefore characteristic for tin. 10 γ was easily detected. A minumum of 50 γ was similarly found in a volume of 2 ml. if an excess of the reagent was added. The red precipitate was soluble in various organic solvents, including butyl acetate, giving a very pale green solution, that yielded the red precipitate again on evaporation. Moderate amounts of tin (<2 mg.) were successfully estimated by comparing the precipitates, recovered from butyl acetate extracts by evaporation in small porcelain basins, with those similarly derived from known amounts of tin. When the amounts were large, suitable portions of the solutions were taken.

With dithiol, antimony and tellurite gave, instantaneously, pale yellow precipitates, lead, an orange precipitate, bismuth, a brown (see p.23), molybdate, a green, and tungstate, a peacock green only on heating, unless the concentration of tungstate/

tungstate was high. With vanadate, a pale green colour probably indicated merely a reduced vanadium ion. The interference of these reactions with the test for tin was investigated. The antimony compound was formed preferentially to that of tin, but an excess of the reagent permitted, in general, the detection of amounts of tin exceeding 50 γ in the presence of twice the amount of antimony. The same applied to tellurite and bismuth, but a six-fold excess of lead was permissible. Molybdate interfered most seriously by blotting out all but excessive amounts of tin. The interference was lessened by the addition of more thioglycollic acid, which gave with the molybdate a blue colour, less intense than that of the green dithiol compound. By this means it was possible to detect tin in the presence of not more than the same amount of molybdenum. Phosphate, vanadate, oxalate and tartrate did not interfere, and the last could be added to eliminate interference from tungstate.

Molybdenum (as molybdate) and Tungsten (as tungstate).— The colour reaction between dithiol and molybdenum was studied by C.C. Miller in 1937 (unpublished research), and the test for tungsten was discovered, and its importance realised, by the writer, some time before the recent publication of Hamence's paper (Ref. 15).

When/

When the test was applied in the same manner as for tin, molybdenum gave immediately a green precipitate, while tungstam gave a peacock green, on heating. Both complexes dissolved readily in butyl acetate, or chloroform without colour change. 25 γ of tungsten gave in one ml. of the solvent quite a strong green colour, and towards molybdenum the reagent was ten times more sensitive. Owing to the high sensitivity of the tests, such extracts could be used only to estimate small amounts of the elements, and only portions of solutions containing appreciable amounts could be examined.

Both complexes were unaffected by even 6N hydrochloric acid. Large amounts of phosphate, tartrate and vanadate did not prevent the reaction with molybdenum. Tartrate prevented the reaction with tungstate, and a combination of phosphate and vanadate greatly reduced the sensitivity, although the substances singly had comparatively little effect. In the slightly acid aqueous solution, tin in quantity obscured the test for tungsten, but the performance of the test in a much stronger acid solution prevented this. Extraction with butyl acetate also rectified matters, by forming merely a very pale green solution with the tin complex. The addition of concentrated hydrochloric acid, after the reagent, also broke down the/

the red tin complex, leaving the green due to tungsten. If to the aqueous solutions containing the green complexes concentrated ammonia was added, the colour due to tungsten disappeared and molybdenum gave a blue colour.

A Study of some Separation Processes within the Tungsten Group.

The method of separating the tungsten and tantalum groups adopted by Noyes and Bray (Ref. 5, p. 70) led to a division of the phosphate, whereas that adopted by the writer caused the whole of the phosphate, which might be present in considerable amount, to be concentrated in the tungsten group. A great many experiments were done before a satisfactory scheme of analysis was devised. As in the case of the tantalum group, tests were carried out on synthetic mixtures, prepared by evaporating just to dryness with a little sulphuric acid, suitable amounts of standard solutions of the components of the tungsten group, and dissolving them in 1 ml. of 7N sodium hydroxide.

The Precipitation of Antimony, Tin, Tellurium and Molybdenum Sulphides in Tartaric Acid Solution.— The alkaline synthetic mixture was acidified with tartaric acid to prevent the precipitation of tungstic acid, if there was no, or insufficient, phosphate to hold it in solution as phosphotungstic acid, and the sulphides of antimony, tin, molybdenum and tellurium were then precipitated/

precipitated by means of hydrogen sulphide. Tungsten, vanadium and phosphate remained in solution. Troublesome features consequent on this separation were the necessity for removing tartaric acid before testing for tungsten with dithiol, or for phosphate by precipitating it as ammonium phosphomolybdate. In the presence of much phosphate, a little molybdenum escaping precipitation with sulphide upset the test for tungsten. A small amount of tin might similarly escape and fail to be detected. The method was abandoned.

The Removal of Phosphate as Zirconium Phosphate.— An attempt was made to prevent the complications due to the presence of phosphate by removing it at the start of the analysis. Curtman, Margulies and Plechner (Ref. 16) removed phosphate from solutions 0.3N in hydrochloric acid by slowly adding a small excess of a 5% solution of zirconium oxychloride to the boiling solution containing phosphate. Accordingly the caustic soda solution of the tungsten group metals was acidified with hydrochloric acid until the normality was 0.3. Tungstic acid separated if phosphate was absent or in insufficient amount to retain it in solution. The separation of antimony oxychloride also occurred if the concentration of antimony was high. These precipitates could be removed by centrifuging, and the oxychloride extracted with stronger hydrochloric acid. Phosphate was then precipitated under the prescribed conditions, along/

along with any tungstic acid liberated by the breaking down of the phosphotungstic acid, leaving antimony, tin, tellurium, vanadium and molybdenum in the solution. From the zirconium phosphate, tungstic acid was extracted by means of warm, moderately concentrated ammonia, and confirmed with dithiol (p.48). To confirm phosphate, the zirconium phosphate precipitate was fused with sodium carbonate, the cold melt extracted with 2N sodium hydroxide, and the extract acidified with nitric acid, and tested with ammonium molybdate.

The separation and confirmation of phosphate, even in the minimum amount of 0.25 mg., proved to be very satisfactory, but small amounts of tungsten were lost, either because they were not precipitated, or were inadequately extracted from the zirconium phosphate precipitate. The low acidity required for the precipitation of zirconium phosphate was a distinct disadvantage, and this method too was eventually abandoned.

The Removal of Molybdenum with Thiocyanate. — By the methods of the preceding sections antimony, tin, tellurium and molybdenum were associated together, without or with vanadium. Vanadium was easily removed in the second method by precipitating the sulphides of the other four elements. In testing this group of sulphides an extraction with 1:1 hydrochloric acid was usually made in order to obtain antimony and tin in solution. The dithiol test for tin was then applied,/

applied, directly if the amount of antimony was small, or after a further separation (see p. 57) if the amount was large. It was found that a little molybdenum escaping into the hydrochloric acid extract might prevent the detection of tin. Consequently a better mode of separation had to be found. Since molybdenum also seriously interfered with the detection of tungsten by dithiol, a very complete separation from tungsten was likewise required. Very satisfactory results were obtained by converting molybdenum to the red thiocyanate complex, $Mo(OH)_2(SCN)_3$, and extracting it with butyl acetate. It is customary to effect the preliminary reduction of molybdate with zinc or stannous chloride, but these not being permissible here, thioglycollic acid was successfully employed. The method which was ultimately adopted as the first step in the analysis of the tungsten group was applied as follows. The caustic soda solution of the tungsten group ions in a centrifuge tube was acidified with hydrochloric acid and maintained near the boiling point by immersing the tube in the water-bath. If a precipitate, supposedly tungstic acid, separated, it was removed and examined as described later (p. 61). The solution at this stage might have a normality of two and a volume of 3 ml. The strength of the acid was not critical, but sufficient had to be present to/

to hold the oxychlorides of tin and antimony in solution, and to form the thiocyanate complex. To the solution were added a few drops of a 10% solution of potassium thiocyanate followed by a few drops of a 10% aqueous solution of thioglycollic acid. The development of a pink colour indicated the presence of molybdenum. The addition of more of one or other, or both of the reagents might be necessary to form the complex with all of the molybdenum, and when the amount was large, it might be necessary to extract part of the complex with butyl acetate, before it could be seen whether or not sufficient of the reagents had been added. Butyl acetate readily dissolved the complex, and the ester layer separated very cleanly from the aqueous layer, particularly if the tube was centrifuged for a few seconds. The top layer was removed with the aid of the pipette described on p. 9 . Several washings with small quantities of the solvent ensured the complete removal of the molybdenum.

When tellurium was present in mixtures treated by this method it was partly or completely precipitated in the elemental form by the reducing action of the thioglycollic acid. It was best to remove it by centrifuging and to transfer the solution to another cone before extracting with the ester, otherwise it was attracted to the interface between the two liquids and made complete removal of the ester layer difficult.

The/

The bulk of the precipitated tellurium was compared with a standard. The extraction method for molybdenum was very well suited for estimating its quantity, provided that the standard was also prepared in butyl acetate.

Even in mixtures containing large amounts of phosphate the extraction of molybdenum was very complete, and if a minor quantity remained in the aqueous solution it was precipitated as sulphide in the subsequent treatment with sulphuretted hydrogen. By direct test with dithiol it was found that the amount of molybdenum escaping precipitation altogether was about 25%.

The Separation of Antimony, Tin and Tellurium (part).— The aqueous layer that remained after the removal of molybdenum and part of the tellurium contained tin wholly or partly in the stannous state, antimony, the remainder of the tellurium, vanadium, tungsten (whole or part) and phosphate. In order to precipitate antimony, tin and the remainder of the tellurium as sulphides the acidity was reduced to 0.3N by the careful addition of a dilute solution of sodium hydroxide. Methyl violet was used to indicate this normality, a green colour being given when a tiny drop of the solution was spotted on filter paper impregnated with the/

the indicator solution. A current of hydrogen sulphide was then passed into the warm solution until the precipitation was complete. In the presence of a large amount of phosphate a little tin might escape separation but provision was made for its subsequent detection (see p. 59). From the centrifuged and washed precipitate the sulphides of antimony and tin were extracted with a small amount of hot 1:1 hydrochloric acid leaving a (usually) small black precipitate of tellurium. The latter was dissolved in a few drops of nitric acid, the latter expelled by heating with hydrochloric acid, and tellurium confirmed by means of calcium hypophosphite in the presence of a little tartaric acid (p. 46). A trace of molybdenum that accompanied the tellurium did not, in general, require to be tested for.

If the amount of sulphide precipitate dissolved by the 1:1 hydrochloric acid was quite small a separation of tin and antimony was unnecessary, and the solution could be evaporated on the steam bath to a volume of 0.1 ml., one half then being tested for antimony with rhodamine -B (p. 44) and the other for tin with dithiol (p. 46). If, however, a considerable amount of precipitate dissolved it was generally necessary to separate tin and antimony. in order to confirm/

confirm the presence of tin. The separation was very satisfactorily effected as follows: Bromine water was added dropwise to the solution until it was yellow in colour, in order to convert tin to the stannic form. The solution was then diluted to reduce the normality in hydrochloric acid to one, 0.5 g. of oxalic acid added to form a complex oxalate of tin, and antimony reprecipitated as the sulphide, its quantity being assessed if it was large. If the amount was small it was redissolved in hydrochloric acid and tested with rhodamine -B. The oxalate solution containing tin could be directly tested with dithiol, a portion being taken if a large amount of tin were anticipated. The oxalic acid did not interfere with the test or the assessment of quantity (see p. 47).

On p. 15 it was mentioned that a maximum of 1.5 mg. of lead might be present in the tungsten group. This would separate as sulphide and be associated with antimony and tin. It would not interfere with the detection of antimony with rhodamine -B, nor with the detection of tin with dithiol, if an excess of the latter were added (see p. 48). If antimony were separated from tin, lead would accompany the former, and it would be essential to dissolve any small precipitate in hydrochloric acid and test with rhodamine -B.

The/

The Separation of Vanadium, Tungsten, Phosphate and a Trace of Tin. — The solution, after the sulphide treatment, contained all of the vanadium and phosphate

that might be present in the group, any tungsten escaping the first separation (p. 53), principally as phosphotungstic acid ($xH_2O.24WO_3.P_2O_5$),

and, occasionally, a little tin, carried through by an excess of phosphate. Since vanadium in association with phosphate interfered with the detection of tungsten (p. 49), it was necessary to separate amounts in excess of about 0.5 mg. The tannin test (p. 45) was applied to about 5% of the solution, and the quantity of vanadium, if seen to be small, assessed. If the estimated amount of vanadium was more than 0.5 mg., its separation from tungsten and phosphate was required, the cupferron method of Clarke (Ref. 17) being adopted. Hydrogen sulphide was expelled from the main solution, a little bromine water added to oxidise reducing ions, which might be in the solution at this stage, and the excess expelled by evaporation. The solution (3 ml.) was then cooled and four drops of 40% hydrofluoric acid were added, followed by excess of an aqueous solution of cupferron. The vanadium was precipitated as the brown vanadium-cupferron complex, which was found to be soluble in butyl acetate, giving a dark brown solution. This solution faded/

faded in colour rather rapidly, but if dealt with immediately could be compared with a standard similarly prepared. The extraction with butyl acetate also removed most of the excess cupferron from the solution. In order to destroy the remainder of the cupferron or its decomposition products, the solution was evaporated to fumes with a few drops of concentrated sulphuric acid, and again diluted to about 3 ml. with water.

This solution had to be tested for tungsten, tin (small), and phosphate. For the first two it was intended to use dithiol, and for the last ammonium molybdate. As all the tests were sensitive, it was thought that each could be applied to a third of the solution. Tin was tested for with dithiol in the presence of tartaric acid to mask tungsten (cf. p.48), and its quantity assessed. If tin was present, tungsten was tested for in a solution about 6N in hydrochloric acid (p.49).

In the absence of more than 0.5 mg. of tungsten, the remaining portion of the solution was tested directly for phosphate (see below). If more than 0.5 mg. of tungsten was present, the phosphate was separated in a solution, 0.3N in acid, by slowly adding to the boiling solution a small excess of a 5% solution of zirconium oxychloride (cf. p.51). The/

The presence of phosphate was usually indicated by the appearance of a precipitate, but a very small amount might not be visible. The solution was then rendered ammoniacal and heated in the water bath. Zirconium phosphate and zirconium hydroxide from the excess of zirconium oxychloride added were completely precipitated, and most of the tungsten was retained in solution as tungstate. The precipitate was separated by centrifuging, washed, and fused with five times the bulk of sodium carbonate in a platinum crucible. It was extracted with a little 2N sodium hydroxide. According as the precipitate of zirconium phosphate in acid solution had been small or large, the whole or part of the extract was tested for phosphate. It was strongly acidified with nitric acid, solid ammonium nitrate was added, and then to the warm solution an excess of a 10% solution of ammonium molybdate. If a yellow precipitate of ammonium phosphomolybdate was produced it was compared with a standard.

The Recovery of a Small Amount of Earth Acid from the Tungsten Group Solution. — As the tantalum and tungsten groups were inter-related, many analyses were done, after first separating the tungsten group by the sodium hydroxide treatment (p.19), from mixtures containing/

containing the components of both groups. In a few of these, acidification led to the separation of a precipitate, supposedly tungstic acid, which was, however, incompletely soluble in 2N sodium hydroxide. The residue, consisting of earth acids, in particular niobic acid, was therefore washed with a little more sodium hydroxide and combined with the tantalum group precipitate. To part or all of the solution containing tungstate (according as the amount of the latter had been seen to be large or small), dithiol was added, the solution acidified with hydrochloric acid, heated, and the green dithiol complex of tungsten, when fully formed, extracted with butyl acetate. Its quantity was assessed by comparison with a standard (p. 49).

The final scheme of analysis for the tungsten group is given in outline on pp. 62 and 63.

As a check on the methods of analysis developed for the tantalum group (pp. 42 and 43) and the tungsten group, six mixtures of unknown composition, containing the components of both groups, were submitted to the writer for analysis. The results obtained are given on p. 64 and discussed on p. 65.

TUNGSTEN GROUP Scheme of Analysis

SOLUTION contains sodium tungstate, molybdate, tellurite, hypovanadate and phosphate, and complex salts of antimony, tin, lead, and perhaps niobium and tantalum in NaOH solution. Acidify with HCl until the N is about 2 and the volume 3 ml. Dissolve SbO_2Cl and digest in boiling water (p. 53).

PRECIPITATE - Digest with 2N NaOH. Wash any residue with more NaOH and combine with Tantalum Group. To part or all of solution add dithiol and HCl. A blue-green ppt. shows W. Extract with butyl acetate to assess (p. 61).

SOLUTION- Add 10% aq. KCNS and 10% aq. thioglycollic acid. A red colour shows Mo, and a black ppt., Te. Extract with butyl acetate, and separate ppt., and ester and aq. layers.

(1) **ESTER LAYER** - Compare with a standard for Mo in butyl acetate (see p. 55)

(2) **PRECIPITATE** - Te. Compare with a standard.

(3) **AQUEOUS LAYER** - Adjust N in HCl to 0.3, and pass H_2S (p. 55).

PRECIPITATE - sulphides of Sn, Sb, Pb, Te and Mo(traces). Digest with 1:1 HCl.

PRECIPITATE - Te and Mo in traces. Dissolve in aqua regia and expel HCl. Test for Te with hypophosphite (p. 56). A trace of Mo may be neglected.

SOLUTION contains chlorides of Sb, Sn^{++}, and Pb. If the ppt. dissolved was small, evaporate to 0.1 ml. Test 0.05 ml. with rhodamine-B. A purple ppt. shows Sb. Test 0.05 ml. with an excess of dithiol. A red ppt. shows Sn. If the ppt. dissolved was large, oxidise Sn^{++} with Br_2 water, reduce to N in HCl, add 0.5 g. of oxalic acid and pass H_2S.

PRECIPITATE - Sb_2S_5 & PbS. Dissolve in 1:1 HCl. Test for Sb with rhodamine-B (pp. 44 & 57) Pb not tested for.

SOLUTION - Add dithiol to all or part. A red ppt. shows Sn. Extract with butyl acetate and assess (pp. 47 & 57).

* SOLUTION. see next page.

*See preceding page.

SOLUTION contains hypovanadate, tungstate, phosphate and perhaps some Sn^{++}. Test 5% for V with tannin and ammonium acetate (p. 58). If more than 0.5 mg. is present in the whole solution, remove it as follows. Expel H_2S, oxidise with Br_2 water, and remove the excess. Cool, and to the solution (3 ml.) add 4 drops of 40% HF and an excess of aq. cupferron.

PRECIPITATE - Brown cupferron complex of V. Extract with butyl acetate. Compare immediately with a standard and assess. (p.58).	SOLUTION - Evaporate to fumes with a few drops of H_2SO_4, and dilute to 3 ml. with water. Divide into three equal parts.
	(1) Add tartaric acid and dithiol and heat. A red ppt. shows Sn. Extract with butyl acetate and assess (pp. 48 & 59).
	(2) Test with dithiol in the presence of 6N HCl, heating for several minutes. A peacock green colour shows W. Extract with butyl acetate and assess (pp. 49 & 59).
	(3) If more than 0.5 mg. of W is present, add slowly to the boiling solution at an acidity of 0.3 N, excess of 5% aq. $ZrOCl_2$, make ammoniacal and heat. Separate the ppt. and fuse with 5 times the bulk of Na_2CO_3. Extract with 2 N NaOH. To all or part of the extract add conc. HNO_3, NH_4NO_3 and 10% aq. ammonium molybdate. Heat at 50°. A yellow ppt. shows PO_4. Assess (see p. 60).

TANTALUM AND TUNGSTEN GROUPS

Results of the analyses of unknown mixtures

The quantities of ions present and found are expressed in mg.

No.	Ta	Nb	Ti	Zr	Bi	Sb	Te	Sn	Mo	V	W	PO_4
1. Present.	10	0.5	-	-	-	0.5	0.25	0.5	-	-	10	-
Fnd. Ta Gp.	10	o	o	o	o	o	o	o	-	-	-	-
Fnd. W Gp.	-	-	-	-	-	0.25	0.5	0.25	o	o	6.5	o
2. Present.	0.5	-	0.25	10	0.25	20	-	0.25	0.5	-	-	10
Fnd. Ta Gp.	0.25	o	0.25	5	0.25	6	o	o	-	-	-	-
Fnd. W Gp.	-	-	-	-	-	4.5	o	tr.	0.5	o	o	9
3. Present.	5	0.5	-	-	-	-	10	25	-	0.25	0.25	0.25
Fnd. Ta Gp.	6	1	o	o	o	o	1	tr.	-	-	-	-
Fnd. W Gp.	-	-	-	-	-	o	4	10	o	0.25	o	0.25
4. Present.	1	-	10	0.25	-	-	1	1	10	1	-	1
Fnd. Ta Gp.	1.5	o	6	0.25	o	o	0.75	o	-	-	-	-
Fnd. W Gp.	-	-	-	-	-	o	o	0.25	7.5	1	o	0.5
5. Present.	0.5	5	0.5	0.5	0.5	1	-	-	0.25	2	4	0.5
Fnd. Ta Gp.	tr.	5	1	0.5	0.25	0.25	o	o	-	-	-	-
Fnd. W Gp.	-	-	-	-	-	0.5	o	o	0.75	2	6	0.5
6. Present.	2	3	-	-	0·5	15	0.5	0.5	1	0.5	0.5	25
Fnd. Ta Gp.	1.5	3.5	o	o	0.25	0.5	o	0.5	-	-	-	-
Fnd. W Gp.	-	-	-	-	-	10	o	o	1.25	0.25	0.25	18

One of the most satisfactory features of these analyses is that in no case has an element been reported when it was not present in the mixture. On three occasions small quantities of elements were missed. In No. 1, it will be observed that the 0.5 mg. of niobium that was present along with 10 mg. of tantalum was not reported. On p. 37 it was indicated that difficulty might be experienced in detecting 1 part of tantalum or niobium in the presence of a 20-fold excess of the other. In No. 3, 0.5 mg. of niobium was detected with certainty when tantalum was present in only a 10-fold excess, and in No. 5, 0.5 mg. of tantalum, although not adequately assessed, was reported as a trace, in the presence of 10 times the amount of niobium, because when tannin was first added to the oxalate solution, the latter became yellow, but yielded no precipitate on boiling. The limiting proportions for the detection of tantalum in the presence of niobium, and vice-versâ, ought therefore to be 1:10, the minimum amount of each element detectable being 0.5 mg.

As the minimum quantity of tungsten (0.25 mg.) in No. 3 was not reported, the analysis of the tungsten group was repeated, but it was again not found. In No. 3, a small amount of the large quantity of tin present, and in No. 6, all of the small quantity, were found in the tantalum group when the dithiol test/

test for bismuth was applied. Hence tin is unlikely to be missed even when a little passes into the tantalum group.

In No. 6, the tellurium presumably went into the tantalum group precipitate which was dark in colour, but when the sulphide group was analysed it was not confirmed. It will be observed that in No. 4 most of a small quantity of tellurium was found in the tantalum group.

The estimation of quantities, though generally satisfactory, was in some instances particularly good. This was true of vanadium, for example, where an estimate was made both on the drop of the solution removed for the tannin-test, and on the depth of colour of the butyl acetate extract of the cupferron complex. Tantalum and niobium were also satisfactorily apportioned on the bulk of the tannin precipitates thrown down from the oxalate solution.

In no case did a leakage of molybdenum cause tungsten to be wrongly reported, or did the interference of tantalum affect the test for zirconium with p-hydroxyphenylarsonic acid.

ANALYSIS OF THE GOLD GROUP.

(Au, Hg, Pt, Pd, Rh and Ir).

As a result of the experience gained in dealing with the tantalum and tungsten groups, it was expected that a fairly complete scheme of separations would have to be evolved before confirmatory tests could be applied with confidence for the members of the gold group, namely, gold, mercury, platinum, palladium, rhodium and iridium. Prior to considering the possible schemes of separation, it was necessary to examine certain of the reagents applicable to these elements. The results for those that proved to be of greatest importance are given below.

Gold - A 1% solution of rhodamine -B in 8N hydrochloric acid gave with gold a reaction similar to that given with pentavalent antimony, i.e. a purple precipitate was formed, and the solution had a blue colour when viewed by transmitted light (Ref. 13). The concentration of hydrochloric acid had an important influence on the sensitivity of the test towards gold. Thus 25γ of gold gave a purple precipitate in solutions, the final normality of which was 3-4, but did not give any in 6N acid. Of the ions which might be present in the gold group, only the mercuric ion/

ion gave a similar reaction to gold, when present in excess, and if the acidity was low, but the addition of hydrochloric acid to bring the normality up to 3 or 4 eliminated this effect. The presence of nitric acid in a concentration greater than normal, when hydrochloric acid was also present, spoiled the test for gold by decomposing the reagent.

Conditions under which the interference of mercury was prevented, while the test remained adequately sensitive to gold were obtained by adding 1 drop of the 1% reagent in 8N hydrochloric acid (as used for antimony, see p.44) to 2 drops of the test solution, in nitric acid of normality not greater than unity. By this means 25 γ of gold were detected in the presence of a 200-fold excess of mercury. Small amounts of gold could be assessed by centrifuging the precipitates, and comparing them with standards.

Mercury.-- The use of diphenylcarbazone as a reagent for mercury was investigated (Ref. 18). A saturated solution in alcohol was found to give a strong purple-coloured precipitate when mixed with a solution containing mercuric ions. The solution, which must not contain more than a trace of chloride ion, and must also be of pH 7-8 was neutralised by the addition of solid sodium acetate. The test might also be applied on spot-test paper, when the greatest sensitivity was desired, but its use in solution was of greater interest, and it was found that 100 γ of mercury gave a distinct precipitate from 1 ml.

of/

of solution.

Palladium gave a precipitate similar to that of mercury but of a bluer shade. The amount produced from a given amount of palladium was about half of that obtained from an equal amount of mercury. Neutral solutions of platinum, rhodium and iridium gave faint violet colours. A solution of gold also gave a violet-coloured precipitate on mixing, which decomposed almost immediately into a black precipitate of the metal. If more than 0.5 mg. of gold was present, this obscured the precipitate derived from small amounts of mercury.

In the absence of an excess of gold, the bulk of the precipitate derived from mercury, could be judged by centrifuging, or it might be dissolved in ethyl or butyl acetate, separated, and compared with a standard. If this method were adopted, care had to be taken to avoid an excess of the reagent, which also dissolved in the ester to give a strong red solution (at pH >7) which upset the assessment.

Platinum.— Of many reagents applied to the detection of platinum, the most valuable was dimethylphenylbenzyl-ammonium chloride, which was used by Maynard, Barber and Sneed (Ref. 19). The reagent was made by mixing equimolecular amounts of benzylchloride and dimethylaniline, and allowing the mixture to stand at ordinary temperature until/

until a crystalline mass was formed. The crystals were washed with ether and dissolved in water to form a 10% solution. This reagent forms compounds with the platinum metals in a manner similar to ammonium or potassium chloride.

e.g. $\left[(CH_3)_2 (C_6H_5) (C_6H_5CH_2) N\right]_2 Pt Cl_6$

When a few drops of the reagent solution were added to the same amount of a solution of platinum in 4N hydrochloric acid in a small test-tube, a copious pale buff precipitate was formed. 25 γ, the smallest quantity investigated, gave a distinct precipitate immediately on mixing. 250 γ of mercury, 1000 γ of gold, 500 γ of rhodium and 250 γ of iridium gave pure white, yellow, pale violet and red-brown precipitates, respectively, similar in bulk to those formed with 25 γ of platinum. Palladium gave a light brown precipitate as copious as that formed with platinum. When the tubes containing the mixtures were placed in boiling water for a few minutes the precipitates due to mercury, palladium and rhodium dissolved and that due to iridium greatly diminished in bulk; they came down again on cooling. The solution containing gold gave a few globules of yellow liquid on heating. As the bulk of the platinum complex was not seriously affected by heating at 100° there was no difficulty in ascertaining the presence of platinum even if moderate excesses of the other group components were in admixture. The precipitate/

precipitate, might, however be discoloured by small amounts of iridium. Comparison with a standard permitted the assessment of quantity.

Iridium.— (1) A solution of leuco-malachite green, 1% in acetic acid, was turned green by the action of a neutral solution of iridium (Ref. 20). The reaction was sensitive down to 25γ, and the only interference encountered among the metals of the gold group was due to the masking effect of strongly coloured ions, notably palladium and rhodium. 50γ of iridium could be found in the presence of a twenty-fold excess of rhodium, which is greater than would ever be found in practice (cf. p. 15). The need for rigid adherence to neutral conditions before the test would work for small amounts of iridium was a disadvantage.

(2) A test proposed by Maynard, Barber and Sneed (Ref. 19) was investigated. The test-solution was evaporated to fuming with sulphuric acid in a porcelain crucible, and a few drops of concentrated nitric acid added, and the evaporation continued. A bright blue colour indicated the presence of iridium. If small quantities of iridium were being sought, it was usually necessary to repeat the addition of the nitric acid two or three times before the colour appeared. This test was more reliable than the l-malachite/

l-malachite green reaction, and was at least as sensitive; moreover, it depended upon a characteristic property of iridium, the formation of a blue oxide. As in the other test, the only interference found was from the strongly coloured ions, but with a ten-fold excess of rhodium, the final colour of the solution was a brownish-purple, which could safely be interpreted as being due to the presence of iridium.

Palladium.— With dithiol solution (p. 46), palladium alone of the metals in the gold group gave a reaction, a brown precipitate being produced when a drop of its solution was mixed on the spot-tile with a drop of the reagent solution, and then acidified. 25 γ was easily detected.

The characteristic reaction of palladium with dimethylglyoxime is described under the section dealing with the separations (p.81).

Rhodium.— No satisfactory test for rhodium was found, apart from the reduction by titanous chloride, which could only be applied in the absence of gold, platinum, and palladium, and which will be described later (p.83).

Evolution of a Scheme of Analysis.

The scheme devised by Noyes and Bray (Ref. 5, pp. 110 et seq.) for the analysis of the gold group, commences with the separation of the gold and mercury from the remaining elements by extraction with ethyl acetate from a solution of low chloride ion concentration. The mercury/

The mercury is then separated from the gold by shaking the ester layer with a solution of high chloride ion concentration, so that the $HgCl_4$" ion is formed and passes into the aqueous layer. The subdivision of the platinum, palladium, rhodium and iridium which remain in the aqueous solution during the first treatment is based on the different solubilities of their ammonium chloride complexes, the platinum and iridium being precipitated, and the palladium and rhodium remaining in solution. This separation has been criticised by Gilchrist and Wichers (Ref. 21) on the grounds of incomplete precipitation, and comtamination of the precipitate by palladium and rhodium.

Gilchrist and Wichers have worked out a scheme of analysis for the six platinum metals (Ref. 22) in which the separation of palladium, rhodium, and iridium from platinum is accomplished by the precipitation of the former as insoluble hydrated dioxides from a solution neutralised to approximately pH 7. The precipitated dioxides are dissolved up, and the palladium is then precipitated as the dimethylglyoxime complex (Ref. 23), a method of which Gilchrist and Wichers speak highly.

It was thought that a scheme of analysis could be devised in which the methods adopted by Gilchrist and Wichers for separating palladium, platinum, rhodium and iridium could be applied to a solution from/

from which gold and mercury had been removed by Noyes and Bray's method.

The results given by the latter (Ref. 5, p. 362) show that the extraction of gold and mercury from a solution of low chloride ion concentration and moderate hydrogen ion concentratipn is almost complete, and that a very small amount of palladium, but no platinum, may be removed. The chloride concentration must be very small in order that mercury may be satisfactorily extracted, but has no influence on the extraction of the gold. A small concentration of hydrogen ions is necessary in the case of the gold to prevent the hydrolysis of the chloride, but beyond this its concentration has little influence upon the extraction of either gold or mercury.

The Extraction of Gold and Mercury.— The initial removal of gold and mercury was, accordingly investigated by means of the following experimental procedure, which was based on that of Noyes and Bray.

The solution containing the elements of the gold group in the form of their chlorides was evaporated down in a 25 mm. porcelain crucible with the addition of concentrated nitric acid until a volume of about three drops remained. 3 Ml. of water and 1 drop of N hydrochloric acid were then added, and the mixture was/

was transferred to a centrifuge tube and extracted twice with 1½ ml. portions of alcohol-free ethyl acetate (see p. 13), a good separation of the layers being obtained by the use of the centrifuge. The two ester extracts were then evaporated carefully to dryness in a small porcelain crucible which was placed on a hot-plate. When several milligrams of gold were present, the expulsion of the last traces of ester led to the formation of a violet deposit of the metal. In order to avoid this happening, and the consequent necessity of using hydrochloric as well as nitric acid to dissolve up the deposit, the evaporation by heat was stopped when a thick yellow syrup was seen, and completed by means of a jet of air from a pipette held in the mouth. When a large amount of mercuric salt was present, it deposited in white rings round the side of the crucible, and could be roughly assessed. This was of importance when the diphenylcarbazone test was applied.

The residue was taken up in the minimum volume of N nitric acid. Unless the quantities of mercury and gold were very large, not more than 0.5 ml. was required. The amount of gold present was assessed on the strength of the yellow colour of the solution if this was intense, but if weak, or not visible, two drops of the solution (representing perhaps one fifth of the total) was tested for gold by adding

one/

one drop of rhodamine -B solution (p. 67). If a precipitate was formed it could be centrifuged into a fine cone and its bulk compared with a standard. In this way any ambiguity arising from the presence in this section of traces of the highly coloured palladium, rhodium or iridium ions was removed.

Before the diphenylcarbazone test for mercury could be applied, it was, in general, necessary to remove the gold from the solution. The remainder of the solution was transferred to a porcelain crucible, and the nitrate driven off by means of hydrochloric acid. The solution was then diluted to about 1 ml. in a centrifuge tube, and a stream of sulphur dioxide passed in. When the solution was saturated, it was heated in the water-bath for a few minutes and the precipitated elemental gold removed by centrifuging. The solution was returned to the crucible, the sulphur dioxide expelled, and the chloride ion removed by evaporation with nitric acid. If the amount of gold present was of the order of 0.5 mg. it was essential to remove it.

If the mercuric salt had been seen to be present in large quantity, a portion of the solution judged to contain 2-3 mg. of mercury was used for assessment by the diphenylcarbazone test; if not, the whole solution was tested. By this means, the use of

a/

a reasonable amount of reagent was ensured. The volume of the solution was adjusted to 2 ml., 0.25 g. of solid sodium acetate added and the reagent added dropwise until the purple colour or precipitate, if any, was seen to be fully developed. The quantity of mercury present was estimated by centrifuging or extraction as described on p. 69.

By this procedure, numerous mixtures of known and unknown composition, containing any or all of the components of the gold group were analysed successfully for gold and mercury. The detection of large and small quantities of gold was satisfactory, as long as the precautions necessary to eliminate the interference of mercury were taken (cf. p.68), and the extraction of gold from the aqueous layer was so complete that in no later operation was its presence detected. The detection of mercury was equally good, the only noticeable interference being from palladium which, if present in maximum amount (10 mg.), was found in the extract to the extent of giving with diphenylcarbazone a distinct blue colour. This, however, was less than that derived from 0.25 mg. of mercury, and was never confused with mercury. With large quantities of mercury, a small amount (0.25 mg. out of 20 mg.) was not extracted by/

by the ester, and remained in the solution, from which it was later removed along with the platinum, by hydrogen sulphide (see p.79).

The Hydrolytic Precipitation of Palladium, Rhodium and Iridium.— The dilute nitric acid solution from which gold and mercury had been removed contained platinum, palladium, rhodium and iridium, and perhaps a small amount of mercury. When the nitrate was expelled by evaporating the solution almost to dryness with concentrated hydrochloric acid, in a porcelain crucible, and then making up the volume to 20 ml. with water, a solution was formed to which Gilchrist and Wichers's hydrolytic procedure could be easily adapted. This was done in the following manner. The solution, in a 50 ml. beaker covered with a watch-glass, was brought to the boiling point, and 2 ml. of a 10% solution of sodium bromate were run in, followed by the dropwise addition of a 10% solution of sodium bicarbonate until the pH of the solution was 6. This was indicated by the use of bromo-cresol purple test-paper, the colour of which was changed to blue when spotted with a small drop of the solution at pH 6. Another ml. of bromate was then added, and the solution gently boiled for 5 minutes. By this time a dark flocculent precipitate of hydrated dioxide had formed in the solution, which, if palladium was present alone or was the dominant constituent,/

constituent, was brown in colour, if rhodium, green, and if iridium, dark blue.

More bicarbonate solution was then added till a pH of 8 was reached, as indicated by a violet colour on cresol-red test-paper, a further ml. of bromate was run in, and the mixture kept at the boiling-point for 15 minutes. The whole was then transferred to a centrifuge tube and the precipitated dioxides removed and washed with water. Those of palladium and iridium separated rapidly, but when rhodium was present, the supernatant liquid remained green, due to traces of the finely dispersed hydrated dioxide, and prolonged centrifuging was only partly successful in bringing this into the precipitate. The supernatant solution thus might contain the platinum, along with not more than 0.5 mg. of mercury, if a large quantity had originally been present and perhaps traces of rhodium and iridium.

The Separation, Detection, and Assessment of Platinum.— In order to concentrate the platinum it had to be separated as sulphide, but before this could be done, it was necessary to destroy the bromate present in the solution. Gilchrist and Wichers (Ref. 22) accomplished this by boiling with hydrochloric acid, but it was thought that it would be easier to expel the liberated bromine if a slight excess of hydrobromic acid/

acid were added. According to the equation:-

$$5HBr + HBrO_3 \longrightarrow 3Br_2 + 3H_2O,$$

it was calculated that 3 ml. of 46% hydrobromic acid would be sufficient. This volume was therefore run in, and the bromine liberated was removed by gently boiling. Hydrogen sulphide gas was then passed into the solution without further preparation, and a black precipitate separated. This precipitate was dissolved in a small amount of aqua regia, the nitrate expelled by evaporation with hydrochloric acid, and the residue dissolved in a little concentrated hydrochloric acid. All or a portion was then taken for the platinum test, depending upon the size of the sulphide precipitate, which, however, could not be taken as an accurate guide to the quantity of platinum present owing to the possible contamination already referred to. The normality of the solution, which had been transferred to a test-tube, was adjusted to four by dilution with water, and a volume of the dimethylphenylbenzylammonium chloride reagent equal to that of the test solution was added, so that the final normality was two. The tube was placed in boiling water and examined after a few minutes (p. 70). The presence of platinum was shown by the formation of the characteristic buff precipitate of the complex, which/

which settled at the bottom of the tube so well that its bulk could be assessed without centrifuging. Occasionally the precipitate was coloured red as a result of contamination with a trace of the iridium complex; this did not affect the assessment, as the amount of iridium present could never be large, and the reagent was much more sensitive towards platinum than towards iridium.

The Detection, Separation and Assessment of Palladium.—

The precipitate containing the hydrated dioxides of palladium, rhodium and iridium was dissolved in about 1 ml. of hot concentrated hydrochloric acid (the complete solution of iridium requiring about half an hour), and diluted to 30 ml. in a beaker. A 2% alcoholic solution of dimethylglyoxime was then added drop by drop until the bulky, yellow precipitate, indicative of the presence of palladium, was fully formed (Ref. 23). After standing in contact with the mother liquor for one hour, the precipitate was removed by centrifuging and estimated by comparison with a standard similarly prepared. It was essential to centrifuge the precipitates for 10 minutes in order to ensure the maximum reduction in bulk, and to avoid erratic results.

The method was found to be satisfactory for large and small amounts of palladium. If confirmation were desired/

desired for a small precipitate, the complex could be destroyed by means of nitric and sulphuric acids, the nitrate expelled, and the dithiol test applied (p.72), but this was never necessary. The possibility of the loss of small amounts of rhodium and iridium in the bulky palladium precipitate was investigated, but was found to take place to a small extent only. For example, 0.05 mg. of iridium could not be detected by the leuco-malachite green test (p.7/), after 10 mg. of palladium had been removed from the solution, but 0.1 mg. gave a good positive indication.

The Detection of Rhodium and Iridium.— The filtrate from the palladium-dimethylglyoxime precipitate was evaporated to dryness with the addition of a few drops of concentrated hydrochloric and nitric acids, which destroyed the organic matter satisfactorily, and the residue taken up in a few drops of concentrated hydrochloric acid.

The method adopted by Gilchrist and Wichers (Ref. 22) for the separation of rhodium from iridium is to remove the former as metal by reduction with titanous chloride, and the excess titanium by means of cupferron, and then to destroy the organic matter, and precipitate the iridium as hydrated dioxide. In order to circumvent the cupferron treatment, with its consequent risk of loss of minimal amounts of iridium, it was decided to divide/

divide the solution into two portions and test separately for the one in the presence of the other.

Rhodium.— One half of the solution was evaporated to dryness again in order to expel any remaining nitrate, taken up in 1 ml. of dilute hydrochloric acid and transferred to a centrifuge cone. A 15% solution of titanous chloride was added dropwise until the violet colour was seen to remain, and the cone was heated in the water-bath for a few minutes. A black precipitate indicated rhodium. Assessment was made in the usual manner. If gold, platinum or palladium had not been completely separated, they would also be precipitated by the titanous chloride, and give a false indication of the presence of rhodium. It was found, however, by analysing mixtures containing several mg. of these elements and no rhodium, that no black precipitate was formed when the titanous chloride was introduced.

Iridium.— The other half of the solution was transferred to a small porcelain crucible, a few drops of sulphuric and nitric acids were added and the mixture was evaporated to fuming. A blue, or in the presence of an eight-fold excess of rhodium, a brownish-purple colour, indicated the presence of iridium, and with a little practice, the quantity could be assessed.

On p. 84 the full scheme of analysis for the group is tabulated.

GOLD GROUP Scheme of Analysis.

SOLUTION contains the chlorides of Au, Hg, Pd, Pt, Rh and Ir in HCl, Evaporate to small volume, add 1 ml. of conc. HNO_3 and evaporate again to about 0.1 ml. Take up in three ml. of water, add one drop of N HCl, and extract with 1½ ml. of ethyl acetate. Repeat the extraction (p. 74).

ESTER LAYER - Evaporate carefully to dryness and take up in N HNO_3. Assess Au on yellow colour. If necessary test 1/5thh with rhodamine-B (p.76). Expel NO_3', pass SO_2 into Cl' soln, remove Au, expel Cl'(p.76). Test all or part with diphenylcarbazone. Assess, (p.69).

AQUEOUS LAYER - Evaporate almost to dryness with HCl and take up in 20 ml. of water. Heat to the boiling point, add 2 ml. of 10% aq. $NaBrO_3$ and then 10% aq. $NaHCO_3$ dropwise to pH 6. Add 1 ml. more of $NaBrO_3$, boil for 5 minutes, increase the pH to 8, add a further ml. of bromate and boil for 15 minutes (see p. 78).

SOLUTION - Add 3 ml. of 46% HBr, expel Br_2 and pass H_2S. Dissolve ppt. of impure PtS_2 in aqua regia, expel HNO_3, take up in 4 N HCl and confirm and assess Pt, in all or in part, by precipitating its buff dimethyl-phenylbenzylammonium chloride, and heating in boiling water (p.80).

PRECIPITATE - Dissolve in 1 ml. of hot conc. HCl, dilute to 30 ml. with water, and add 2% alcoholic dimethylglyoxime.

PRECIPITATE - Pd as dimethyl-glyoxime complex. If desired, destroy organic matter with HNO_3 and H_2SO_4 and test with dithiol (p.81).

SOLUTION - Evaporate to dryness with HCl and HNO_3, take up in a minimumoof HCl and divide into two equal parts.
(1) Evaporate to dryness to expel NO_3', take up in 1 ml. of 2N HCl and ppt. black Rh with $TiCl_3$ (p.83). Assess.
(2) Evaporate to fumes with H_2SO_4. Add a few drops of HNO_3. A blue colour shows Ir. Assess.

Analysis of Mixtures

Several mixtures of composition unknown to the operator were analysed with the following results.

The quantities are expressed in milligrams.

No.		Au	Hg	Pt	Pd	Rh	Ir
1.	Present	-	-	0.25	10	0.25	0.25
	Found	0	0	1	15	0.5	0
2.	Present	-	40	-	0.25	10	10
	Found	0	32	0	0.25	5	10
3.	Present	-	-	10	-	-	5
	Found	0	0	4	0	0	10
4.	Present	7.5	0.25	-	-	2.5	0.25
	Found	15	0.25	0	0	5	0.5
5.	Present	2	1.5	0.25	1.5	1	0.5
	Found	6	0.5	0.5	1	2.5	0.5
6.	Present	-	-	0.5	7.5	2.5	0.25
	Found	0	0	1	6	2	0.25

As with the tantalum and tungsten groups, a very satisfactory feature is that no metal absent from the mixture has been reported. The failure to report iridium in No. 1 was due to the employment of the leuco-malachite green test instead of the much more reliable reaction with sulphuric and nitric acids. It is interesting to note that mercury was not reported in No. 1, which contained a maximum amount of palladium, and that platinum was not found in No. 2, which contained large amounts of mercury, rhodium and iridium. On the whole, the assessments are satisfactory.

CONCLUSION

Satisfactory schemes for the analysis on the semi-micro scale of the tantalum, tungsten and gold groups of Noyes and Bray have been evolved.

It was necessary to separate completely most of the components of the groups before final confirmation and assessment of quantity could be made. This result, which is in line with the findings of Fischer and co-workers (Ref. 3) when dealing with an analagous group, was a consequence partly of the lack of specificity in the tests available, and partly of the unsatisfactory limiting proportions, one ion in small amount not being detectable when other ions were present in the maximum excess under consideration. This factor has made it necessary to draw up schemes of a more exhaustive character than would have been required had equal quantities only of the elements been considered. A scheme suitable merely for similar amounts of the various components is, however, of little real value.

It is important to notice that, while many of the organic reagents were unsatisfadory as far as their specificity was concerned, their sensitivity was more than adequate for work on the semi-micro scale. As a result, it was frequently possible to divide a solution containing a number of constituents into

several portions and treat them by different methods for the detection of the individual ions. Thus further complicated separations were avoided. Examples of this have been given in the treatment of parts of the tungsten and gold groups. In the tantalum group, in which the peculiar nature of the reactions of the earth acids necessitated three different modes of treatment for the detection of all the group components, the sensitivity of the tests employed permitted the division.

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