

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXIX. The Separation of Tungsten from Titanium, Niobium, Tantalum, and Zirconium

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IN an earlier Section, Schoeller and Jahn¹ have shown that tungsten cannot be included in any of the groups obtained in our proposed scheme for the analysis of earth-acid minerals, because it is partially precipitated with the earth acids by tartaric hydrolysis, as well as by tannin and by cupferron from tartrate or oxalate solutions. Hence there arose the need for a method which would quantitatively separate small amounts of tungsten from large amounts of earth acid as well as from associated earths, chiefly titania and zirconia. It was mentioned in the paper referred to above that such a method had been worked out. This Section contains a description of the procedure (which is based upon Bedford's work² on the separation of tungsten from niobium) and an account of our investigations into the separation of tungsten from titanium.

A. SEPARATION OF TUNGSTEN FROM TITANIUM.—Of all the metallic oxides which occur in earth-acid minerals, tungstic oxide alone forms stable, soluble alkali salts. The more basic earths are unaffected by alkali,³ whilst the earth acids form sodium salts which are sufficiently insoluble to be used for the separation of tungsten from tantalum and niobium.⁴ Titania appears to hold an intermediate position between the earth acids and the more basic earths, since Schoeller and Deering⁵ have shown that its behaviour in an alkali fusion is strongly affected by association with niobic oxide. Hence an inquiry into the separation of tungsten from titanium formed the first step in this investigation.

No deviation from time-honoured practice could be found by reference to recent literature. The few published methods need not be discussed here, the essential information being fairly summarised in the following passage taken from Bull. 212 of the U.S. Bureau of Mines⁶: "The separation of Ti from W presents little difficulty, so that both may be easily determined in the same sample. Fusions with alkalis, followed by water leach of the melt, offer a simple method for the separation. The W is obtained in the filtrate, while the Ti remains in the residue. In the fusion with pyrosulphate the conditions are reversed, in that the W remains in the insoluble residue as WO_3 , and the Ti passes into the filtrate as the sulphate. This separation is best accomplished if a few drops of concentrated H_2SO_4 are added to the H_2O in which the pyrosulphate fusion is dissolved. This precaution assists in keeping the W in the insoluble portion."

We considered it necessary to investigate the effect of these procedures on oxide mixtures of low tungsten-content.

(a) *Pyrosulphate fusion*.—The mixed oxides were fused with potassium pyrosulphate (3 g.), and the product was leached with 5 per cent. sulphuric acid (Exp. 1). The melt dissolved to a *perfectly clear solution*. The liquid was then treated with cinchonine solution and warmed, but even this specific reagent did not induce a normal tungsten precipitation. The small precipitate obtained overnight (0.0080 g.) contained more titanium than tungsten.

This single experiment disposes of the procedure under discussion as a means for separating tungsten from titanium. No doubt, with oxide mixtures of low titanium-content, tungstic acid may remain substantially insoluble but, we venture to predict, contaminated with titania. The case is plainly analogous to that of titania in association with the earth acids⁷: if tantalum and niobium, whose power of forming soluble complexes is weak, undergo "loss of individuality" when associated with sufficient titanium, then tungsten, a complex-former *par excellence*, may be expected to behave as it did in the above experiment, when it dissolved to a clear solution which gave a negative reaction for tungstic acid, even with cinchonine. Rose⁸ was aware of the ineffectiveness of the pyrosulphate separation process. He states that in the lixiviation of the melt the titania dissolves first, but that subsequently the tungstic oxide also dissolves (complex-formation). He resorts to treatment of the solution with ammonia, although the titanium precipitate thus produced occludes tungstic acid.

| Exp. | WO ₃ g. | TiO ₂ g. | WO ₃ recovery: |
|------|-----------------------|------------------------|---|
| 1 | 0.0224 | 0.2028 | Nil |
| 2 | 0.0546 | None | Nil |
| 3 | 0.0220 | 0.1040 | R ¹ : 0.0288 g. R ² : 0.0216 g. |

In Exp. 2 pure tungstic oxide was fused with bisulphate, and the product was lixiviated with water. The cloudy liquid thus obtained cleared completely on warming, and remained clear while boiling. After cooling, it gave a characteristic precipitate with cinchonine solution. This test proves that, even by itself, tungstic oxide does not remain insoluble after bisulphate fusion. Re-fusion of the bisulphate melt of 0.0534 g. of tungstic oxide with 1 ml. of strong sulphuric acid previous to leaching led to the same result.

In Exp. 3 we tested the application of the pyrosulphate and tannin method⁹ to this separation case. The tannin prevented the formation of a soluble tungsten complex just as in the case of the earth acids and titania,⁹ but the weight of the ignited residue, R¹, was excessive; re-treatment of R¹ gave a seemingly good result, but R² was still contaminated with 2 to 3 mg. of titania. The tests with pyrosulphate were then abandoned.

(b) *Alkali fusion*.—In Exps. 4 to 8, sodium carbonate was used as flux. The mixed oxides were fused with 3 g. of this salt until the fused mass was quite clear. The cold mass was extracted with water in Exp. 4, and with half-saturated sodium chloride solution in Exp. 5. In each case the tungsten recovery showed a negative error of about 40 per cent., and the titania residue gave a positive

tungsten reaction. Hence the other procedure recommended in the above quotation was also found to be defective.

| Exp. | Taken | | Tungstic oxide | | Titania | |
|------|-----------------------|------------------------|----------------|-------------|-------------|-------------|
| | WO ₃ g. | TiO ₂ g. | Found g. | Error g. | Found g. | Error g. |
| 4 | 0.0205 | 0.2010 | 0.0126 | -0.0079 | | |
| 5 | 0.0212 | 0.2043 | 0.0130 | -0.0082 | | |
| 6 | 0.0200 | 0.2030 | 0.0202 | +0.0002 | 0.2034 | +0.0004 |
| 7* | 0.0360 | 0.1685 | 0.0362 | +0.0002 | 0.1686 | +0.0001 |
| 8* | 0.0061 | 0.2387 | 0.0056 | -0.0005 | 0.2386 | -0.0001 |

* Quantities taken not known to operator.

Re-treatment of the titania residue by the same process did not recommend itself, in view of the very imperfect separation achieved by the first fusion. We inferred that occlusion of tungsten by the titania during lixiviation might be counteracted by the use of caustic alkali instead of water. Experiments in this direction proved successful at fairly high alkali concentrations (*i.e.* 10 per cent. sodium hydroxide; see Exps. 6, 7). The separation was carried out as follows:

(c) *Authors' caustic-soda method.*—The mixed oxides (about 0.25 g.) are fused with 3 g. of sodium carbonate in a platinum crucible over a Tecu burner for 20 minutes or until the fused mass is clear. The cold crucible is transferred to a nickel dish containing a solution of 10 g. of sodium hydroxide in 50 ml. of water. The covered dish is kept on a boiling water-bath for 2 to 3 hours, the water lost by evaporation being replaced. The crucible is cleaned and rinsed with 50 ml. of hot water. The liquid is allowed to stand until cold or overnight, and filtered. The residue, *P*¹, is washed with half-saturated sodium chloride solution, and reserved.

The filtrate is submitted to bicarbonate hydrolysis,¹⁰ *i.e.* treatment with phenolphthalein indicator and dilute hydrochloric acid until the red colour disappears. The solution is heated on the water-bath, the red colour being discharged from time to time with a few drops of acid. The small flocculent precipitate, *P*², is collected, and washed in the same way as *P*¹.

The filtrate from *P*² is treated with 0.5 g. of tannin,¹¹ etc., for the determination of the tungstic oxide. For the quantitative recovery of the titania, the filters containing *P*¹ and *P*² are pulped with a little *N* hydrochloric acid. After dilution to 100 ml., the liquid is warmed and made slightly ammoniacal; the precipitate is collected, washed with ammonium nitrate solution, and ignited. It is advisable to leach the ignited precipitate, unless small, with a little dilute acid; after addition of a slight excess of ammonia, the precipitate is again collected, ignited strongly, and weighed.

It will be noted that Exp. 8 gave a less complete tungsten recovery, which we ascribe to the use of caustic alkali of one-half the strength specified above.

B. SEPARATION OF TUNGSTEN FROM TITANIUM, NIOBIUM, TANTALUM, AND ZIRCONIUM.—Having quantitatively separated tungsten from titanium by our caustic-soda method, we proceeded to apply the method to the separation of tungsten from large amounts of titanium and niobium. The case is of importance in its application to titanoniobate minerals (*e.g.* samarskite).

The method applied to that ternary mixture proved a failure, because of the modified behaviour of titania and niobic oxide in association. Each oxide without the other remains insoluble in the treatment; but a mixture of the two in approximately equal quantities gives a considerable fraction soluble in caustic soda to a semi-colloidal solution which is not completely flocculated by bicarbonate hydrolysis. Exp. 9 illustrates the course of an attempted separation:

| | | Taken | |
|--------|---|--------------------------------|--|
| Exp. 9 | { | TiO ₂ | 0.1202 g. P ¹ : 0.1630 g. |
| | | Nb ₂ O ₅ | 0.1244 „ P ² (contains Ti and W): .. 0.0720 „ |
| | | WO ₃ | 0.0304 „ Tannin-cinchonine ppte.: .. 0.0406 „ |
| | | Σ | 0.2750 „ Recovery: 0.2756 „ |

Exp. 10, in which a small addition of tantallic oxide was made, gave the same result:

| | | Taken | |
|------------------------------------|------------|--------------------------------|-------------|
| TiO ₂ | 0.1070 g.; | Nb ₂ O ₅ | 0.1139 g. } |
| Ta ₂ O ₅ | 0.0325 „; | WO ₃ | 0.0134 „ } |
| Tannin-cinchonine ppte.: 0.0236 g. | | | |

After experimenting with various other schemes, we turned our attention to the action of ammoniacal magnesium solutions upon alkaline solutions of the metallic acids. Bedford,² who first applied the reaction in the analysis of a niobotungstate, found that it precipitates the niobic acid, the alkali tungstate remaining in solution. He determined the niobium in the ignited precipitate by fusing it with bisulphate and extracting the product with boiling water. He did not attempt the recovery of the tungstic oxide, the quantity of which he obtained by difference.

We succeeded in utilising Bedford's reaction for the separation of tungsten from titanium and niobium, recovering the two earths as a mixed tannin precipitate, and determining the tungsten by our tannin and cinchonine method (Exps. 12 to 14). The whole process, which will be referred to as the *Magnesia Method*, is fully described under C below. (The results obtained are shown on page 510.)

The niobium experiments (12 to 14) were more satisfactory than the test separations of ternary mixtures containing tantallic oxide (15 to 17). In Exp. 15, a single treatment gave a negative tungsten, and a positive tantalum, error; this was again the case in Exp. 16 (WO₃ error -0.0016, Ta₂O₅ error +0.0016 g.), but re-treatment of the ignited TP¹ (0.4090 g.) gave the final errors recorded in the Table. As for Exp. 17, the separation succeeded in one treatment, in which the precipitant was added at about 50° C., and the further heating of the suspension of the magnesia precipitate was omitted (*infra*, under C).

The more complex mixtures of Exps. 18 and 19 were successfully treated in a single operation; this we ascribe to niobic oxide forming a substantial proportion of the mixed earths (as in Exps. 12 to 14), zirconia not interfering in the magnesia method (see Exps. 26, 27).

C. THE MAGNESIA METHOD.—The mixed oxides (0.2 to 0.5 g.) are fused with 4 g. of potassium carbonate in a platinum crucible over a strong burner for 10 to 15 minutes. The fused mass is taken up in 200 ml. of hot water, care being taken to disintegrate any lumps by gentle boiling and manipulation with a glass rod. The crucible is rinsed and discarded, and the hot solution is treated with

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freshly-prepared reagent (1 g. of crystallised magnesium sulphate, 2 g. of ammonium chloride, 25 ml. of water, 4 drops of ammonia). The covered beaker is kept on a covered water-bath for an hour. The flocculent precipitate is collected on an 11-cm. No. 40 Whatman filter, and washed with quarter-saturated ammonium chloride solution.

| Exp. | Earths taken g. | | Tungstic oxide taken g. | Amounts found g. | Error g. |
|------|--------------------|--------------------------------|-------------------------------|------------------------|-------------|
| 11 | None | | 0.0310 | 0.0311 | +0.0001 |
| 12* | { | TiO ₂ | 0.0324 | 0.0320 | -0.0004 |
| | | Nb ₂ O ₅ | | | |
| | | Σ | 0.3093 | 0.3095 | +0.0002 |
| 13* | { | TiO ₂ | 0.0341 | 0.0337 | -0.0004 |
| | | Nb ₂ O ₅ | | | |
| | | Σ | 0.4204 | 0.4202 | -0.0002 |
| 14* | { | TiO ₂ | 0.1016 | 0.1008 | -0.0008 |
| | | Nb ₂ O ₅ | | | |
| | | Σ | 0.2076 | 0.2084 | +0.0008 |
| 15* | { | TiO ₂ | 0.0242 | 0.0225 | -0.0017† |
| | | Ta ₂ O ₅ | | | |
| | | Σ | 0.4059 | 0.4072 | +0.0013† |
| 16* | { | TiO ₂ | 0.0225 | 0.0228 | +0.0003‡ |
| | | Ta ₂ O ₅ | | | |
| | | Σ | 0.4078 | 0.4073 | -0.0005‡ |
| 17* | { | TiO ₂ | 0.0228 | 0.0228 | 0.0000† |
| | | Ta ₂ O ₅ | | | |
| | | Σ | 0.4047 | 0.4045 | -0.0002† |
| 18* | { | TiO ₂ | 0.0248 | 0.0243 | -0.0005 |
| | | Nb ₂ O ₅ | | | |
| | | Ta ₂ O ₅ | | | |
| | | Σ | 0.4278 | 0.4280 | +0.0002 |
| 19* | { | TiO ₂ | 0.0315 | 0.0312 | -0.0003 |
| | | Nb ₂ O ₅ | | | |
| | | Ta ₂ O ₅ | | | |
| | | ZrO ₂ | | | |
| | | Σ | 0.3844 | | |

* Quantities taken not known to operator.
† Single treatment
‡ Double treatment

} see text below.

* Quantities taken not known to operator.

† Single treatment

‡ Double treatment

} see text below.

Determination of the mixed earths.—The precipitate is rinsed back with the same wash-liquor; the filter is placed in the platinum crucible intended for the ignition of the tannin precipitate, *TP*¹. The suspension of the magnesia precipitate (150 ml.) is acidified with hydrochloric acid and digested on the water-bath for an hour. An equal volume of saturated ammonium chloride is then added, and the reaction is adjusted with ammonia to slight acidity to litmus paper. The liquid is now treated with 2 g. of ammonium acetate and heated to boiling, and fresh 5 per cent. tannin solution is added until flocculation is complete. The precipitate,

TP^1 , is allowed to settle on the water-bath, collected with the help of gentle suction, washed with the ammonium chloride solution, and ignited with the filter from the magnesia precipitate.

If TP^1 requires re-treatment, it is again fused with potassium carbonate, and the operations above described are repeated, yielding a second magnesia precipitate and a filtrate therefrom, which is added to the first. The magnesia precipitate is again treated with tannin as for TP^1 , giving TP^2 , which is ignited, leached as usual,¹² and weighed as mixed earths.

Determination of the tungsten.—The filtrate or combined filtrate from the magnesia precipitate or precipitates is treated by the tannin and cinchonine method. This procedure, as originally described, is carried out in a solution of high sodium chloride concentration; in the magnesia method we add a filtered, hot-saturated solution of 20 to 30 g. of ammonium chloride before precipitating the tungsten complex.

D. COMPARATIVE TESTS ON THE SEPARATION OF BINARY MIXTURES BY THE METHODS DESCRIBED.—Having solved the most complex of the above-mentioned separation problems by the use of the magnesia method, we surmised that it might do duty as a general method applicable to all the separation cases under discussion. Exps. 20 to 28 were carried out with a view to deciding that question.

| Exp. | | Taken g. | Found in | | Final errors g. |
|------|---|--|-----------------------|--------------------|-----------------------|
| | | | first treatment g. | re-treatment g. | |
| 20 | { | WO ₃ 0.0337 TiO ₂ 0.2078 | 0.0281 | 0.0047† | −0.0009 |
| 21* | { | WO ₃ 0.0320 TiO ₂ 0.2614 | 0.0306 | Not done | −0.0014 |
| 22* | { | WO ₃ 0.0236 Nb ₂ O ₅ 0.2536 | 0.0266 | 0.0235‡ | −0.0001 |
| 23* | { | WO ₃ 0.0307 Nb ₂ O ₅ 0.2140 | 0.0328 | 0.0308‡ | +0.0001 |
| 24 | { | WO ₃ 0.0259 Ta ₂ O ₅ 0.2274 | 0.0247 | 0.0011† 0.2271† | −0.0001 −0.0003 |
| 25 | { | WO ₃ 0.0229 Ta ₂ O ₅ 0.2056 | 0.0213 | 0.0016† 0.2051† | 0.0000 −0.0005 |
| 26* | { | WO ₃ 0.0316 ZrO ₂ 0.2898 | 0.0320 | | +0.0004 |
| 27* | { | WO ₃ 0.0147 ZrO ₂ 0.2783 | 0.0150 | | +0.0003 |
| 28* | { | WO ₃ 0.0320 TiO ₂ 0.1822 ZrO ₂ 0.2206 | 0.0296 | Not done | −0.0024 |

* Quantities taken not known to operator.

† Obtained by re-treatment of TP^1 .

‡ Obtained by re-treatment of WO₃ product.

Exps. 20 to 25 prove that the separation of tungsten from the three individual earths in one operation is less satisfactory than that from the mixed earths: titania

and tantallic oxide both occluded tungsten, whilst the precipitation of the niobic oxide by the magnesia reagent was not quite quantitative. Re-treatment of *TP*¹ in Exps. 20, 24 and 25, and of the ignited tannin-cinchonine precipitate in Exps. 22 and 23, gave good results. The mixture of titania and zirconia in Exp. 28 comported itself like titania. The separation of tungsten from zirconium by the magnesia method (Exps. 26, 27) is satisfactory.

In order to obtain data for subsequent discussion (see E), we also carried out a few more tests by the caustic-soda method:

| Exp. | | Taken g. | Found g. | Errors g. |
|------|---|------------------|------------------|--------------------|
| 29* | { WO ₃ Nb ₂ O ₅ | 0.0156 0.2753 | 0.0158 0.2742 | +0.0002 -0.0011 |
| 30* | { WO ₃ Ta ₂ O ₅ | 0.0344 0.2096 | 0.0341 0.2083 | -0.0003 -0.0013 |
| 31* | { WO ₃ Ta ₂ O ₅ | 0.0206 0.2271 | 0.0208 0.2276 | +0.0002 +0.0005 |
| 32* | { WO ₃ ZrO ₂ | 0.0334 0.2224 | 0.0369 0.2175 | +0.0035 -0.0049 |
| 33* | { WO ₃ ZrO ₂ | 0.0342 0.2000 | 0.0358 0.1960 | +0.0016 -0.0040 |

* Quantities taken not known to operator.

The separation from niobium and from tantalum gave a satisfactory tungsten recovery in one operation; 10 g. of sodium hydroxide were used in the extraction of the melt. We were surprised to find that the method did not give a quantitative separation of tungsten from zirconia (Exps. 32, 33). This must be due to incomplete hydrolysis, in the strongly alkaline solution, of the sodium zirconate present in the melt. The small amount of zirconia which thus accompanies the tungsten into the alkaline filtrate is not precipitated therefrom by bicarbonate hydrolysis, and most of this soluble fraction becomes occluded in the tannin cinchonine precipitate. Hence the tungsten results show a positive, the zirconia results a larger negative, error. The above deduction was confirmed by Exps. 34 and 35, in which the oxides were fused with alkali carbonate, and the melt was extracted with hot water instead of caustic soda; the recovered tungstic oxide was now free from zirconia:

| Exp. | WO ₃ taken g. | ZrO ₂ added g. | Flux | WO ₃ found g. | Error g. |
|------|-----------------------------|------------------------------|---------------------------------|-----------------------------|-------------|
| 34* | 0.0311 | 0.2045 | Na ₂ CO ₃ | 0.0306 | -0.0005 |
| 35* | 0.0328 | 0.2056 | K ₂ CO ₃ | 0.0328 | 0.0000 |

* Quantities taken not known to operator.

E. ANALYTICAL APPLICATION.—As a result of the experimental work here recorded, an appropriate method from amongst four can be selected for the quantitative separation of tungstic oxide from certain earths and mixtures thereof.

(a) The magnesia method is generally applicable to the separation of tungsten from titanium, niobium, tantalum, or zirconium, and from binary, ternary, and quaternary mixtures of these earths. The separation from zirconium alone is

complete in a single precipitation. Although in our test analyses the separation of tungstic oxide from mixed earths containing a substantial proportion of niobic oxide was complete in one operation, we think it advisable to repeat the treatment in doubtful cases where the quantity of tungstic oxide exceeds a few mg. In fact, in accurate work the completeness of the separation should always be ensured by a repetition of the procedure. With oxide mixtures in which niobic oxide preponderates, the purity of the tungstic oxide should be tested by solution in caustic soda, filtration, and precipitation of the filtrate with tannin and cinchonine.

(b) Sodium-carbonate fusion and extraction with caustic soda (caustic-soda method) separates tungstic oxide from titania in one operation, also from niobic or tantallic oxide or both, but not from titania *plus* earth acid or from zirconia.

(c) Sodium-carbonate fusion and extraction with water separates tungstic oxide from zirconia, beryllia, ferric oxide, thoria, ceria, and yttria in one operation.⁸

(d) Sodium-chloride precipitation separates tungstic oxide from niobic or tantallic oxide or both,⁴ and from mixed pentoxides containing subordinate amounts of zirconia,¹⁷ the latter remaining unaffected.

Although, strictly speaking, the magnesia method could be applied in all the cases under review, we do not feel disposed to advocate it to the exclusion of the other three processes. The caustic-soda method (outside the province of earth-acid analysis) is the simplest means for the separation of tungsten from titanium. Sodium-carbonate fusion and extraction with water form a valuable procedure of extensive applicability.¹⁸ Lastly, precipitation by sodium chloride is a specific earth-acid reaction which also permits of a rapid approximate volumetric determination of tantalum and niobium. Schoeller and Jahn, the originators of the volumetric method, rightly considered the results too wide to recommend it for the actual determination of the two elements.¹⁰ We revert to it here because Britton and Robinson¹⁴ have described the tannin separation of tantalum from niobium as "extremely difficult, requiring considerable experience and skill before accurate results can be obtained." We do not dispute that all fractionation processes as such are difficult, but we hold that the tannin method under discussion is comparatively easy, thanks to the characteristic colour changes which mark the progress of the fractionation. However that may be, we would remind operators not too familiar with the tannin separation that they may obtain a preliminary approximation, at the same time as a separation from tungsten, by converting the mixed pentoxides into the sodium salts, titrating the alkali in the precipitate, and recovering the oxides as explained in Section VI.¹⁰ The weighed recovered oxides (P^1)¹⁵, together with the small bicarbonate-hydrolysis precipitate (P^2), are then fused with bisulphate, etc., for the separation of tantalum and niobium by tannin.¹⁶

The following unpublished determinations, by Schoeller and Jahn, of "unknown" quantities of mixed oxides, illustrate the degree of approximation of which the volumetric method is capable. (See table on page 514.)

With the exception of Exp. 1, the tantalum results show a negative error. We ascribe this to adsorption of alkali by the 9 cm. filter paper used. If so, closer results should be obtained by filtration on a small pad of filter pulp or a sintered glass crucible.

| Exp. | | Taken g. | P ¹ (ex NaCl ppt.) g. | 0.1 N HCl ml. | Found g. | Errors g. |
|------|---|--|--|------------------|------------------|--------------------|
| 1 | { | Ta ₂ O ₅ 0.2816 Nb ₂ O ₅ 0.2300 | 0.5054 | 36.53 | 0.2865 0.2251 | +0.0049 -0.0049 |
| 2 | { | Ta ₂ O ₅ 0.2132 Nb ₂ O ₅ 0.3102 | 0.5182 | 39.95 | 0.2015 0.3219 | -0.0117 +0.0117 |
| 3 | { | Ta ₂ O ₅ 0.3510 Nb ₂ O ₅ 0.1230 | 0.4670 | 31.65 | 0.3433 0.1307 | -0.0077 +0.0077 |
| 4 | { | Ta ₂ O ₅ 0.1752 Nb ₂ O ₅ 0.3220 | 0.4879 | 38.12 | 0.1725 0.3247 | -0.0027 +0.0027 |
| 5 | { | Ta ₂ O ₅ 0.2822 Nb ₂ O ₅ 0.1742 | 0.4512 | 32.20 | 0.2708 0.1856 | -0.0114 +0.0114 |
| 6 | { | Ta ₂ O ₅ 0.1952 Nb ₂ O ₅ 0.2747 | 0.4640 | 35.62 | 0.1864 0.2835 | -0.0088 +0.0088 |

SUMMARY.—A separation of tungsten from titanium cannot be achieved by fusion of the mixed oxides with bisulphate and extraction of the melt with water or dilute acid. Fusion of the mixed oxides with sodium carbonate and extraction with water is likewise ineffective, but extraction of the carbonate melt with 10 per cent. sodium hydroxide solution affords a quantitative separation.

The only procedure found to separate tungsten from titanium and niobium, with or without tantalum and zirconium, consists in fusing the mixed oxides with potassium carbonate, and treating the aqueous extract of the melt with a slightly ammoniacal magnesium salt solution; the earths are precipitated, whilst alkali tungstate remains in solution. A repetition of the procedure is necessary unless the mixed earths contain a large proportion of niobic oxide; for accurate work, however, double treatment is recommended in all cases. Zirconia may be separated from tungstic oxide by fusion with alkali carbonate and extraction with water. The applicability of the methods available for the separation of tungsten from the individual earths and from the mixed earths is discussed. If the mixed earth acids are separated from tungsten by sodium-chloride precipitation, titration of the alkali in the precipitate furnishes a preliminary approximate determination of tantalum and niobium.

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