234. *Qualitative Semimicro-analysis with Reference to Noyes and Bray's System: The Tantalum and the Tungsten Group.*

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The elements composing the tantalum and the tungsten group of Noyes and Bray's system have been divided into two groups differing slightly from those of Noyes and Bray. For mixtures containing not more than 50 mg. referred to the cations, satisfactory methods have been evolved for the detection and approximate estimation of 0·25—50 mg. of antimony, tin, and phosphate, 0·25—10 mg. of molybdenum, tellurium, titanium, tungsten, and zirconium, 0·5—10 mg. of tantalum and niobium, and minor amounts of vanadium (0·25—2 mg.) and bismuth (0·25—0·5 mg.).

In 1927 Noyes and Bray (" A System of Qualitative Analysis for the Rare Elements ") published a precise scheme of separations for nearly all the elements occurring as cations. It refers to the analysis of 1 g. of a non-metallic material or 500 mg. of an alloy, containing a maximum of 500 mg. of any one common element or 100—200 mg. of any one rarer element, and a minimum of 1—3 mg. of any element.

The introduction within recent years of many sensitive and selective organic and inorganic reagents has led to considerable changes in the methods of qualitative analysis, *e.g.*, a reduction in the amount of material taken for an analysis, and the simplification of the separation processes that ordinarily precede the final confirmation of the presence of a metal. Numerous books on semimicro-qualitative analysis have been published. Most refer to the systematic detection of the common elements, but Nieuwenburg and Dulfer (" A Short Manual of Systematic Qualitative Analysis," 1938) also include several less common elements; 20—100 mg. of material may be taken for such analyses. On the micro-scale, Benedetti-Pichler and Spikes (" Introduction to the Microtechnique of Inorganic Qualitative Analysis," 1935) have given a scheme of analysis for very varied proportions of the common metals in 1 mg. of material, and with their co-workers are gradually extending their methods to include all the metals, using as a basis Noyes and Bray's scheme (see *Mikrochem.*, 1935—38; *Ind. Eng. Chem., Anal.*, 1937—39). There has been no corresponding development on the semimicro-scale, despite the greater simplicity of the technique. Fischer, Dietz, Brünger, and Grieneisen (*Angew. Chem.*, 1936, **49**, 719) published a scheme of analysis for the ammonium sulphide group of Noyes and Bray's system, using a maximum of 200 mg. of material, which is rather in excess of the semimicro-limit, and appear not to have continued their investigations.

It was accordingly proposed to develop semimicro-methods for mixtures containing a maximum of 50 mg. of metal ions, common and uncommon. The methods adopted by Noyes and Bray for preparing solutions and grouping the elements were assumed to be applicable, with relatively the same results as in the original scheme. For the first investigation the tantalum and the tungsten group were selected. The elements composing these groups, which are separated together in a solution 5N in hydrofluoric acid, are tantalum, niobium, titanium, zirconium, antimony, bismuth, tin, tellurium, tungsten, molybdenum, vanadium, lead, and phosphorus, all, except tellurium and vanadium, which are in the quadrivalent form, being in their highest state of oxidation. A few are found only in association with certain others; *e.g.*, the occurrence of zirconium, tellurium, or bismuth depends on the presence of phosphorus, tin, or antimony, respectively. Of some, only a fraction of the total amount in the original mixture may be present. In approximate accordance with Noyes and Bray's findings (*op. cit.*, pp. 18, 19, 47, 50, 71), and on the basis throughout of the reduction of all their quantities to one-tenth, consideration was given to the detection and approximate estimation in the combined groups of a maximum of 50 mg. of tin, antimony, or phosphate (PO_4), 10 mg. of tantalum, niobium, titanium, zirconium, tungsten, molybdenum, or tellurium, about 2 mg. of vanadium, and 0·5 mg. of bismuth. Lead did not require to be tested for, but the influence on tests for the other elements of 1—2 mg. had to be known. The minimum amount of any element considered was 0·25 mg.

EXPERIMENTAL.

Preliminary Separation of the Elements composing the Tantalum and the Tungsten Group.—The mixture containing these elements was first evaporated nearly to dryness, in a 6 ml. platinum crucible, with a few drops of sulphuric acid to remove hydrogen fluoride. Instead of Noyes and Bray's procedure, in which the mixture is now made alkaline with ammonia and digested with aqueous ammonium sulphide, the residue was boiled and stirred for several mins. with 1 ml. of 7N-sodium hydroxide, giving an insoluble and a soluble portion, which were separated by centrifuging. These contained : *Insoluble portion*, tantalum, niobium, zirconium, titanium, bismuth, and antimony (part) mainly as oxides or hydroxides, and elementary tellurium (part) ; very occasionally tin was present. *Soluble portion*, sodium tungstate, molybdate, tellurite (part), hypovanadate, and phosphate, and complex salts of antimony (part), tin, lead, and occasionally a little niobium and tantalum.

The first, designated the " tantalum group," differed from that of Noyes and Bray's scheme in that it contained part of the antimony and tellurium, and no phosphate or vanadate. The second, designated the " tungsten group," contained the same elements as Noyes and Bray's corresponding group, and, in addition, a small amount of earth acids which was recovered and included in the tantalum group (see p. 1260).

Analysis of the Groups.—The methods of separation devised by Schoeller (" The Analytical Chemistry of Tantalum and Niobium," 1937) for the analysis of materials containing tantalum and niobium were utilised in the analysis of the tantalum group (see tabulated scheme). The three modes of treatment of the residue constituting this group facilitated the detection of small amounts of all the group components.

Tantalum Group.

<table>
<tr><td colspan="5"><i>Residue.</i> Wash twice with 1% aq. NH_4NO_3 to remove $Na^{\cdot}$, and suspend in water. Divide into three equal parts (1).</td></tr>
<tr><td colspan="5">(<i>a</i>) Evaporate to dryness in a silica crucible. Fuse with 10 times the bulk of $KHSO_4$, cool, and extract with 3—4 ml. of hot, 10% aq. tartaric acid. Keep warm and stir, and saturate with H_2S (2).</td></tr>
<tr><td colspan="4"><i>Precipitate.</i> Sulphides of Te, Sb, Bi, and Sn. Digest with hot 1 : 1 HCl.</td><td rowspan="4"><i>Solution.</i> Expel H_2S. Add to the cold solution a drop of perhydrol. A yellow colour shows Ti. Compare with a standard (8).</td></tr>
<tr><td rowspan="3"><i>Precipitate.</i> Dissolve in HNO_3. Evaporate with HCl and heat with 0·1 g. of calcium hypophosphite to form black Te. Assess (3).</td><td colspan="3"><i>Solution.</i> If the sulphide precipitate was quite small ($<$1 mg.), evaporate to small volume. Test part with rhodamine-B. A red precipitate shows Sb; assess (4). Test another part with dithiol in the presence of HF. A brown precipitate shows Bi; assess (5). Test the remainder with an excess of dithiol. A red precipitate shows Sn; assess (6).
If the sulphide precipitate was not small, dilute and reprecipitate the sulphides with H_2S. Separate and digest with warm, 2N-yellow ammonium sulphide.</td></tr>
<tr><td rowspan="2"><i>Precipitate.</i> Bi_2S_3. Dissolve in 1 : 1 HCl. Test for Bi with dithiol and assess. See (5).</td><td colspan="2"><i>Solution.</i> Reprecipitate the sulphides of Sb and Sn, separate, dissolve again in HCl, reduce the acidity to N, add solid oxalic acid and saturate with H_2S (7).</td></tr>
<tr><td><i>Precipitate.</i> Sb_2S_5. If large, estimate Sb on the bulk of this precipitate. If small, dissolve in HCl, test with rhodamine-B and assess. See (4).</td><td><i>Solution.</i> Expel H_2S. To all or part add dithiol and heat. Estimate Sn. See (6).</td></tr>
<tr><td colspan="5">(<i>b</i>) Fuse with $KHSO_4$ [cf. (<i>a</i>)]. Take up in 10 ml. of 1% aq. tannin in 10% H_2SO_4 and heat gently to precipitate the yellow and red tannin complexes of Ta and Nb. Separate, wash with 2N-H_2SO_4, dissolve in HNO_3 and evaporate to dryness. If more than 0·5 mg. of Ti has been found, repeat the whole procedure, estimating the amount of Ta + Nb on the bulk of the second tannin precipitate. Fuse the residue with $KHSO_4$, dissolve in 10 ml. of hot, saturated, aq. ammonium oxalate, and test for and apportion Ta and Nb by fractional precipitation with tannin (9).</td></tr>
<tr><td colspan="5">(<i>c</i>) If Ta and Nb are absent, evaporate, fuse with $KHSO_4$, take up in a few drops of 4N-H_2SO_4 and test with <i>p</i>-hydroxyphenylarsonic acid in the presence of HCl and H_2O_2. A white precipitate in a boiling solution shows Zr. Compare with a standard.
If Ta and Nb are present, evaporate, fuse in a platinum crucible over a blowpipe with 0·2 g. of K_2CO_3, and take up in 1 ml. of hot 2N-KOH. Separate and wash the residue, and repeat the treatment. Proceed as in the absence of Ta and Nb (10).</td></tr>
</table>

In the tungsten group (see tabulated scheme) the presence of phosphate complicated the analysis, and made it necessary to test in two places for tungsten and tin. The figures in parentheses in the two schemes are referred to in " Notes on Methods and Tests " (p. 1260).

Tungsten Group.

<table>
<tr><td colspan="5"><i>Solution</i> (containing NaOH). Add HCl until the acidity is 2N. Dissolve SbO_2Cl and digest in boiling water.</td></tr>
<tr><td rowspan="7"><i>Precipitate.</i> Digest with 2N-NaOH. Combine the residue with the tantalum group. Test the solution with dithiol and H_3PO_4. A blue-green precipitate shows W. Extract with butyl acetate to assess (11).</td><td colspan="4"><i>Solution.</i> Add 10% aq. KSCN and 10% aq. thioglycollic acid. A red colour shows Mo; a black precipitate, Te. Extract the former with butyl acetate and separate the precipitate, ester, and aqueous layers, comparing the first two with standards (12).</td></tr>
<tr><td colspan="4"><i>Aqueous layer.</i> Adjust the acidity to 0·3N, warm and saturate with H_2S (13).</td></tr>
<tr><td colspan="2"><i>Precipitate.</i> Sulphides of Sn, Sb, Pb, and Te and Mo in traces. Digest with hot 1 : 1 HCl.</td><td colspan="2"><i>Solution.</i> Contains vanadyl salt, phosphoric and phosphotungstic acids, and perhaps some Sn. Test 5% for V with tannin and ammonium acetate. If any is present remove it as follows. Expel H_2S, oxidise with Br_2, aq., and remove the excess. Cool, and to the solution (3 ml.) add 4 drops of 40% HF and an excess of cupferron. Extract with butyl acetate (14).</td></tr>
<tr><td><i>Precipitate.</i> TeS_2 and MoS_2 in traces. Dissolve in <i>aqua regia</i> and expel HNO_3. Test for Te and estimate with hypophosphite (3). Neglect Mo.</td><td><i>Solution.</i> If the precipitate dissolved was small, evaporate to small vol. and remove any $PbCl_2$ that separates. Test part for Sb with rhodamine-B (4), and part for Sn with dithiol (6). If the precipitate dissolved was large, oxidise $Sn^{\cdot\cdot}$ with Br_2, aq., expel excess, reduce to N in HCl, add oxalic acid and pass H_2S (7).</td><td rowspan="4"><i>Ester layer.</i> Brown. Compare immediately with a standard V solution similarly prepared (15).</td><td><i>Aqueous layer.</i> Destroy organic matter and expel HF by evaporating to fumes with a few drops of H_2SO_4. Dilute to 3 ml. with water.</td></tr>
<tr><td rowspan="3"><i>Precipitate.</i> Sb_2S_3 and PbS. Dissolve in 1 : 1 HCl, expel H_2S, and test all or part for Sb with rhodamine-B (4). Pb need not be tested for (see p. 1258)</td><td rowspan="3"><i>Solution.</i> Expel H_2S. Add dithiol to all or part and estimate Sn (6).</td><td>(<i>a</i>) To 1 ml. or less (W must not exceed 1 mg. per ml.) add tartaric acid and dithiol in the cold, and leave for 10 mins. A red precipitate shows Sn. Assess [see (6)].</td></tr>
<tr><td>(<i>b</i>) To 1 ml. or less add 2N-NaOH to alkalinity. Test for W with dithiol and H_3PO_4. If Sn is present add the same vol. of conc. HCl and heat. Extract with butyl acetate and assess [see (11)].</td></tr>
<tr><td>(<i>c</i>) If more than 0·5 mg. of W is present, add slowly to the boiling solution, at an acidity of 0·3N, excess of 5% aq. $ZrOCl_2$, make ammoniacal and heat. Separate the precipitate and fuse with 5 times the bulk of Na_2CO_3. Extract with 2N-NaOH. To all or part of the extract add conc. HNO_3, NH_4NO_3 and an excess of 10% aq. ammonium molybdate. Heat at 50°. A yellow precipitate shows PO_4. Compare with a standard (16).</td></tr>
</table>

Notes on Methods and Tests.

For separating precipitates and solutions a centrifuge with tubes ranging in capacity from 0·5 to 15 ml. was employed. Precipitates were in general washed twice with volumes of wash liquid suited to their bulk, the second washing being rejected. The volumes of liquid taken to dissolve precipitates, or for digestion processes, were commonly twice the bulk of the precipitate. For a description of suitable pipettes, stirrers and various devices, see, *e.g.*, Benedetti-Pichler and Spikes (*op. cit.*).

Note 1. Excess of sodium ions was washed out in order to prevent any subsequent separation of insoluble sodium tantalate or niobate. A solution of ammonium nitrate prevented peptisation.

Note 2. This procedure was based on that of Schoeller (*op. cit.*, pp. 38, 39).

Note 3. By the reduction of tellurous acid with hypophosphite (Feigl, " Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 1938, 346), in a solution 2N in hydrochloric acid, 10γ of tellurium were easily detected in 0·05 ml. Large excesses of antimony, bismuth, and tin were without effect, and tellurium was separated from them only because it interfered with the tests used for bismuth and tin. A small amount of molybdenum did not interfere. The precipitate was compared with a standard for the estimation of quantity.

Note 4. The selectivity of Eegriwe's test for antimony with rhodamine-B (*Z. anal. Chem.*, 1927, **70**, 400) was increased by making it in a solution ~3N in hydrochloric acid with a 1% solution of the reagent in 3N-hydrochloric acid. If to 0·5 ml. of a solution containing 50γ of antimony, a drop of saturated, aqueous potassium nitrite and a drop of the reagent were added, it soon became red-purple and then blue in transmitted light. A finely-divided red precipitate separated on centrifuging. As little as 5γ of antimony was detectable. If the supernatant liquid was not pink, more reagent was added until it was (one drop of reagent precipitated ~25γ of antimony), and the precipitate was compared with a standard. Of solutions containing much antimony only a small portion was examined. Large excesses of tin, bismuth, lead, tellurite, molybdate, and many other radicals, tartaric acid and phosphoric acid did not interfere. Molybdate gave a deep-red colour but no precipitate.

Note 5. For the detection of bismuth in solutions up to ~2N in hydrochloric acid, toluene-3 : 4-dithiol (" dithiol ") was excellent (cf. Clark, *Analyst*, 1936, **61**, 242). The reagent was made up fresh, 0·2% in 0·25N-sodium hydroxide, one drop corresponding to 25—50γ bismuth. Bismuth formed a brown complex, 10γ being detectable in 0·5 ml. of solution. The complex dissolved readily in butyl acetate with a reduction in the intensity of the colour. Small amounts of bismuth were detected and directly assessed on a spotting tile. A little hydrofluoric acid did not influence the test and permitted the detection of 10—50γ of bismuth *in the cold* in the presence of 500γ of tin. Although bismuth could be detected in the presence of a 50-fold excess of antimony, which gave a pale yellow complex, reasonable assessment of a small amount was possible only if the excess was much less (5-fold). Tellurite interfered by giving a buff precipitate that deposited tellurium on heating.

Note 6. With dithiol, tin gave under similar conditions to bismuth, but preferably with heating (Clark, *loc. cit.*), a scarlet precipitate which dissolved in butyl acetate to form a pale yellow solution: 5γ were readily detected in 1 ml. of aqueous solution. Moderate amounts were estimated from the bulk of precipitates formed with a minimum excess of the reagent. Owing to the sensitivity of the test only portions of solutions containing much tin were examined. The complex dissolved in hot, 6N-hydrochloric acid. 20-, 4-, 10-, and 100-Fold excesses of antimony, bismuth, tellurium and lead respectively did not prevent the detection of tin, but the first three, except in much smaller excesses, interfered with its estimation. Molybdate, which gave a dark-green complex, interfered badly. Large amounts of phosphoric, oxalic, and tartaric acids were without influence. The presence of the last in an unheated solution prevented interference from tungsten (~1 mg. per ml.), which formed an emerald-green complex (see note 11).

Note 7. Oxalic acid converted stannic tin into a complex ion which did not react with hydrogen sulphide in slightly acid solutions.

Note 8. The centrifugate from the sulphide precipitate contained titanium, zirconium, tantalum, niobium, tartaric acid and potassium hydrogen sulphate. With perhydrol even 10γ of titanium gave a definite pale yellow colour in a volume of several ml. Assessment was made by comparison with a standard containing similar amounts of tartaric acid and sulphate, which slightly bleached the yellow colour. None of the other constituents of the tantalum group interfered.

Note 9. The bisulphate–tannin treatment was based on Schoeller's method (*op. cit.*, p. 118) : 100γ of tantalum and niobium gave a distinct precipitate. Titanium alone gave no precipitate, but in association with tantalum or niobium it was partly precipitated, colouring the precipitate red, and sometimes masking tantalum or falsely suggesting the presence of niobium. Repetition of the treatment greatly reduced its influence. The assessment of tantalum *plus* niobium was best made on the bisulphate–tannin precipitate. They were apportioned by adapting as follows Schoeller's quantitative separation process based on the differential stability of oxalotantalic and oxaloniobic acids in the presence of tannin (*op. cit.*, pp. 123 *et seq.*). To the ammonium oxalate solution a 2% solution of tannin was added dropwise in 0·5 ml. portions, and after each addition the mixture was boiled and any precipitate removed. If none appeared, a little solid ammonium chloride and a few drops of 2N-ammonia were added in order to bring it down, and it was removed. The addition of tannin was continued until precipitate formation ceased.

In the absence of titanium, yellow tantalum precipitates separated first, without the addition of ammonia and ammonium chloride; then came mixed tantalum and niobium precipitates, orange in colour, and, finally, red niobium precipitates, all requiring the addition of ammonium chloride and ammonia. A very small amount of tantalum might be indicated by only a yellow solution, and a very small amount of niobium by a final " mixed " precipitate. Only with practice was it possible from an examination of a set of such precipitates to detect 0·15 mg. of tantalum or niobium in 3 mg. of their mixture. If a little titanium was present, it complicated the detection of a small amount of tantalum by depositing as a red complex, after the first addition of tannin from a solution containing *no* ammonum chloride and ammonia. If subsequent additions of tannin failed to produce yellow tantalum complexes it was necessary to destroy the first red complex and try to detect tantalum by the original bisulphate–tannin treatment. Minimal amounts of tantalum were not satisfactorily found.

Note 10. Tests for zirconium required the absence of other than a minor amount of tantalum, which was most effectively removed by the treatment cited. The residue containing all the zirconium, some or all of the titanium, bismuth, and antimony, and not more than traces of tantalum and perhaps niobium, was readily fused with potassium hydrogen sulphate and dissolved in sulphuric acid. 1—3 Drops of a 4% aqueous solution of *p*-hydroxyphenylarsonic acid (see Simpson and Chandlee, *Ind. Eng. Chem.*, *Anal.*, **1938**, **10**, 642) added to such a solution, containing 40γ of zirconium, readily yielded on boiling a colourless precipitate that could be compared in bulk with a standard. The presence of a drop of 2N-hydrochloric acid in *boiling* solutions prevented precipitate formation by even 3 mg. of antimony or bismuth, and a drop of perhydrol prevented the reactions of niobium and titanium. Towards tantalum the reagent was not very sensitive, 400γ, an amount unlikely to be present, giving the same result as 40γ of zirconium.

Note 11. The presence of phosphate prevented the separation on acidification of part or all of the tungsten as tungstic acid. In its absence a small amount of tungsten might also fail to be precipitated. Tantalic and niobic acids escaping from the tantalum group were precipitated in the acid solution, and did not dissolve in 2N-sodium hydroxide, which readily dissolved tungstic acid. For the detection and estimation of tungsten in this solution, dithiol was most successfully used for some time before the publication of Hamence's paper (*Analyst*, **1940**, **65**, 152). The conditions under which the emerald-green complex was formed were critical; *e.g.*, its quantitative production by adding the reagent to acid solutions was slow and uncertain. The following method was satisfactory. To a solution of tungstate in 2N-sodium hydroxide (1 ml. or more), containing an excess of a fresh 0·5—1% solution of dithiol in 0·5N-sodium hydroxide, 2—4N-phosphoric acid was added dropwise slowly with constant shaking until a turbidity just appeared. If tungsten was absent, or present in only a minute amount, the turbidity was white; with much tungsten it was violet, and further small additions of acid produced a buff and then a blue-green suspension. Whenever the latter appeared, time was given for full colour development before another drop of acid was added. When no further change occurred a little more acid was added (an excess did no harm), and the mixture was heated in boiling water for several minutes. The green complex was readily and completely extracted with butyl acetate and compared with a similar standard : 5γ of tungsten were easily found. For colour comparison it was undesirable to have more than 40γ of tungsten per ml. of solvent.

If hydrochloric acid replaced phosphoric acid, more careful control of the addition was required, and with larger amounts of tungsten the separation of tungstic acid complicated matters. After the formation of the complex in phosphoric acid solutions, however, the addition of concentrated hydrochloric acid, even up to 6N, had no adverse effect, and, in a hot solution, it served to eliminate interference from at least a 20-fold excess of tin (cf. note 6). Molybdenum interfered by forming an olive-green complex of similar intensity of colour. Vanadium hindered the formation of the tungsten complex.

Note 12. Before dithiol could be utilised for the confirmation of tin, and tungsten escaping the initial separation, it was essential to remove molybdenum almost completely. This was accomplished by converting it into its complex thiocyanate, $Mo(OH)_2(SCN)_3$ (Noyes and Bray, *op. cit.*, p. 346), and extracting it with butyl acetate. For the reduction, thioglycollic acid was an excellent substitute for zinc. To the solution, $\sim$2N in hydrochloric acid, a few drops of a 10% aqueous solution of potassium thiocyanate were added, followed by a few drops of a 10% solution of thioglycollic acid. If a pink colour developed, the addition of the reagents was continued until it was certain that conversion of the molybdenum was complete. Butyl acetate readily extracted the complex. Even in mixtures containing much phosphate the separation was very effective, and if a trace of molybdenum escaped, it was caught in the subsequent sulphide precipitation. The thiocyanate reaction was sufficiently sensitive for the detection of a minimum amount of molybdenum, and the butyl acetate extract served for a colorimetric estimation.

Note 13. The acidity was adjusted by adding 2N-sodium hydroxide until a drop of the solution spotted on paper impregnated with methyl-violet gave a green colour. In the presence of much phosphate a little tin escaped precipitation as sulphide, and had to be detected later.

Note 14. As vanadium interfered with the detection of tungsten with dithiol, and with the precipitation of phosphate as ammonium phosphomolybdate, its removal was necessary, cupferron in the presence of hydrofluoric acid being a suitable precipitant (Clarke, *Analyst*, **1927**, **52**, 466, 527). Butyl acetate was employed to remove the complex and most of the excess cupferron. As these steps could be omitted in the absence of vanadium, the latter was first tested for in a small portion of the solution with a 5% aqueous solution of tannin, one drop of which, followed by ammonium acetate to reduce acidity, gave with 10γ of vanadium in 1 ml.

of solution a blue colour. Larger amounts of vanadium gave blue-black precipitates. Only small amounts could be satisfactorily estimated. Interference from an excess of tungstate, which gave a brown precipitate, was counteracted by the addition of tartrate.

Note. 15. The cupferron complex of vanadium gave a brown ester layer. Although the colour faded rapidly, a colorimetric estimation was possible.

Note 16. The separation of phosphate with zirconium oxychloride was based on the method of Curtman, Margulies, and Plechner (*Chem. News*, **1924**, **129**, **299**). The presence of phosphate was usually indicated by the appearance of a precipitate in the acid solution, but tungstic acid might also separate. Ammonia added in excess dissolved the latter, completed the precipitation of phosphorus as zirconium phosphate, and brought down the residual zirconium as hydroxide. Fusion of the precipitate with sodium carbonate separated the phosphate from the zirconium, which retards its precipitation as ammonium phosphomolybdate. 50γ of phosphate were satisfactorily detected and estimated in 1 ml. of a solution containing a 100-fold excess of tungsten.

Analysis of Mixtures.—Mixtures of unknown composition containing components of the tantalum and tungsten groups were supplied to the junior author, and analysed substantially according to the methods prescribed, with the results recorded below. The figures indicate the weight in mg. of each element and of phosphate.

	Element.	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	—
	Found	10	0	0	0	0	0·25	0·5	0·25	0	0	6·5	0
2	Present	0·5	—	0·25	10	0·25	20	—	0·25	0·5	—	—	10
	Found	0·25	0	0·25	5	0·25	10·5*	0	trace	0·5	0	0	9
3	Present	5	0·5	—	—	—	—	10	25	—	0·25	0·25	0·25
	Found	6	1	0	0	0	0	5*	10	0	0·25	0	0·25
4	Present	1	—	10	0·25	—	—	1	1	10	1	—	1
	Found	1·5	0	6	0·25	0	0	0·75†	0·25	7·5	1	0	0·5
5	Present	0·5	5	0·5	0·5	0·5	1	—	—	0·25	2	4	0·5
	Found	trace	5	1	0·5	0·25	0·25	0	0	0·75	2	6	0·5
6	Present	2	3	—	—	0·5	15	0·5	0·5	1	0·5	0·5	25
	Found	1·5	3·5	0	0	0·25	10·5*	0	0·5†	1·25	0·25	0·25	18

* Part in tantalum group. † All in tantalum group.

The most satisfactory feature of these analyses is that no element was *erroneously* reported as present in the mixtures. On three occasions small quantities were not detected. 0·5 Mg. of niobium was missed in No. 1, the maximum amount of tantalum making detection difficult (see note 9); 5 mg. of tantalum did not prevent detection (No. 3). The failure to find the minimum amount of tungsten in No. 3 was probably attributable to a faulty method of applying the dithiol test, the correct conditions of application of which were found afterwards (note 11). There was no obvious reason for the non-detection of tellurium in No. 6. Its presence in the tantalum group was suspected, but the confirmatory test failed. Estimations of quantity were essentially of the correct order of magnitude. The schemes therefore satisfy the conditions proposed on p. 1258, except for tantalum and niobium. Of these, the detection of 0·25 mg. is doubtful, and neither can be detected with certainty in the presence of more than a ten-fold excess of the other.

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[*Received, July 5th*, **1940**.]