653. *Inorganic Chromatography on Cellulose. Part XIII.* Determination of Tantalum and Niobium in Low-grade Phosphatic and Siliceous Ores.*

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The chromatographic method of determination of tantalum and niobium (*J.*, 1952, 3155) has been extended to ores containing less than 0·1% of the oxides of these metals. Chemical pre-treatment is required. The method has been applied to Nigerian granites containing up to 0·3% of niobium pentoxide and to phosphatic soils from Sukulu, Uganda. Phosphate ions are partially extracted with niobium in the chromatographic procedure and are removed thereafter.

Chromatographic methods have been described for the quantitative separation and determination of tantalum and niobium in medium- and high-grade minerals and ores (Part XII, *loc. cit.*). The sample, prepared in a dilute solution of hydrofluoric acid to which ammonium fluoride was added, was placed on a column of cellulose. Tantalum was extracted with ethyl methyl ketone saturated with water; the column was equilibrated with ethyl methyl ketone containing 1% of hydrofluoric acid which arrested movements of titanium, zirconium, and tin; and niobium was then extracted with ethyl methyl ketone containing 12·5% (v/v) of hydrofluoric acid (40% w/w aqueous solution). In one procedure the sample was chromatographed directly, and in the other a preliminary chemical treatment, involving "acid hydrolysis," was given in order to remove the bulk of the common metal ions from the earth acids (oxides of tantalum and niobium). For low-grade materials samples of 10 g. were needed, to yield weighable quantities of the earth acids. As these could not be directly transferred to columns of cellulose preliminary separation of the earth acids, together with small amounts of other constituents, was necessary.

Two types of ore have been examined in detail and it is considered that the principles involved could be extended to any type of low-grade material. One ore examined was a granite from Nigeria, containing small amounts of pyrochlore and about 70% of silica, together with iron, aluminium, alkali metals, and small amounts of titanium, tin, and zirconium. Silica was removed first, by repeated evaporation with hydrofluoric–nitric acids; fluoride ions were then removed by addition of sulphuric acid and evaporation to fuming; after dilution, two "acid hydrolyses" were made, thereby precipitating the earth acids together with some titanium, zirconium, and other impurities (cf. *loc. cit.*). The ignited crude earth acids were dissolved in hydrofluoric acid, and tantalum and niobium determined chromatographically.

The second ore, from Sukulu, Uganda, contained much phosphate (as apatite) and ferric oxide, minor constituents being about 0·2% of niobium (about 0·004% of tantalum) (as pyrochlore), titanium, and zirconium. It was not found practicable to separate phosphate ions completely before chromatography and, since phosphate is partly extracted with the niobium by the solvent mixture used, the niobium could not be determined by direct ignition (*loc. cit.*). Separation of the earth acids from phosphate ions was achieved by prior precipitation with ammonia solution (cupferron and tannin were unsatisfactory for this purpose). The difficulty did not affect determination of tantalum since phosphate ions are not extracted by ethyl methyl ketone saturated with water.

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* Part XII, *J.*, 1952, 3155.

The chromatographic procedure has also been applied to the determination of niobium in phosphatic pyrochlore concentrates derived from Sukulu soils. However, a second precipitation of the extracted earth acid with ammonia was needed for complete separation from phosphate ions. The amount of niobium present in such samples is considerably greater than the amount obtained from the analysis of the original ore.

EXPERIMENTAL

Determination of Tantalum and Niobium in Low-grade Phosphatic Ores : Analysis of Soil from Sukulu, Uganda.—(a) *Separation of niobium from phosphate ions by ammonia solution.* A known amount of metallic niobium was weighed into a platinum dish, and a measured amount of ammonium phosphate solution added. Hydrofluoric acid was added together with a few drops of nitric acid, and solution effected by heating on the steam-bath. After evaporation to dryness sulphuric acid (50% v/v; 10 ml.) was added and the whole evaporated until sulphur trioxide was freely evolved (to remove fluoride). The solution was transferred to a 400-ml. beaker, diluted to 200 ml., and then neutralised with ammonia solution, and an excess of 5 ml. (*d* 0·880) was added. The solution was heated to the b. p. and set on the edge of a hot-plate for about 20 minutes. The precipitate was filtered on a No. 541 Whatman filter-paper after addition of a little cellulose pulp, washed with dilute ammonia–ammonium nitrate solution, ignited, and weighed (as Nb_2O_5). The amount of phosphate present in the filtrate was determined by the standard molybdate method. In order to test the degree of separation of niobium from phosphate ions, a second precipitation of the niobium oxide with ammonia solution was made after the ignited oxide from the first precipitation had been dissolved in hydrofluoric–nitric acid and the procedure described above was then repeated. During this work it was noticed that on ignition of niobium residues to the pentoxide in the presence of comparable amounts of phosphate ions, the resulting material was extremely resistant to attack by hydrofluoric acid, possibly owing to the formation of niobium pyrophosphate. Results obtained are shown in Table 1 (values are mg.). The figures for phosphate are not quantitative (some phosphoric acid is lost during the evaporation with sulphuric acid) but serve as a guide to the degree of separation.

TABLE 1.

		Nb_2O_5 found	P_2O_5 in filtrate	Nb_2O_5 found	P_2O_5 in filtrate	Nb_2O_5 found	P_2O_5 in filtrate
Nb present	P_2O_5 present	1st pptn.		2nd pptn.		3rd pptn.	
99·6	*ca.* 90	109·5	74	98	11·0	—	—
102·6	,, 50	107	41·6	100·7	6·0	—	—
100·2	,, 25	102·1	18·9	98·7	4·0	98·3	nil
31·6	,, 60	31·7	60·2	29·8	2·8	29·0	nil
32·8	,, 50	37·0	41·0	32·5	3·2	—	—
37·5	,, 25	41·3	20·2	37·0	2·2	—	—

The results show that two precipitations with ammonia suffice for the separation of the earth acid from phosphate ions but that there is a small loss of niobium. Nevertheless, it is considered that the process is sufficiently accurate for most analytical purposes. Preliminary investigations of cupferron and tannin as reagents for the precipitation of niobium showed only poor separation from phosphate ions.

(b) *Behaviour of phosphate ions in the chromatographic procedure.* The movement of phosphate ions during the chromatographic extraction of tantalum and niobium was examined for two types of sample, namely, (1) calcium phosphate, and (2) calcium phosphate together with tantalum and niobium.

The samples were decomposed with hydrofluoric–nitric acid in the usual way, and the chromatographic procedure described earlier (*loc. cit.*) was then carried out. The tantalum and niobium were determined in the appropriate fractions and all fractions were analysed for phosphate content. The niobium was reprecipitated twice with ammonia to test the completeness of the separation from phosphate ions. Results obtained are given in Table 2. They show that phosphate ions are only extracted by the solvent employed for extraction of niobium. Two precipitations with ammonia are required for the separation of niobium from 100 mg. of P_2O_5 such as might be present after extraction of a phosphatic niobium concentrate (see also Tables 1 and 5). In the analysis of low-grade Sukulu soil, where relatively small amounts of Nb_2O_5 (and correspondingly small amounts of P_2O_5) are present, one precipitation of niobium was sufficient (see Table 3).

The results show that phosphoric acid is not extracted by the solvent employed for extraction of tantalum, so the direct ignition procedure may be employed for the final determination of tantalum as Ta_2O_5.

TABLE 2. *Sample* (1) : 137 *mg. of* P_2O_5 (*as calcium phosphate*). *Sample* (2) : 140 *mg. of* P_2O_5 (*as calcium phosphate*), 57·2 *mg. of* Ta, *and* 101·5 *mg. of* Nb.

Sample	Ta fraction : 250 ml. of COMeEt satd. with H_2O		Intermediate fraction : 400 ml. of COMeEt containing 1% of HF		Nb fraction : 400 ml. of COMeEt containing 12·5% of HF					
					1st pptn.		2nd pptn.		3rd pptn.	
	Ta found (mg.)	P_2O_5 extracted (mg.)	" Nb " found (mg.)	P_2O_5 extracted (mg.)	" Nb " (mg.)	P_2O_5 in filtrate (mg.)	" Nb " (mg.)	P_2O_5 in filtrate (mg.)	" Nb " (mg.)	P_2P_5 in filtrate, (mg.)
1	Nil	Nil	Nil	trace	Nil	31	—	—	—	—
2	57·8 *	Nil	Nil	Nil	113·4	81	101·4	14·8	100·0	1·4

* Ta determined by pptn. with ammonia.

TABLE 3.

Sample no.	Nb_2O_5 (mg.) added as concentrate	1st precipitation		2nd precipitation	
		Nb_2O_5 (mg.)	P_2O_5 in filtrate (mg.)	Nb_2O_5 (mg.)	P_2O_5 in filtrate (mg.)
S.1	Nil	26·8	—	24·4	—
S.1	Nil	23·7	—	22·7	—
S.1	24·5	48·2	—	46·5	—
S.2	Nil	19·0	21·0	18·0	0·3
S.3	Nil	13·4	20·0	11·4	0·2

(c) *Procedure for analysis of phosphatic Sukulu soil.* The method adopted was as follows : A sample (10 g.) was treated with hydrochloric acid (18%; 100 ml.), vigorously boiled, and evaporated, finally to dryness; a further small quantity of hydrochloric acid was then added, and the solution again evaporated to dryness. The residue was baked under an infra-red lamp for 1 hour to effect removal of small quantities of fluoride (possibly originating in cryolite). As is shown below (p. 3402) for analysis of Nigerian granite, hydrochloric acid treatment followed by baking does not remove gross amounts of fluoride such as remain after hydrofluoric acid treatment for removal of silica. If fluoride is present during " acid hydrolysis," low results are obtained.

To the dry residue obtained, concentrated hydrochloric acid (5 ml.) was added, followed by water (250 ml.) and saturated sulphur dioxide solution (30 ml.), and the solution boiled for 20 minutes and then set aside overnight (see Bagshawe and Elwell, *J. Soc. Chem. Ind.*, 1947, **66**, 398). The precipitate, containing the earth acids, was filtered on No. 541 Whatman filter-paper and, after being washed with warm 0·5N-hydrochloric acid, treated with 18% hydrochloric acid (100 ml.) and hydrogen peroxide (100-vol.; 30 ml.). The filter-paper was ashed in a platinum dish, and the ash added to the above mixture, which was then warmed for a few minutes, diluted to about 600 ml., and boiled gently for about 30 minutes : during this process the volume of the solution was not allowed to fall below *ca.* 500 ml. After being kept for *ca.* 1 hour the precipitate was filtered off (paper pulp was added) on No. 541 Whatman filter-paper, washed with 0·5% hydrochloric acid and reserved for further treatment. The filtrate was neutralised with ammonia, and concentrated hydrochloric acid (10 ml.) then added, followed by saturated sulphur dioxide solution (*ca.* 30 ml.). The volume of solution at this stage was 500—600 ml. The solution was boiled for 30 minutes and then set aside overnight. After filtration, the precipitate, combined with the first precipitate, was ignited in a platinum dish. The ignited precipitate contained, in addition to earth acids (mainly niobium), silica, phosphates of calcium and common metal ions, and small amounts of titanium and zirconium. The ignited precipitate was dissolved in hydrofluoric acid and treated as a sample for chromatographic analysis (*loc. cit.*). The fraction of solvent used for extraction of tantalum and the intermediate solvent fraction were discarded, as the tantalum content of Sukulu soil was of the order of the blank, and the intermediate solvent fraction was free from metal ions. After removal of solvent the niobium fraction was transferred to a platinum dish, sulphuric acid (50% v/v; 10 ml.) was added, and the whole evaporated to fuming. After about 30 minutes' fuming, niobium was determined as above after precipitation with ammonia. Table 3 shows some results for the determination of niobium in Sukulu soil (the tantalum content was too low for determination). In one case pyrochlore concentrate (derived from the soil) was added. A single precipitation of earth acid with ammonia is seen to suffice for separation of niobium from phosphate ions. A small loss of niobium occurred during the second precipitation with ammonia.

Table 4 shows results for a range of Sukulu soil samples. In a number of analyses known amounts of niobium were added in the form of pyrochlore concentrate and good recoveries were obtained. In two further experiments, analysed ferrotantalum–niobium alloy was added, and in another a known amount of columbite. The results showed good recoveries of tantalum.

TABLE 4.

Sample no. (10 g.)	Nb–Ta added as:	added		found		Nb_2O_5	
		Ta_2O_5 (mg.)	Nb_2O_5 (mg.)	Ta_2O_5 (mg.)	Nb_2O_5 (mg.)	present (%)	found (%)
4	Nil	Nil	Nil	*ca.* 1·0	19	0·19	0·19
4	Ferro–Ta–Nb	5·7	26	7·6	46	0·45	0·46
4	Pyrochlore	—	23·5	*ca.* 1·0	44	0·43	0·44
7	Nil	Nil	Nil	*ca.* 1·0	23	0·23	0·23
7	Columbite	15·6	19	15·1	35	0·42	0·35
7	Pyrochlore	—	24·5	*ca.* 1·0	48	0·48	0·48
7	,,	—	49	,,	72	0·68	0·72
7	,,	—	76	,,	105	0·99	1·05
7	,,	—	20·0	1·7	45·1	0·43	0·45
7	,,	—	38·0	3·1	60·0	0·61	0·60

TABLE 5.

	1st pptn.		2nd pptn.		3rd pptn.			
Ta_2O_5 found (mg.)	" Nb_2O_5 " (mg.)	P_2O_5 in filtrate (mg.)	Nb_2O_5 (mg.)	P_2O_5 in filtrate (mg.)	Nb_2O_5 (mg.)	P_2O_5 in filtrate (mg.)	Ta_2O_5 (%)	Nb_2O_5 (%)
3·2 *	103·7 †	59·0	96·4	7·6	94·6	Nil	0·2	9·6

* Blank = 1 mg.

† 4·5 Mg. included from last 200 ml. of " intermediate solvent " fraction.

Typical results of spectrographic analysis of separated Nb_2O_5 : Ta, 0·1; Fe, 0·1; Sn, 0·01; Ti, 0·3; Zr, 0·3—1·0%; P, trace. The total impurities in the Nb_2O_5 are thus negligible.

(d) *Analysis of phosphatic pyrochlore concentrate from Sukulu soil.* The concentrate obtained from the soil was analysed by the chemical-chromatographic procedure (*loc. cit.*). Niobium was determined in the appropriate solvent fraction (from a 1-g. sample) by ammonia precipitation. The results, in Table 5, show that two precipitations with ammonia are necessary (see also Tables 1 and 2) for separation of earth acid from phosphate ions.

Determination of Tantalum and Niobium in Low-grade Siliceous Ores from which Phosphates are Absent : Application to Nigerian Granite.—Nigerian granite containing small amounts of pyrochlore comprises about 70% of silica together with iron, aluminium, potassium, and sodium, with small amounts of other common metals, titanium, and zirconium. The content of niobium pentoxide ranged from 0·2 to 0·3%, tantalum being approx. 1/12th of this. From a sample (*ca.* 10 g.) in a platinum dish (diam. 5″, to avoid spraying) silica was removed by repeated evaporation with hydrofluoric acid after the addition of a few ml. of concentrated nitric acid. Sulphuric acid solution (50% v/v; 40 ml.) was added and the mixture evaporated under an infra-red lamp until sulphur trioxide was freely evolved, and finally to dryness by bringing the dish close to the lamp. A further 40 ml. of sulphuric acid were added and the mixture was again evaporated to fuming and allowed to fume for a further 20—30 minutes. [In early experiments attempts were made to remove fluoride ions by evaporations with hydrochloric acid (the sample being finally taken to dryness and baked) but very low results were obtained in the subsequent determination of niobium. This indicated that fluoride ions were present during the acid hydrolysis and caused solubility of the earth acids.] The contents of the dish were transferred to a 1-l. beaker with the aid of water. Insoluble material adhering to the dish was removed by digestion with a little hydrochloric acid. The crude earth acids were then precipitated by two acid hydrolyses as described on p. 3401. Apart from a few ml. of hydrochloric acid employed to clean the dish, no more was added for the first precipitation since sufficient acid was present as sulphuric acid. After ignition of the crude earth acid precipitate, tantalum and niobium were determined chromatographically. It was found that the intermediate solvent fraction (ethyl methyl ketone containing 1% of hydrofluoric acid) could be discarded. Results obtained on a sample of the Nigerian granite with and without the addition of known amounts of pyrochlore concentrate (analysed by the direct procedure, *loc. cit.*), separated from the source of the sample, are given in Table 6. They show excellent recoveries of the earth acids.

TABLE 6. *Pyrochlore concentrate contains* 3·01% *of* Ta_2O_5 *and* 36·6% *of* Nb_2O_5. *Samples taken,* 10 *g.*

Concentrate added equiv. to :		Found ·		Present		Found	
Ta_2O_5 (mg.)	Nb_2O_5 (mg.)	Ta_2O_5 (mg.)	Nb_2O_5 (mg.)	Ta_2O_5 (%)	Nb_2O_5 (%)	Ta_2O_5 (%)	Nb_2O_5 (%)
Nil	Nil	3·0 *	28·0	—	—	0·02	0·28
Nil	Nil	2·5	25·1	—	—	0·02	0·25
6·1	73·5	9·6	99·5	0·08	1·00	0·09	1·00
6·6	79·0	8·8	103·0	0·09	1·05	0·08	1·03

* Blank = 1 mg.

As a precautionary measure niobium was determined in the appropriate solvent fraction by precipitation with ammonia before chromatography in case small amounts of potassium salts had been occluded by the crude earth acids, for potassium ions are extracted by the solvent employed for extraction of niobium. Spectrographic analysis of the ignited niobium pentoxide showed that the impurities present were negligible.

The authors thank Dr. R. B. F. Temple and Mr. J. R. Moore, who carried out the spectrographic work, and Miss Patricia Swain for experimental assistance. The work was carried out on behalf of the Ministry of Supply and is published by permission of the Director of the Chemical Research Laboratory.

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[*Received, May* 26*th*, 1952.]