603. *Inorganic Chromatography on Cellulose. Part XII.* The Quantitative Determination of Tantalum and Niobium in Complex Minerals, Ores, and Synthetic Materials.*

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A new chromatographic method based on cellulose as adsorbent and ethyl methyl ketone containing hydrofluoric acid as solvent, has been described (Part XI *) for the quantitative separation of tantalum from niobium and for their determination in certain types of mixtures. This method has been modified so that it is now applicable to the quantitative determination of these elements in complex materials containing appreciable amounts of titanium, tin, and zirconium. A solution of the sample in hydrofluoric acid containing ammonium fluoride being used, tantalum is extracted first in ethyl methyl ketone saturated with water. The column is then washed with ketone containing 1% (v/v) of hydrofluoric acid (40% w/w aqueous solution) which arrests the movement of titanium, tin, and zirconium. Niobium is then extracted with the ketone containing 12·5% of hydrofluoric acid. After removal of solvent the tantalum and niobium are determined in the appropriate fractions by ignition to the pentoxides.

The procedure is simple and accurate and has been used for the analysis of a wide range of natural and synthetic materials.

In Part XI * a method was described for the quantitative separation of tantalum from niobium by chromatographic extraction of the fluorides in the presence of ammonium fluoride, cellulose adsorbent and ethyl methyl ketone solvents being used. Tantalum was extracted first with ethyl methyl ketone saturated with water; niobium was then extracted with ethyl methyl ketone containing 7·5% (v/v) of hydrofluoric acid (40% aqueous solution). The same procedure was applied to minerals and ores but, whereas the tantalum fraction was obtained free from other ions, the niobium fraction was contaminated with appreciable amounts of titanium, tin, and zirconium when these metals were present in the original sample. The degree of contamination was reduced by re-extraction of the niobium fraction, but it was realised that a simple modification of the procedure was desirable if it was to be of general application in earth-acid analysis, for tantalum and niobium frequently occur in association with titanium, tin, and zirconium.

A modification of the above procedure has now been found so that niobium can be extracted free from titanium, tin, and zirconium.

It has been shown that extraction with ethyl methyl ketone containing 2% of hydrofluoric acid after extraction of tantalum prevents movement of titanium, etc., in the solvent subsequently employed for niobium (ethyl methyl ketone containing 7·5% of hydrofluoric acid) when this element is absent. When niobium was present, however, these elements were partially extracted but to a less degree than when the intermediate solvent was omitted; also a much larger volume of solvent was required to effect complete extraction of niobium (*J.*, 1952, 1504). The reduction in movement of titanium, etc., under these modified conditions appeared to be due to removal of water from the cellulose by the low-acidity solvent, the presence of water (in addition to hydrofluoric acid) in the solvent being necessary for extraction of these elements. Further research on these lines has led to modifications such that the procedure can now be applied to a wider range of materials than was hitherto possible. The new chromatographic procedure involves the following operations: (*a*) Tantalum is extracted with the solvent originally employed (*J.*, 1952, 1497) but the volume has been reduced to 250 ml., no advantage being gained by employing a greater amount. (*b*) The column is next conditioned by washing it with 400 ml. of ethyl methyl ketone containing 1% of hydrofluoric acid (40% aqueous solution). In this way, the quantity of water present in the cellulose is reduced to a value which is too small to permit extraction of titanium, tin, and zirconium by the solvent next employed for

* Part XI, *J.*, 1952, 1497.

extraction of niobium. (*c*) Niobium is extracted with a solvent consisting of ethyl methyl ketone containing 12·5% of hydrofluoric acid instead of 7·5% as originally used and amounts equivalent to 200 mg. of niobium metal are readily extracted in a volume of *ca.* 400—500 ml. (*d*) The earth acids are finally determined as oxides in the first and the last fraction respectively, by ignition of the residual solutions obtained after removal of the solvent. The entire process is simple and can be carried out by a relatively unskilled analyst.

Although the types of complexes formed in the chromatographic system have not yet been intensively studied, the following conditions seem to be involved. (*a*) Tantalum is extracted as fluoride by ethyl methyl ketone saturated with water but free from added hydrofluoric acid. Niobium is not extracted, neither are commonly occurring metal ions such as Th, Ce, lanthanons, Fe, Al, Mn, Cu, Ni, Ti, Sn, Zr, W, Pb, Ca, Mg, etc. (*b*) Increase in concentration of hydrofluoric acid and water in the solvent favours extraction of Nb, Ti, Sn, Zr, and small amounts of metal ions which form soluble fluorides. (*c*) A low concentration (*e.g.*, 1%) of hydrofluoric acid in the solvent and a very low concentration of water give unfavourable conditions for extraction of niobium and other metal ions; hence the use of such solvent for removal of water after extraction of tantalum. (*d*) Increase in concentration of hydrofluoric acid in the solvent favours extraction of niobium. Provided that water is absent or present in only a very low concentration, as when the intermediate solvent (1% of hydrofluoric acid) has previously been used, metal ions other than niobium are not extracted (except tungsten, which is partly extracted).

The procedure has now been extensively applied to complex synthetic materials (*e.g.*, ferro–tantalum–niobium alloys) and minerals such as pyrochlore and columbite. It has been shown that in many instances, particularly in the presence of certain foreign ions, there is a small hold-up of tantalum during its extraction by the water-saturated solvent. This was recovered by re-extraction of the niobium fraction (*J.*, 1952, 1504). Improvements in technique have reduced this effect, and it has been completely overcome by making a simple acid hydrolysis on the sample, before chromatographic extraction. This was found to be necessary only when very high accuracy was required, since the extent of the hold-up was usually less than 2% of the amount present in the original sample. This preliminary chemical step was also employed when the earth acids present in the sample were less than about 1%. The analysis of low-grade ores and the treatment of phosphatic materials will form the subject of a paper shortly to be submitted.

So far, the only metal ion which has caused difficulty is tungsten, because it is partly extracted with the niobium. This metal is easily determined in the ignited niobium pentoxide by the colorimetric thiocyanate procedure. In the early work on the separation of tantalum from niobium it was found that when tantalum was present in excess of niobium it was partly retained in the cellulose wad (*J.*, 1952, 1497). This peculiarity is being reinvestigated and the first experiments showed that tantalum was quantitatively recovered from a mixture containing 150 mg. of Ta and 50 mg. of Nb. Such results are no doubt due to improvements in the chromatographic technique since the method was first devised. Further investigations on high-grade tantalum ores are continuing.

EXPERIMENTAL

(1) *Study of the Movements of Titanium, Tin, and Zirconium under the Solvent Conditions employed for Extraction of Niobium.*—Early experiments had shown that the best conditions for the preparation of the sample solution from the material under analysis before transfer to the chromatographic column, involved a final solution in 8 ml. of dilute hydrofluoric acid (25% of 40% w/w solution) and addition of 1 g. of ammonium fluoride. The addition of the latter was found to be essential in order to obtain complete extraction of the earth acid fluorides and it was also essential as complexing agent for certain impurities such as titanium and tin. Time has not permitted an intensive study of its exact rôle in the chromatographic process. The solvent originally employed for extraction of tantalum (ethyl methyl ketone saturated with water) has not been changed, since almost complete extraction of tantalum with a high degree of purity can be obtained from extremely complex mixtures. Variations in solvent conditions which have been carried out in order to find a suitable modification which would lead to extraction of niobium without extraction of impurities were always made after the extraction of

tantalum, and even in its absence the solvent used for tantalum extraction was always first passed through the column.

A number of experiments was carried out in order to observe whether additional ammonium fluoride in the sample solution would lead to complete retention of titanium, etc., and at the same time the effect on extraction of niobium was examined. The results of these experiments showed that increase in concentration of ammonium fluoride brought about a more rapid extraction of niobium in the earlier stages of the extraction with the solvent (ethyl methyl ketone containing 7·5% of hydrofluoric acid) but a volume of 400—500 ml. was still required to effect complete extraction. Under these conditions there was no effect on the extraction of impurities (titanium, etc.) but tantalum proved more difficult to extract with the water-saturated solvent. All further experiments were therefore made with sample solutions containing 1 g. of ammonium fluoride.

Further experiments were carried out upon a complex mixture (concentrate V) containing titanium, tin, and zirconium in addition to other metal ions, both with and without added niobium. The metals and ratios in which they were present are as follows: TiO_2, 30; SnO_2, 15; ZrO_2, 10; MnO_2, 5; Fe_2O_3, 5; WO_3, 10 parts.

0·07 G. of this mixture being used, about 40% was extracted in the first 150 ml. of the solvent first used for niobium extraction (ethyl methyl ketone containing 7·5% of hydrofluoric acid) with only slight extraction in later fractions. The ignited oxides from this extraction contained about 30% of titania with tin, zirconium, and tungsten forming the major constituents of the residual elements. A similar experiment was carried out with addition of about 200 mg. of niobium (as metal) to the same amount of concentrate V. Approximately half the niobium was extracted in the first 150 ml. of solvent. This niobium fraction contained about 30% of the original concentrate (mainly TiO_2, SnO_2, ZrO_2, and WO_3). Niobium extracted in later fractions was found to be very pure, and this gave an important clue to the mechanism of the movement of other metals and confirmed that water played an important part in the movement of impurities. Experiments were made in which the effect of hydrofluoric acid concentration in the solvent, and the volume of solvent employed, on the movement of impurities and extraction of niobium were studied. In this way, it was hoped to find the lowest concentration of hydrofluoric acid in the solvent and the volume required to arrest movement of impurities without causing extraction of niobium.

(2) *Extraction of Niobium and Retention of Impurities. Study of Volume and Acidity of Ethyl Methyl Ketone Solvent.*—In the following experiments, the sample solution was prepared in the manner described on p. 3161, where a full description of the method is given. The solvent used for tantalum extraction was always employed before using the solvent containing hydrofluoric acid. A known weight of concentrate V being used, usually about 70 mg. (see above for composition), extractions were carried out after the addition of niobium to the sample. Extractions were made in the manner described on p. 3161. Niobium and any metal ions, if extracted, were determined by direct ignition to oxide after removal of solvent (see p. 3162). The oxides so obtained were analysed colorimetrically for titanium (and sometimes tungsten), since this metal also gave an indication of the behaviour of tin and zirconium but was more easily determined. Spectrographic analyses were also made on a number of the fractions.

In the experiments which follow (Table 1) tantalum was extracted with 250 ml. of ethyl methyl ketone, saturated with water. Hydrofluoric acid was then added to the dry solvent, and in the different experiments the concentration was progressivly decreased from 3·5% v/v of acid (40% w/w aqueous solution) and a given volume of such solvent was passed through the column. After collection of the eluant in fractions, niobium was extracted with solvent of higher acidity. The results of spectrographic analyses are shown in Table 2.

Comparison of the results obtained shows that the progressive reduction of acidity of the intermediate solvent from 3·5% to 1% causes a decrease in the amount of niobium extracted and also in the amount of impurities. The results show that, in order to extract niobium in a reasonable volume of solvent (400—500 ml.), after use of the intermediate solvent, a higher concentration of hydrofluoric acid than that hitherto employed is required for complete extraction of niobium.

The procedure used in experiment (*d*) was adopted, apart from minor modifications, in all further experiments and applications. It is fully described on p. 3163. The only impurity in the extracted niobium, for which a correction needs to be applied, is tungsten, when present in the original sample.

(3) *Application of the New Chromatographic Procedure to the Determination of Tantalum and Niobium in Synthetic Mixtures.*—Having established the conditions for obtaining pure niobium

(except for tungsten) from a complex base mixture, we examined the same conditions for extraction of niobium in the absence of impurities. It was known that impurities could alter the behaviour of niobium fluorides on extraction with ethyl methyl ketone–hydrofluoric acid solvents.

TABLE 1.

Expt.	Wt. of concentrate V, mg.	Wt. of Nb, mg.	Solvent COMeEt : HF, %	No. of fraction	Vol. of fraction, ml.	Wt. of oxides derived from fraction, mg.	TiO_2 content of oxides (colorimetric determinations), mg.	
(*a*)	70	205	3·5	1	100	<1	—	
			,,	2	100	89·3	2·7	
			,,	3	100	39·2	2·8	
			,,	4	100	24·3	<0·02	
			7·5	5	200	116·9	0·03	
(*b*)	70	190·4	2·5	1	200	nil	—	
			,,	2	100	20·0	1·6	
			,,	3	100	4·0	nil	
			,,	4	100	3·3	nil	
			7·5	5	200	73·6	nil	
			,,	6	200	111·3	nil	
			,,	7	150	44·3	nil	
			,,	8	50	9·6	nil	
						266·1 (≡ 186·3 mg. Nb)		
(*c*)	70	201·5	1	1	200	trace	—	
			,,	2	100	,,	—	
			,,	3	100	,,	—	
			10	4	200	208·0 } 200·5 mg. Nb	nil	
			,,	5	200	73·1	nil	
			,,	6	200	5·2	nil	
			,,	7	100	2·0	—	
							TiO_2, mg.	WO_3, mg.
(*d*)	80	193·5	1	1	400	nil	—	—
			12·5	2	200	192·7 } 193·2 mg. Nb after correction for W	nil	—
			,,	3	100	69·7	nil	0·8
			,,	4	100	14·4	nil	0·6
			,,	5	100	1·4	—	1·1

Note.—The volume of low-acidity solvent was not reduced below 400 ml. in experiment (*d*) since preliminary experiments had shown that a smaller volume could lead to subsequent extraction of impurities in the solvent employed for niobium.

TABLE 2.

		Amount of impurity in separated niobium oxide :					
Expt.	Fraction	Fe_2O_3, %	MnO, %	SnO_2, %	TiO_2, %	ZrO_2, %	WO_3 % (or mg. in whole fraction)
(*a*)	2	1·0	0·1—1·0	0·3—1·0	>5·0	1·0—3·0	—
	5	0·03—0·1	<0·1	0·01	0·03	<0·1	1·1%
(*b*)	5	0·03—0·1	<0·1	<0·01	0·1—0·03	<0·3	—
	6	0·03—0·1	<0·1	<0·01	0·01	<0·3	—
(*c*)	4	0·01—0·03	<0·1	<0·01	<0·01	0·1—0·3	—
	5	0·03—0·1	<0·1	<0·01	0·01—0·03	0·3—1·0	—
	7	—	—	—	—	—	1·0 mg.
(*d*)	2	0·03—0·1	0·1	0·01	0·01—0·03	0·3—1·0	—
	3	0·1 —0·3	0·1	0·01	0·01—0·03	0·1—0·3	0·8 mg.
	4	—	—	—	—	—	0·6 ,,
	5	—	—	—	—	—	1·1 ,,

Note.—Tungsten was determined by the standard colorimetric thiocyanate procedure.

Results obtained in two experiments showed that in one case, where niobium only was present in the sample, niobium was partly extracted in the last 200 ml. of the solvent containing 1% of hydrofluoric acid, and in the second case, where tantalum was present in addition to niobium, the same effect was again observed. It thus appeared that the presence of some foreign ions is necessary to prevent partial extraction of niobium with this solvent. However, this phenomenon was not considered to be serious since it was easy to collect the final 200 ml. of the low-acidity solvent and combine it with the high-acidity solvent containing the main niobium fraction. This procedure would, of course, be unnecessary when analysing samples containing appreciable amounts of foreign ions, particularly in a routine laboratory when similar samples are under analysis, since it is possible to check whether any niobium is extracted in the low-acidity solvent for one particular type of sample.

The results shown in Table 3 were obtained by the new chromatographic procedure for pure Ta–Nb mixtures.

TABLE 3.

Solvents employed : Ethyl methyl ketone (*a*) saturated with water, (*b*) containing 1% of hydrofluoric acid, (*c*) containing 12·5% of hydrofluoric acid.

Taken			Nb, mg.			
Ta, mg.	Nb, mg.	Ta found, mg., in 250 ml. of solvent (*a*)	1st 200 ml. of solvent (*b*)	2nd 200 ml. of solvent (*b*)	400 ml. of solvent (*c*)	Total Nb, mg.
nil	172·8	1·0 (blank)	—	14·4	158·9	173·2
nil	200·2	0·5	1·0	1·0	199·0	201·0
79·6	212·2	80·9	—	10·5	201·3	211·8
17·6	211·0	18·5	1·0	25·8	185·7	212·5

Spectrographic analysis : All tantalum fractions contained $<0{\cdot}1\%$ of Nb; all niobium fractions contained $<0{\cdot}1\%$ of Ta.

The results shown in Table 4 were obtained for samples of various synthetic concentrates to which tantalum and niobium had been added. Presumably because of the presence of foreign ions, the low-acidity solvent did not cause extraction of niobium in amount greater than about 2 mg.

TABLE 4.

Concentrate I : equal amounts of TiO_2, SnO_2, ZrO_2, Fe_2O_3, ThO_2, Al_2O_3, SiO_2, and Ce and lanthanons.
Concentrate V : TiO_2, 30; SnO_2, 15; ZrO_2, 10; MnO_2, 5; Fe_2O_3, 5; WO_3, 10 parts.

	Taken, mg.		Concentrate		Ta found,	Nb found, mg.		Total Nb,
Expt. no.	Ta	Nb	taken,	g.	mg.	Solvent (*b*)	Solvent (*c*)	mg.
1	—	21·5	V	0·113	<1·0	<1·0	22·5	22·5
2	107·2	202·4	I	0·25	107·3	2·2	199·9	202·1
3	11·6	20·3	I	1·0	12·1	<1·0	(Not determined)	
4	4·4	20·6	I	1·0	4·6	<1·0	20·5	20·5
5	44·7	208·7	TiO_2	0·074	47·0	2·3	203·0	205·3

Notes on Results.—Expt. (1). The excess of niobium found over that added was shown to be due to tungsten. Spectrographic analysis indicated that all other impurities were less than 1 mg.

Expt. (2). Both the separated Ta and Nb contained less than 1 mg. of impurities. The last 200 ml. of the intermediate solvent (*b*) contained 2·2 mg. of Nb.

Expt. (3). The Ta and Nb fractions were spectrographically pure.

Expt. (4). The Nb contained <1 mg. of impurity.

Expt. (5). The Ta and Nb fractions were free from titanium.

The results show that tantalum and niobium can be directly determined by the chromatographic procedure, in the presence of comparatively large amounts of other ions including titanium, tin, and zirconium. Any tendency for niobium to be extracted by the intermediate solvent is overcome by collecting the last 200 ml. of this solvent, which is then combined with the main niobium fraction.

(4) *Chemical Treatment of Samples before Chromatographic Separation of Tantalum and Niobium, and its Comparison with the Direct Chromatographic Procedure*.—During the analysis of a number of samples of columbite and ferro-tantalum–niobium alloys it was found that direct application of the chromatographic procedure as described above gave slightly low results owing to small hold-ups of tantalum and sometimes niobium in the column (*J*., 1952, 1497). Further experiments indicated that this was due to the presence of foreign ions, some of which, depending upon the amount present, may be more troublesome than others. The difficulty has been overcome by making a simple chemical separation, before chromatography (see p. 3162); in this way the bulk of metals such as iron, cobalt, nickel, etc., are easily removed. In most cases, in routine work, this separation is probably unnecessary.

The chemical separation, based in part on the procedure described by Bagshawe and Elwell (*J. Soc. Chem. Ind.*, 1947, **66**, 398), involves separation of the earth acids in dilute hydrochloric acid. Depending upon the amount of earth acids present and also the grade and type of sample, one or sometimes two separations were made. The major portion of tantalum and niobium were precipitated in hydrochloric acid containing 10% (v/v) of acid of *d* 1·18, which also ensures solubility of part of the titanium, tin, and zirconium and effects almost complete separation of common ions such as Fe. The residual earth acids were then precipitated after the acid concentration in the filtrate had been reduced to 2%. The combined earth-acid precipitate was ignited, and the oxides treated as a sample for the chromatographic determination of tantalum and niobium (see p. 3162).

Typical results obtained by this double precipitation procedure for synthetic samples are given in Table 5. In Table 6 results obtained by the direct chromatographic procedure after chemical separation are compared for a number of standard types of sample (including columbite and ferro–tantalum–niobium alloys).

The results shown in Tables 5 and 6 indicate the general usefulness of the chomatographic procedure for the determination of tantalum and niobium in complex materials. In most cases a direct determination without chemical separation is sufficiently accurate, particularly for medium-grade samples. In such cases the intermediate solvent can usually be discarded. When, however, a very accurate result is required, and particularly with high-tantalum–niobium samples, it is preferable to make the simple chemical separation before chromatography. In this way the bulk of ions such as iron, which may cause a small hold-up of earth acids

TABLE 5.

Concentrate I : See Table 4.
Concentrate III : Equal amounts of Al_2O_3, ThO_2, Fe_2O_3, lanthanons, SiO_2.
Concentrate IV : ,, ,, CaF_2, WO_3, MgO, PbO, MnO_2.
Concentrate VI : ,, ,, ThO_2, Al_2O_3, CaF_2, SiO_2, lanthanons ; 25 parts of this mixture together with Fe_2O_3, 10; MgO, 3; PbO, 2; MnO_2, 2 parts.

	Taken, mg.		Concentrate		Ta found,	Nb oxides	Nb found,
Expt. no.	Ta	Nb	No. and wt., g.		mg.	found, mg.	mg.
1	nil	207·6	I III IV	0·17 0·77 0·11	<1·5	296·9	205·0
2	51·8	151·2	VI	1·0	51·4	—	149·0
3	95·0	192·8	I	1·0	93·2	—	193·2

Notes.—Ta_2O_5 : In all cases the impurities were negligible and <0·1% of Nb was present.
Nb_2O_5 : From Expt. (1). Ta, <0·1; Fe, 0·03—0·1; Sn, 0·01—0·03; Ti, <0·1; Zr, <0·3%. (The weight of niobium in the last column has been corrected for tungsten, since the oxides contained 5 mg. of WO_3.) From Expt. (2). All impurities <0·1%. From Expt. (3). The Nb_2O_5 contained 1 mg. of TiO_2 as impurity. The last 200 ml. of the intermediate solvent contained 19·3 mg. of oxides; this was combined with the main niobium fraction which was free from titanium.

TABLE 6. *Volume of solvent used for extraction of niobium* (*ethyl methyl ketone containing* 12·5% *of hydrofluoric acid*).

In Expts. 1 and 2, 400 ml. of solvent were taken, but in Expt. 3, 500 ml. were required.

Expt.	Type of sample and weight taken :		Type of	Found, %		Found, %	
no.	Type	G.	determination	Ta_2O_5	Ta	Nb_2O_5	Nb
1	Pyrochlore	0·6246	Direct	3·01	—	36·66	—
2	Columbite	0·4585	,,	29·85	—	36·75	—
							corr. for W
3	,,	0·5047	Initial chemical sepn.	30·61	—	36·60	—
4	Ferro–Ta–Nb (Standard sample)	0·4577	Direct	—	13·03	—	51·85 (corr. for W, 51·20)
5	,,	0·4373	Initial chemical sepn.	—	13·27	—	52·30 (corr. for W, 52·0)
6	Ferro–Ta–Nb	0·3004	Direct	—	5·74	—	60·60 (corr. for W, 60·02)
7	,,	0·4616	Initial chemical sepn.	—	5·85	—	61·26 (corr. for W, 60·76)
8	Steel (Cr, 18; Ni, 8; Mo, 3%)	4·0 g.	,, ,,	—	<0·05	—	0·85
9	Steel (Cr, 18; Ni, 8%)	4·0 g.	,, ,,	—	<0·05	—	0·91

For notes see p. 3161.

Notes.—Expt. 1. Total impurities in both oxides were less than 0·1%. The same pyrochlore, when analysed by the original technique (*J.*, 1952, 1504), gave niobium oxide which contained 5% of titanium oxide.

Expt. 2. Tungsten extracted with the niobium was equivalent to 0·37% (WO_3) on the original sample; otherwise the oxides were spectrographically pure.

Expt. 3. Apart from tungsten in the extracted niobium, the oxides were spectrographically pure. The last 200 ml. of the intermediate solvent contained 2·0 mg. of oxides.

Expt. 4. The niobium oxide contained 1·25% of WO_3; other impurities were absent. The last 200 ml. of the intermediate solvent contained 3·1 mg. of oxides.

Expt. 5. The niobium oxide contained 0·56% of WO_3 but no other impurity.
Expt. 6. ,, ,, 0·96% of WO_3 ,, ,,
Expt. 7. ,, ,, 0·82% of WO_3 ,, ,, The last 200 ml. of the intermediate solvent contained 1·0 mg. of oxides. At least 500 ml. of the solvent containing 12·5% of hydrofluoric acid were required for extraction of niobium; the final 100 ml. gave 7·8 mg. of oxides.

Expt. 8. The chemical pre-treatment employed in the analysis of this sample was shorter than that applied in Expts. 1—7 in that only one precipitation of the earth acids was made in a volume of 250 ml. at an acidity of 2% of hydrochloric acid (*J. Soc. Chem. Ind.*, 1947, **66**, 398) (see p. **3163**). A sample weight of 4 g. was used. Owing to the presence of molybdenum in the sample extracted by the solvent used for niobium, the niobium was determined by a precipitation procedure employing ammonia, before ignition to oxide. This procedure has also been used for samples containing phosphorus and will be described more fully in a later paper. The niobium oxide from this analysis contained less than 1% of impurity.

Expt. 9. The pre-chemical separation employed was similar to that used in Expt. 8; niobium was determined by direct ignition, since molybdenum and phosphorus were absent from the original sample.

(especially tantalum) in the column, are removed at the outset. These effects are well illustrated by Expts. 2 and 3, and 4 and 5 (Table 6). When the sample contains less than about 2% of earth acids, it is usually preferable to make a chemical separation (see Expts. 8 and 9), otherwise the large sample which may be required would be extremely difficult to handle on the column.

Experience has shown that a sample weight should be chosen such that not more than about 175—200 mg. of each earth-acid element is present, otherwise the capacity of the cellulose may be exceeded. In general, it has been found that these quantitites of the metals are easily extracted in the volumes of solvents recommended, *i.e.*, 250 ml. of water-saturated solvent for tantalum and 400—500 ml. of the ethyl methyl ketone–12·5% hydrofluoric acid solvent for niobium.

Method for the Direct Chromatographic Determination of Tantalum and Niobium in their Mixtures with Other Metal Ions (including Ti, Sn, Zr, Th, *lanthanons,* Fe, Al, Ca, Mg, Pb, Ce, etc.).

Solvents.—*Ethyl methyl ketone.* The commercial product was purified as described in Part XI (*J.*, 1952, 1501).

Solvent A (for extraction of tantalum). This was prepared as already described (*ibid.*).

Solvent B (intermediate solvent). 1 Ml. of hydrofluoric acid solution (40% w/w) was added to each 99 ml. of ethyl methyl ketone.

Solvent C (for extraction of niobium). 12·5 Ml. of hydrofluoric acid solution (40% w/w) were added to each 87·5 ml. of ethyl methyl ketone.

Decomposition of Sample and its Preparation for Chromatography.—Samples (pyrochlore, columbite, ferro–tantalum–niobium, etc.) were decomposed by treatment with hydrofluoric and nitric acid mixtures in large platinum dishes (3″ diam.), and were finally converted into fluorides by repeated evaporation with hydrofluoric acid. Decomposition and evaporations were effected on the steam-bath (see also *J.*, 1952, 1497). 8 Ml. of 25% hydrofluoric acid (40% w/w) were added to the dry residue, and the whole was gently warmed under a platinum cover for about 10 minutes to effect solution. Evaporation was carefully avoided during this operation. Ammonium fluoride (1 g.) was then added, and heating was continued for a few more minutes to effect solution. The final solution was allowed to cool, and 6 g. of cellulose (Whatman standard grade) were then added, and the whole well mixed with a short Polythene rod to form a homogeneous friable mass.

Chromatographic Extraction. A column of activated cellulose was prepared and conditioned with solvent A as already described (*J.*, 1952, 1501). The sample, absorbed on cellulose, was then transferred to the top of the column and the empty dish was allowed to rest in the funnel. Solvent was always poured into the dish with stirring, before transfer to the column. Solvent A was added by this method, in sufficient quantity to reach a level of about 2 cm. above the cellulose wad, which was then agitated by means of a Polythene plunger so that it formed a homogeneous continuation to the main column. The plunger was washed with solvent A, sufficient being used to reach nearly to the top of the tube (to funnel-join). When this first batch of solvent A had reached the level of the cellulose, the addition of solvent was continued until 250 ml. had been used. The eluant containing the tantalum was collected in a 600-ml. Polythene beaker, which was replaced by a similar beaker when the last of solvent A had fallen to the level of the cellulose. Solvent B was next poured into the column *via* the platinum dish, so that it came about half-way to the level of the top of the column tube. When this solvent had fallen to the level of the cellulose, a further similar quantity was added, and the sample wad gently beaten with the plunger, and the extraction continued in the manner described above until 400 ml. of solvent B had been used. Depending on the type of sample under analysis, the last 200 ml. of solvent B could contain some niobium. This possibility is readily established for a particular type of ore by one determination in which the appropriate fraction of solvent B is analysed for niobium. With analyses on medium-grade ores containing appreciable amounts of impurities, the whole of this intermediate solvent fraction could normally be discarded. In the analysis of very high-grade ores or samples where a pre-chemical separation had been made (see below) it was often necessary to collect the last 200 ml. of solvent B and combine it with the main niobium fraction (solvent C).

When the last of solvent B had fallen to the top of the " wad " the extraction was continued in the manner described, with solvent C (in this case the wad was not agitated), 400 ml. being collected for low-grade samples or 500 ml. for medium- or high-grade samples. This fraction contained niobium and if necessary was combined with the last 200 ml. of solvent B.

Removal of Solvents and Determination of Tantalum and Niobium.—The solvent was removed from each of the fractions in the manner already described (*J.*, 1952, 1502) by evaporation in a stream of air. The aqueous residue was then transferred to a weighed platinum dish (diam. about 2″) by means of a fine jet of water and a rubber-tipped rod. Sulphuric acid (2 drops of 50% solution) was added, and the solution gently evaporated to a volume of about 1 ml. under infra-red lamps. Sufficient ashless paper was added to absorb the solution, and the dish was carefully ignited, finally to about 900°. The resulting oxide was then weighed (Ta_2O_5 or Nb_2O_5). This direct ignition procedure was found to be quicker and preferable to the tannin procedure (*J.*, 1952, 1502).

Purity of Tantalum and Niobium Oxides.—Provided that phosphorus and molybdenum were absent from the original sample, the only impurity for which a correction was necessary was tungsten in the niobium oxide. This metal was determined by the colorimetric thiocyanate procedure, carried out in strongly acid solution (HCl) after fusion of the oxide with sodium carbonate.

Method with Chemical Pre-treatment of the Sample, followed by Chromatographic Analysis.

When a high degree of accuracy was required, or when a large amount of sample was needed such as with low-grade materials, most of the common metal ions were first removed by precipitation of the earth acids from an acid solution. Since titanium, tin, and zirconium are very strongly absorbed by earth acids, unless the concentration of the earth acids was very low, this chemical treatment only brought about a small reduction in these ions.

Medium- or high-grade samples (0·3—0·5 g.) were decomposed in the usual manner with hydrofluoric and nitric acids in a large platinum dish (see p. 3160), and after final evaporation to dryness, 20 ml. sulphuric acid solution (50% v/v) were added, and the contents of the dish taken to strong fumes of sulphuric acid under infra-red lamps and then allowed to fume for 1 hour to remove fluoride ions. After cooling, the contents of the dish were washed into a 1-l. beaker, a total of about 100 ml. of being water used. After addition of 50 ml. of hydrochloric acid (*d* 1·18) and 30 ml. of hydrogen perioxde (100-vol.), the beaker was covered with a clock-glass and gently warmed for a short period to assist solution of earth acids and titania. The solution was diluted to about 600 ml. and boiled for 30 minutes; this usually gave a clear solution which gradually deposited earth acids and adsorbed impurities such as TiO_2, SnO_2, WO_3. After cooling, the precipitate was collected on a No. 541 Whatman paper, washed with dilute hydrochloric acid (1% solution), and reserved for further treatment. The filtrate was returned to the original beaker and neutralised by addition of ammonia (*d* 0·88). After addition of 10 ml. of hydrochloric acid (*d* 1·18) and about 50 ml. of a saturated solution sulphur dioxide, the volume was made up to about 600 ml., and the solution then boiled for about 20 minutes and set aside for about 10 hours or overnight. The precipitate was filtered on a No. 541 Whatman paper, washed, and then combined with the main earth-acid precipitate in the original platinum dish. It was then ignited, and the oxides treated as a sample for chromatographic analysis. Tantalum and niobium were determined as described in the first procedure (p. 3161). Depending on the type of sample, it was sometimes necessary to combine part of the intermediate solvent fraction with the main niobium fraction.

Low-grade Materials.—The blank values obtained in the direct procedure on 1-g. samples of mixed ions (Fe, Al, Ti, Zr, etc.) were usually of the order of up to 1·5 mg. (oxide) for tantalum and 2 mg. (oxide) for niobium when the earth acids were absent, so in the analysis of low-grade samples comparatively large amounts (5 g.) were often needed. Such samples were too large for direct chromatographic analysis, so it was always necessary to make a previous chemical separation. The procedure adopted (*e.g.*, the analysis of steels) was that described by Bagshawe *et al.* (*loc. cit.*) which was shorter than that described above since only one precipitation was involved. The procedure adopted for samples of steel involved decomposition of the sample in hydrochloric acid in a 500-ml. beaker, evaporation to dryness, and baking for about 1 hour under infra-red lamps. The residue was moistened with 5 ml. of hydrochloric acid (*d* 1·18), followed by addition of about 20 ml. of water, and the whole then warmed to effect solution. After dilution to 250 ml., about 30 ml. of a saturated solution of sulphur dioxide were added to reduce ferric iron, and the solution boiled for about 20 minutes and then kept overnight. After filtration, the earth-acid precipitate was ignited, and the tantalum and niobium determined chromatographically. The whole of the intermediate solvent fraction could usually be discarded.

Samples which contained large amounts of silica were treated with hydrofluoric acid in order to remove the silica at the outset of the analysis.

The analysis of low-grade samples, particularly those containing phosphorus, will be considered more fully in a future publication.

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