

273. *Inorganic Chromatography on Cellulose. Part XI.* A Study on the Separation of Tantalum from Niobium and its Application to Quantitative Analysis.*

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A new method is described for the separation of tantalum and niobium from each other and from certain other metals. The method is based on their extraction in turn as fluorides, by ethyl methyl ketone in the presence of cellulose adsorbent. Tantalum is extracted first with ethyl methyl ketone saturated with water. Niobium is then extracted with the same organic solvent containing 7.5% (v/v) of hydrofluoric acid (40% aqueous solution). It has been shown that, so long as the amount of tantalum present does not exceed that of the niobium, a sharp and quantitative separation is obtained. The method has been applied to the separation of the earth acids from their mixtures with other metal ions, and to the determination of niobium and tantalum in minerals and alloys.

THE separation of tantalum and niobium together, from other metals is not readily accomplished, particularly from minerals and ores, by existing chemical methods. The quantitative separation of tantalum from niobium may be even more difficult, the method probably most widely employed in analytical chemistry being based on the use of tannin and described in detail by Schoeller ("The Analytical Chemistry of Tantalum and Niobium"). The methods using tannin, however, are difficult and slow in operation and do not always give satisfactory results. Accordingly, attention was directed to chromatographic procedures which have been found valuable in analysis (Arden, Burstall, and Linstead, *J.*, 1949, S 311; Burstall and Wells, *Analyst*, 1951, **76**, 396; Burstall, Davies, Linstead, and Wells, *J.*, 1951, 516; Burstall, Davies, and Wells, *Discuss. Faraday Soc.*, 1949, No. 7, p. 179; Kember and Wells, *Analyst*, 1951, **76**, 570).

Experiments were first made upon complex tantalum and niobium salts with organic acids such as tartrate, citrate, oxalate, and acetate, but these did not prove very satisfactory. With fluorides the method has been found very promising. The method of extraction therefore consisted in getting the niobium and tantalum in solution in aqueous hydrofluoric acid, soaking up this solution in cellulose pulp, and placing the product so formed at the top of a column of cellulose and extracting it with ethyl methyl ketone containing water or aqueous hydrofluoric acid. In this work, platinum vessels were used for preparation of the samples, and Polythene for the chromatographic tube and vessels for collection of fractions. The choice of solvent was determined by tests using a paper-strip technique (Burstall, Davies, Linstead, and Wells, *loc. cit.*); tests were then made with columns packed with cellulose pulp.

It was soon found that the use of ethyl methyl ketone containing a low concentration of hydrofluoric acid favoured the extraction of tantalum, whereas a high acidity was necessary for extraction of niobium; moreover, the presence of ammonium fluoride in the sample "wad" was shown to be beneficial in assisting in the retention of certain other ions present as impurities. Tantalum and niobium were extracted free from impurities which included, calcium, magnesium, thorium, cerium, rare earths, aluminium, iron, and lead, when these were present. In the case of tantalum, no impurity has yet been found which markedly contaminates the extracted fluoride. Other ions which were examined included, tin, zirconium, titanium, tungsten, and manganese. Except for manganese, these ions were found, however, to contaminate appreciably the niobium fraction and work is in progress to reduce this effect. These ions are often present in minerals and ores containing tantalum and niobium.

Quantitative extraction of tantalum and niobium in fluoride solution was difficult. Although it was possible to extract pure tantalum and niobium from a mixture of the two metals by using ethyl methyl ketone containing up to 2% and 7.5% of hydrofluoric acid respectively, neither element could be quantitatively extracted with these solvents, even

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when each was present alone. A systematic study was therefore begun in order to find whether solvents based on the use of ethyl methyl ketone, water, and hydrofluoric acid, could be found which would completely extract the fluorides. With tantalum, the best separation was obtained with ethyl methyl ketone saturated with water and a sample solution containing 25% v/v of hydrofluoric acid (40% w/w solution). In the absence of niobium the recovery of tantalum was of the order of 97%, but in the presence of niobium in amounts equal to or in excess of the tantalum it was quantitative. Addition of hydrofluoric acid to the solvent decreased the recovery of tantalum, and increase in the volume of solvent employed did not improve it. As the amount of hydrofluoric acid in the solvent was increased, the recovery of tantalum decreased still further and with solvent acidity of 20% hydrofluoric acid, the recovery was less than 30%. It thus appeared that the best conditions for the extraction of tantalum necessitated the presence of the minimum quantity of hydrofluoric acid in the chromatographic system. In the presence of niobium a considerable volume of solvent could be employed in excess of that required for extraction of tantalum without causing extraction of niobium, thus ensuring ideal conditions for sharp separation of the two elements.

Experiments on the extraction of niobium indicated that a high concentration of hydrofluoric acid in the solvent was necessary and that the movement of niobium increased with increasing acid concentration. The most convenient concentration of hydrofluoric acid so far found was 7.5% (v/v, 40% aqueous solution). In the presence of niobium only, it was impossible to effect quantitative extraction directly by employing the solvent containing hydrofluoric acid solution: it was necessary to wash the column first with the ethyl methyl ketone-water solvent in the manner employed for extraction of tantalum. Under these conditions extraction of niobium was quantitative.

On employing mixtures of tantalum and niobium in amounts up to 150 mg. of each, provided that the tantalum did not exceed niobium, separations were quantitative and the earth acids were of high purity. When tantalum is present in excess of niobium there is a small retention of tantalum in the column. A similar retention may be obtained (of the order of 4—5%) when tantalum is present with other metal ions. Spectrographic analyses have shown that extraction of other metal ions (so far examined) with the tantalum is very small. The main difficulty with niobium is the prevention of partial extraction of titanium and zirconium and, to a less extent, tin and tungsten, when these elements are present.

The chromatographic technique has been examined so far for the determination of tantalum and niobium in mixtures with one another and when present together with calcium, magnesium, lead, aluminium, iron, manganese, lanthanons (including cerium), and thorium. Recent work has shown that movements of titanium, zirconium, and tin can be greatly suppressed by the use of a low acidity solvent (2% HF) after removal of tantalum but before extraction of niobium with solvent containing 7.5% of hydrofluoric acid. Research on this aspect is continuing.

The method has been applied to the analysis of columbite, pyrochlore, and ferro-tantalum-niobium alloys.

The mechanism underlying the extraction and separation of tantalum and niobium from each other and from other metals has not been fully elucidated. It is a prerequisite for this chromatographic method, however, that the fluorides of tantalum and niobium should be soluble in the respective solvents used for extraction, but since niobium is removed in succession to tantalum, it is essential that niobium be retained during extraction of tantalum. It is reasonable to suppose that the fluorides of these metals are present as complex salts or acids of the type $R(\text{TaF}_6)$ or $R_2(\text{TaF}_7)$ and $R_2(\text{NbF}_7)$ or $R_2(\text{NbOF}_5)$ which are the commonest and most stable complexes formed in solution. Under these conditions of extraction for tantalum, it is supposed that complex tantalum fluoride, probably in association with water and solvent molecules, is extracted as one of the foregoing types of salt, whereas niobium is in the form of the oxyfluoride. However, with solvent containing hydrofluoric acid used for niobium extraction, it is possible for conversion of a niobium oxyfluoride into a salt of the type $R_2(\text{NbF}_7)$ to take place; this is then extracted. It is well established that water and hydrofluoric acid content of the solvents

are critical factors. Partition between complex fluoride in the organic solvent and water in the cellulose adsorbent is probably an important factor in the separation process. Chemical adsorption between complex fluorides and reactive groups in the cellulose may also play a part and may be responsible for the small retention of tantalum observed in the extraction process.

EXPERIMENTAL

I. *Paper-strip Experiments.*—A number of paper-strip extractions were carried out by a standard technique which has been widely employed for separation of many inorganic ions. Polythene boats were, however, employed as solvent containers to prevent silica contamination by the action of hydrofluoric acid on glass vessels. Several different solvents were employed in order to obtain an indication of the feasibility of the separation under consideration and to compare the relative values of the various solvents. It was decided to limit the preliminary investigations to the separation of tantalum and niobium from one metallic impurity. The impurities which were expected to cause difficulty were zirconium, aluminium, iron, titanium, and tin. Titanium was selected from this list for these experiments as the metal most likely to be troublesome.

The procedure adopted was to run two strips simultaneously, one with a fluoride solution of titanium and the other with a fluoride solution of tantalum and niobium. The strips were developed by spraying with tannin solution, followed by exposure to ammonia vapour. A comparison was then made of the distances moved by the titanium on the one hand and the tantalum and niobium on the other.

The solvents examined included a number of esters, ethers, alcohols and ketones, all with the addition of 5% (v/v) of hydrofluoric acid (40% aqueous solution). Of these, the alcohols and ketones caused considerable movement, the ethers a small amount, and the esters practically none. Of the solvents tried, ethyl methyl ketone gave the best separation and was therefore employed for further experiments. A number of strips were then run using a mixture of all three of the metals, tantalum, niobium, and titanium, and the effect of addition of measured quantities of 40% of hydrofluoric acid to the solvent was examined. Strips were run with concentrations of 2, 5, and 10% (v/v) of this acid in the solvent. In all cases, separation into bands was obtained, but the movement of titanium appeared to increase with increasing hydrofluoric acid concentration and the bands became less sharply defined.

II. *Cellulose-column Experiments.*—(1) *Ethyl methyl ketone employed for extractions.* The ethyl methyl ketone used throughout this work was the purified commercial product. Five gallons were digested under reflux with a mixture of 60 g. of potassium permanganate and 100 g. of sodium hydrogen carbonate in 3 l. of water for about 2 hours. The aqueous layer was removed and the solvent layer dried first over calcium chloride and then over sodium hydroxide. The ethyl methyl ketone was then distilled.

(2) *Preparation of sample solution.* In these experiments, pure tantalum and niobium metals or oxides were employed and any other metals added as impurities were usually taken as oxides. Solution was effected by dissolving the metal or oxides in about 10 ml. of hydrofluoric acid (40% w/w) solution with a few drops of concentrated nitric acid in addition. By covering the dish with a platinum cover and gently warming it before repeated evaporations with hydrofluoric acid, solution of the tantalum and niobium was easily effected. The solution was finally evaporated just to dryness after removal of nitric acid by evaporation with hydrofluoric acid and was then taken up in the requisite volume of dilute hydrofluoric acid solution (usually 6 ml. of water and 2 ml. of 40% acid solution). A clear solution was not, of course, obtained with samples containing metal ions added as impurities and which formed insoluble fluorides.

(3) *Extraction technique.* A tube was constructed from Polythene to a pattern similar to that of the glass columns used for the extraction of uranium (*Analyst*, 1951, **76**, 396), and the cellulose pulp used was the standard grade as supplied by Messrs. Reeve Angel Ltd. Full details of the procedure for extraction are given on p. 1501.

(4) *Preliminary experiments.* Early experiments showed that tantalum and niobium could be extracted by ethyl methyl ketone containing hydrofluoric acid (40% w/w aqueous solution), in concentration ranging from 0 to 7.5% v/v, but it was found that titanium was also extracted. The movement of titanium was examined because it forms a water-soluble fluoride and is commonly associated with the earth acids in naturally occurring materials.

The effect of the addition of complexing agents to the sample was investigated before attempting to find conditions for complete extraction of tantalum and niobium but with retention of titanium. After examination of a number of fluorides, it was found that ammonium fluoride

largely prevented the movement of titanium but permitted extraction of the earth acids; moreover, there were indications that tantalum could be separated from niobium by altering the acidity of the organic solvent. A series of experiments was therefore made in which conditions were sought for complete extraction of tantalum and niobium from a number of commonly associated ions. It was hoped then to find conditions for what was at the time considered to be possibly the more difficult separation, namely, that of the tantalum from the niobium.

A synthetic mixture was prepared consisting of equal amounts of an aluminium-iron silicate (granitic material), thoria, lanthanons isolated from monazite, alumina, ferric oxide, tin oxide, titanium oxide, and zirconium oxide. To 1-g. amounts of this mixture, known amounts of tantalum and niobium were added as metals (usually about 150 mg.) and the whole was decomposed as described in (2) (above). After final evaporation to dryness, 8 ml. of a solution of hydrofluoric acid (40%), in concentrations varying from 25 to 100% in different experiments, were added together with 1 g. of ammonium fluoride. Extractions were made in cellulose columns with ethyl methyl ketone containing 7.5% v/v of hydrofluoric acid (40%). Although tantalum and niobium were both extracted with a very good degree of purity with respect to other ions, in no case could quantitative recovery be obtained. Moreover, results were erratic and recoveries were generally poor. There appeared to be continuous extraction of the earth acids up to a volume of 600 ml. of solvent but increase in this volume brought about little further extraction. The process for extraction in the absence of foreign ions was then examined but results again were generally disappointing. Similar erratic results were obtained when tantalum and niobium were taken separately. There appeared to be no relation between the acidity of the sample solution and the amount of acid in the solvent. A systematic investigation of the conditions required for extraction of tantalum when present alone or with ions other than niobium was then carried out and this was followed by an investigation of the extraction of tantalum and niobium from their mixtures with one another.

(5) *Extraction of tantalum.* The first experiments were carried out in order to find the effect of the hydrofluoric acid concentration in the solvent on the degree of extraction of tantalum. These showed that, as the acidity of the solvent decreased, better recoveries of tantalum were obtained. It was also found that the presence of water in the solvent was advantageous and that a low-acidity sample was better. It was found that the minimum acidity and volume conditions for the sample solution which could be reasonably employed consisted of 2 ml. of aqueous hydrofluoric acid solution (40%) and 6 ml. of water (with 1 g. of ammonium fluoride added). Recoveries from 150 mg. of tantalum ranged from 93% down to about 30% when the acidity of the solvent was varied from 1% up to 10% of hydrofluoric acid (v/v) and at the high acidities results tended to be erratic. Results were similar in the presence and absence of foreign ions. Usually no further extraction of tantalum occurred after a volume of 200—300 ml. of solvent had been passed. Extraction with solvent containing water in addition to the acid usually resulted in a better extraction of tantalum.

TABLE I.

Ta added, g.	Nb added, g.	Base material present *	Ta found, g.	Analysis of Ta
0.155	nil	nil	0.149	—
0.151	0.149	nil	0.149	<0.1% Nb
0.148	0.154	nil	0.147	"
0.156	0.005	nil	0.143	—
0.153	0.047	nil	0.140	—
0.149	nil	1 g., No. 3	0.148	—
0.152	0.151	1 g., No. 3	0.148	<0.1% Nb 0.03% Fe
0.151	nil	1 g., No. 2	0.147	0.1% Fe, <0.1% Ti
0.153	nil	1.4 g., No. 4	0.150	0.02% Fe
0.133	nil	1 g., No. 1	0.131	{ 0.03% Fe, 0.01% Ti
0.150	0.153	1 g., No. 1	0.147	{ 0.01% Sn, <0.1% Zr

* No. 1: equal amounts of aluminium silicate, ThO₂, TiO₂, SnO₂, ZrO₂, Fe₂O₃, lanthanons, cerium (from monazite), Al₂O₃. No. 2: equal amounts of Al₂O₃, Fe₂O₃, ThO₂, lanthanons, cerium, TiO₂. No. 3: equal amounts of Al₂O₃, Fe₂O₃, ThO₂, lanthanons, cerium. No. 4: equal amounts of Al₂O₃, Fe₂O₃, ThO₂, lanthanons, cerium, CaF₂, MnO₂, PbO, MgO.

In view of these results it was decided to examine the degree of extraction with ethyl methyl ketone saturated with water but containing no added hydrofluoric acid. This solvent contains approximately 10% of water (by vol.), the exact value depending upon the temperature of the experiment. It was soon found that better extractions of tantalum were obtained than were hitherto possible, and therefore the conditions of employing this solvent were more critically

examined. The results given in Table 1 are typical of many showing the degree of extraction from samples containing tantalum alone, or in the presence of other ions, or present with niobium.

The sample was prepared in a volume of 8 ml. of 25% v/v hydrofluoric acid (40%) with 1 g. of ammonium fluoride added, and it was then absorbed in 6 g. of standard-grade cellulose (Reeve Angel Ltd.) and extracted on a column of cellulose (12" long). Ethyl methyl ketone saturated with water (300 ml.) was employed for extraction although it was usually found that no further extraction of tantalum was obtained after taking 250 ml. Spectrographic results of the analysis of the recovered tantalum are also given in Table 1.

The results show that when tantalum is present alone or together with relatively small amounts of niobium, recoveries are of the order 92—96%, indicating appreciable hold-up of tantalum. However, when tantalum is present with equivalent amounts of niobium or with other foreign ions, the recoveries are reasonably good, being of the order of 98—99%. In all cases spectrographic analyses showed that the extracted tantalum was of a high degree of purity.

(6) *Extraction of niobium.* Preliminary experiments showed that niobium could only be extracted as fluoride in a reasonable volume of solvent by employing high concentrations of hydrofluoric acid in the ethyl methyl ketone solvent, but later work with solvent containing 7.5% of hydrofluoric acid (40%) and employed directly for extraction gave erratic results. It was found, however, that when this solvent mixture was employed after treatment of the column with the solvent used for tantalum extraction, excellent recoveries of niobium were obtained. The reason for this interesting effect has not yet been elucidated but in later experiments the solvent used for tantalum extraction was always employed before that used for extraction of niobium, with beneficial results.

(7) *Quantitative separation of tantalum from niobium.* It has been shown (see Table 1) that complete extraction of tantalum when present alone could not be achieved under the conditions which have been described, but, in the presence of niobium in amount at least equal to that of the tantalum, very good recoveries were obtained. A series of experiments was therefore carried out in which separations were made of tantalum and niobium mixtures (niobium present in similar or greater amount). Tantalum was extracted by using 300 ml. of ethyl methyl ketone solvent (saturated with water) and niobium was then extracted with 400 ml. of ethyl methyl ketone containing 7.5% (v/v) of hydrofluoric acid (40%). No advantage was gained by increasing the volume of 400 ml. of solvent for niobium.

(8) *Method for the determination of tantalum and niobium in their mixtures.* Ethyl methyl ketone was purified as described on p. 1499.

Preparation of Solvent A (as employed for extraction of tantalum). A solution of ethyl methyl ketone saturated with water was prepared by shaking intermittently for about 30 minutes 400 ml. of the solvent with 50 ml. of water in a separating-funnel. When excess of water had completely separated and the organic solvent was clear, the aqueous layer was run off and discarded.

Preparation of Solvent B (as employed for extraction of niobium). A volume of 7.5 ml. of hydrofluoric acid solution (40%) was added to each 92.5 ml. of ethyl methyl ketone, a Polythene measuring cylinder being used. A Polythene bottle was employed for storage of the prepared solvent.

Procedure: Chromatographic extractions. Tantalum and niobium metals or oxides were accurately weighed into a platinum dish and moistened with water, and a few drops of nitric acid followed by 5—10 ml. of hydrofluoric acid (40%) solution were added; decomposition was then continued as described in (2) (p. 1499), and the dry residue was taken up as before but with addition of 1 g. of ammonium fluoride. The mixture was covered and gently warmed for ten minutes to ensure solution of tantalum and niobium fluorides, care being taken to avoid appreciable evaporation. A Polythene rod was used for stirring the contents of the dish. A column of activated cellulose (standard grade, Reeve Angel Ltd.) about 12 in. long was prepared in a Polythene tube (ca. 2 cm. bore, 26 in. long) at the top of which was a funnel to facilitate introduction of the sample. The bottom of the tube terminated in a short length of narrow tubing of about 50-mm. bore which was sealed by a 6-cm. length of polyvinyl chloride tubing with a screw slip. The column was prepared by adding a slurry of the cellulose in ethyl methyl ketone. The cellulose settled under its own weight and the level of the solvent was allowed to fall to the top of the column. A homogeneous column was thus obtained. The column was conditioned by passage of 100 ml. of Solvent A which was finally allowed to fall to the level of the cellulose. Cellulose (6 g.) was added to the sample solution in its platinum dish and the whole well mixed, a Polythene rod being used in order to form a homogeneous friable mass. The mixture was then introduced into the top of the column, and the empty platinum dish allowed to rest in the funnel throughout the subsequent procedure. Solvent A was added in

sufficient amount to reach a level about 2 cm. above the cellulose containing the sample. The wad was then agitated by means of a Polythene plunger so that it formed a homogeneous continuation of 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 a quantity of 300 ml. had been passed. The eluent, containing the tantalum fraction, was collected in a 600-ml. Polythene beaker. When the last of Solvent A had fallen to the level of the cellulose, the beaker was replaced by another similar beaker. Sufficient of Solvent B was poured first into the dish and then into the column in order to come about halfway to the level of the top of the column. It was then allowed to fall to the level of the cellulose. A further similar quantity of solvent was added and the sample was gently beaten with the plunger, care being taken not to penetrate below the actual sample "wad." The plunger was washed with Solvent B, and the extraction of niobium continued as for tantalum, but 400 ml. of solvent were collected.

Removal of solvents and determination of tantalum and niobium. The solvent was removed from each fraction, in a fume cupboard by cautious evaporation under an infra-red lamp, a stream of air being directed into the beaker during evaporation. When the volume of solution had been sufficiently reduced, the contents of the beaker were transferred to a platinum dish and evaporated further to remove the remaining solvent, care being taken to avoid spray. Sulphuric acid (5 ml. of 1 : 1) was then added, followed by 2 ml. of concentrated nitric acid and about 1 ml. of 70% perchloric acid. The solution was evaporated gently to sulphuric acid fumes. The contents of the dish were washed into a 250-ml. glass beaker, the volume at this stage being about 50 ml. After addition of 5 g. of ammonium chloride, the solution was heated to boiling; 0.5—2 g. of tannin (depending on the amount of earth acid present), dissolved in about 5 ml. of hot water, was then added and sufficient solid ammonium acetate to give a solution of pH 4—5 (by test-paper). The beaker was kept at about 80° for about 10 minutes, and the precipitate collected on a No. 541 Whatman filter-paper. The precipitate was finally strongly ignited to oxide, at a temperature preferably above 1000° (Ta_2O_5 or Nb_2O_5). The oxides were spectrographically analysed for impurities. In the recent stages of the work it has been found that this more lengthy tannin procedure could be replaced by a shorter procedure involving direct ignition to the oxides. After removal of solvent and evaporation to a few ml. in a platinum dish, a few drops of 50% sulphuric acid and concentrated nitric acid were added, evaporation continued to about 1 ml., and sufficient ashless cellulose "block" added to absorb the solution. The whole was then carefully ignited to the oxide. This shorter procedure was not employed when the amount of tantalum or niobium present was less than about 5 mg.

TABLE 2.

Expt. no.	Ta, mg. :		Nb content of Ta, mg.	Nb, mg. :		Ta content of Nb, mg.
	Taken	Found		Taken	Found	
1	151.0	149.0	0.15	151.0	—	—
2	50.5	52.0	0.05	150.0	150.5	0.3
3	10.3	10.4	0.01	152.1	153.0	0.15
4	5.0	6.2	0.03	153.1	152.9	0.15
5	nil	0.7	—	152.2	154.4	0.15
6	150.9	151.6	0.15	150.2	151.4	0.15
7	2.0	1.9	0.002	11.1	11.4	—
8	147.9	146.7	0.30	154.2	150.2	0.15
9	49.5	48.7	0.15	154.6	155.5	0.50
10	6.1	6.1	0.03	157.1	157.5	0.15
11	152.4	149.3	0.20	251.5	253.4	1.80

Table 2 shows the results obtained on a range of mixtures. Spectrographic analyses were carried out to determine the niobium and tantalum contents, respectively, of the separated tantalum and niobium oxides. The results indicate that tantalum and niobium can be quantitatively separated from each other in good purity (provided that the amount of tantalum present in the original mixture does not exceed that of the niobium). For high Ta : Nb ratios the procedure is still under investigation, but even in the absence of niobium, tantalum extraction exceeds 90%. It will be seen later, however, that application of the procedure to complex mixtures with other ions leads to a better recovery of tantalum than in the absence of niobium.

(9) *The separation and determination of tantalum and niobium in their mixtures with other ions.* It was established early in the work on the study of the movements of other ions in association with tantalum and niobium that ammonium fluoride would prevent the movement of soluble fluorides such as those of titanium, tin, and zirconium under certain conditions. These conditions were obtained when a direct extraction was made with ethyl methyl ketone containing hydro-

fluoric acid (40%) without addition of water. Unfortunately, there was only partial extraction of niobium. Good and consistent recoveries of niobium were only obtained when the solvent used for tantalum extraction was passed through the column before the extraction with solvent used for niobium as in the procedure already described. It was shown, however, that, of the many ions examined, only traces were extracted with the tantalum, whereas extraction of niobium caused the extraction of certain impurities, mainly titanium, tin, and zirconium, in sufficient amount appreciably to contaminate the niobium fraction. Extraction of commonly occurring ions such as Ca, Mg, Pb, Mn, Th, Fe, Al, Ce, and rare earths was very small. The degree of extraction of titanium, tin, and zirconium was also affected by the amount of the niobium. Experiments have shown that the degrees to which these ions may cause contamination are in the order Ti, Zr, and Sn (least). The work which follows consists of a preliminary survey of the applications of the chromatographic technique to the analysis of complex mixtures of tantalum and niobium. In all cases the initial sample was decomposed by treatment with nitric and hydrofluoric acids with final conversion into fluorides in the manner described on p. 1499. Where insoluble fluorides were present, these were dispersed into the cellulose wad in the same manner as the solution.

A mixture of equal amounts of iron, aluminium, thorium, lanthanons (including cerium), and aluminium silicate was prepared by taking equal amounts of the corresponding oxide (except in the case of aluminium silicate which was added as a naturally occurring silicate). Results obtained for recoveries of added tantalum and niobium from 1 g. of the mixture are given in Table 3. Spectrographic analyses of the separated tantalum and niobium oxides are also shown.

TABLE 3.

Ta, mg. :		Impurities in Ta recovered, mg.	Nb, mg. :		Impurities in Nb recovered, mg.
Added	Found		Added	Found	
149.3	147.7	0.1 Fe	nil	—	—
nil	—	—	151.5	150.4	0.4 Fe
151.7	148.6	0.15 Nb	150.9	150.6	0.4 Ta
					0.15 Fe
5.6	5.0	0.1 Nb	30.0	31.5	0.1 Ta
		0.3 Fe			0.4 Fe
20.2	19.5	0.1 Nb	100.5	100.9	0.2 Ta
		0.2 Fe			0.3 Fe

TABLE 4.

Ta (or Ta fraction), mg. :		Impurities in Ta (or Ta fraction), mg.	Nb (or Nb fraction), mg. :		Impurities in Nb (or Nb fraction), mg.*
Added	Found		Added	Found	
(a) 1 G. of mixture used in Table 3 plus 125 mg. of TiO ₂ .					
150.6	147.5	0.2 Ti 0.2 Fe	nil	40 as oxide	{ Ta = 2 Fe = 1.5 Ti = 30
(b) 1 G. of mixture used in Table 3 plus 125 mg. of ZrO ₂ .					
149.8	144.8	0.2 Zr 0.2 Fe	nil	27 as oxide	{ Ta = 2.5 Fe = 0.8 Zr = 20
nil	nil	—	149.4	162	{ Fe = 0.6 Zr = 12
(c) 1 G. of mixture used in Table 3 plus 125 mg. of SnO ₂ .					
150.1	144	Sn, nil	nil	21 as oxide	{ Ta = 1 Fe = 1.2 Sn = 15
nil	nil	—	150.0	161	{ Fe = 5 Sn = 5
(d) 1 G. of mixture used in Table 3 plus 0.1 g. of each of Ca, Mn, Pb, Mg as oxides.					
153.1	150.1	all impurities	nil	7 as oxide	—
nil	3	0.3 mg. —	155.0	154	Fe = 0.3 Mn = 1.5

* Approximate spectrographic analysis.

It was found necessary to increase to 500 ml. the volume of solvent employed for extraction of niobium in the presence of impurities.

Experiments have also been carried out with mixtures containing titanium, zirconium, and tin in addition to iron, aluminium, thorium, and rare earths. The results are shown in Table 4.

The results given in Tables 3 and 4 show that there is only very slight contamination of

extracted tantalum, the lowest recoveries being obtained from mixtures containing Ti, Zr, or Sn. Part of the remaining tantalum could be recovered from the niobium fraction. Good recoveries of niobium appear to be obtained in all cases but contamination by Ti, Zr, and Sn is appreciable.

Research is in progress to overcome the interference by Ti, Zr, and Sn and also to improve the recovery of tantalum. This work involves a second chromatographic extraction of the niobium fraction under modified solvent conditions. It has been found that complete removal of the aqueous solvent used for tantalum by washing the column with ethyl methyl ketone containing 2% of hydrofluoric acid before extraction with the solvent containing 7.5% of the acid leads to a marked reduction in the movements of Ti, Zr, and Sn. The movements of these metals in the presence of niobium, however, have yet to be examined and also the effect on recovery of niobium. [Added, 6.3.52: Difficulties due to interference by Ti, Zr, and Sn have now been overcome. A modified procedure will shortly be submitted for publication.]

(10) *Application of the chromatographic procedure to minerals and alloys.* The process has not yet been widely applied to naturally occurring materials but results have been obtained on samples of pyrochlore, columbite, and synthetic ferro-tantalum-niobium alloy. Results obtained on a sample of each of these materials are given below. Since all samples were fairly complex materials, a second chromatographic separation of the niobium fraction was made in two instances in order to reduce contamination by impurities such as titanium and also to recover small amounts of tantalum which were not extracted with the main tantalum fraction but were all or partly extracted with the niobium.

(a) *Columbite.*—Wt. of sample = 0.5 g. Decomposed by HF and HNO₃ (insoluble, fused with KHSO₄—tannates precipitated—ignited and added to soluble portion).

Chromatographic separation. Tantalum fraction = 146.7 mg. of oxides, contained: 0.1 mg. Nb, 0.1 mg. Fe, and 0.7 mg. Zr (as oxides) (*i.e.*, total impurity = 0.9 mg.). Niobium fraction = 192 mg. oxides. (500 ml. of solvent used.)

The niobium fraction was subjected to a second chromatographic extraction in order to decrease contamination by Ti, Sn, Zr and recover any tantalum which had passed through in the first separation.

Tantalum fraction = 7.6 mg., contained 0.4 mg. of total impurity. Niobium fraction = 183 mg., contained: 0.2 mg. Ta, 0.2 mg. Fe, 0.2 mg. Sn, 1.8 mg. Ti, and 0.4 mg. Zr (as oxides).

Total Ta₂O₅ = 30.9% (0.3% impurities).

Total Nb₂O₅ = 36.6% (0.4% TiO₂ and 0.2% other impurities).

(b) *Pyrochlore Concentrate.*—Wt. of sample = 0.4992 g. Decomposed by HF-HNO₃.

Chromatographic separation. Tantalum fraction = 20.0 mg. of oxides, contained: 0.1 mg. Nb, 0.2 mg. Fe, 0.02 mg. Zr, 0.1 mg. Sn, 0.2 mg. Ti (as oxides) (*i.e.*, total impurity = 0.5 mg.). Niobium fraction = 245.9 mg. oxides, contained: 0.3 mg. Ta, 0.2 mg. Fe, 0.3 mg. Zr, 0.5 mg. Sn, 12 mg. Ti (as oxides).

Total Ta₂O₅, 4.0% (0.1% impurities).

Total Nb₂O₅, 49.2% (2.4% TiO₂, 0.2% other impurities).

This analysis illustrates the degree of contamination of the separated niobium by titanium. A second chromatographic extraction was not carried out but experiments have shown that this would have effected a considerable reduction in titanium.

(c) *Ferro-tantalum-Niobium Alloy.*—Contains mainly Ta-Nb-Fe, Mn.—Wt. of sample = 0.3719 g. Decomposed by HF + HNO₃.

Chromatographic separation. Tantalum fraction = 58.5 mg. of oxides, contained: <0.1 mg. Nb, 0.1 mg. Fe, <0.1 mg. Mn, <0.1 mg. Sn, <0.1 mg. Ti, <0.1 mg. Zr (as oxides) (*i.e.*, total impurity <0.5 mg.). Niobium fraction = 286.5 mg. oxides. (500 ml. of solvent used.)

As in example (a), the Nb fraction was subjected to a second chromatographic extraction to recover any Ta which had passed through in the first separation and reduce contamination of the niobium fraction.

Tantalum fraction = 2.0 mg., contained 0.1–0.2 mg. Fe (as oxide). Niobium fraction = 274 mg., contained <0.2 mg. Ta, 0.2 mg. Fe, approx. 1 mg. Mn, 0.2 mg. Sn, 0.5 mg. Ti, <0.2 mg. Zr and W—detected (as oxides).

Total Ta₂O₅ = 60.5 mg. = 13.33% Ta (<0.2% impurities).

Total Nb₂O₅ = 274 mg. = 51.56% Nb (about 0.5% impurities).

These results suffice to show that the chromatographic technique has considerable promise for the analysis of complex ores and materials containing tantalum and niobium. Further experiments are in progress, particularly on the application of the chromatographic procedure to the analysis of low-grade materials (*i.e.*, less than 1.0% of earth oxides).

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