Anion-Exchange Separation and Estimation of Thorium in Niobite-Tantalite Type Minerals: A New Approach

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Synopsis. A simple, rapid and quantitative anion-exchange separation of microgram to milligram quantities of thorium has been achieved from milligram quantities of niobium, tantalum, and titanium in citric acid-nitric acid medium. This method is successfully applied for the separation and estimation of thorium in niobite-tantalite type minerals. Sample (0.500 g) is fused with ca. 8 g $KHSO_4$ and is taken in ca. 7% citric acid medium. To a suitable aliquot ca. 8 M (1 M=1 mol dm^{-3}) nitric acid acidity is maintained in ice cold condition, and is passed through a column of Dowex-lX8 (100—200 mesh size). Thorium is eluted with ca. 6 M HCl and estimated spectrophotometrically with arsenazo III. The RSD obtained by this method is 2—3%.

Quantitative separation of thorium from niobium, tantalum and titanium is a difficult task. Tartaric hydrolysis[1)] is a widely quoted method for the separation of niobium and tantalum. However, the separation of thorium is not quantitative. Also titanium, zirconium, and other acid soluble elements accompany thorium along with few milligrams of niobium and tantalum. Fluoride and oxalate precipitations[2)] are used for the quantitative separation of thorium; for smaller quantities calcium or lanthanum is used as carrier. However, in the presence of excess alkali and alkaline earth metals zirconium, titanium, niobium, and tantalum partly co-precipitate as its double salts.[3)] This method cannot separate rare earth elements and other insoluble fluorides. In the presence of niobium, tantalum, and titanium ion-exchange studies are usually carried out in hydrofluoric acid medium,[4—9)] but they are not feasible for thorium separation. Strelow et al.[10)] have performed the separation of lead from tin, antimony, niobium, tantalum, and molybdenum by cation-exchange chromatography in tartaric acid–nitric acid medium. The oxalate or citrate complexes of niobium, tantalum, and titanium remain stable in fairly concentrated nitric acid for a considerable time, and under these conditions they do not adsorb on the anion-exchanger. Anion-exchange separation of thorium[11)] is a well known method and is used for the separation of thorium in silicate rocks.[12—15)] However, a simple specific ion-exchange separation method for thorium from niobite-tantalite type matrix is not available. Therefore it was attempted to study the anion-exchange behavior of thorium in a mixed organic acid–nitric acid medium in the presence of sulfate with a view to separate and estimate thorium in niobite-tantalite type minerals after the $KHSO_4$ fusion. This method is applied to both synthetic and natural samples.

Experimental

Apparatus: A borosilicate glass column of 1 cm internal diameter was used. Spectrophotometric studies were performed on a Varian 634 S model double beam spectrophotometer.

Anion-Exchanger: Dowex-lX8, 100—200 mesh size was used.

Reagents: All reagents and chemicals used were of AR or GR grade. Stock solution of 1000 μg ml^{-1} of ThO_2 was prepared from thorium nitrate in 3% (v/v) nitric acid and was standardized gravimetrically. Niobium, tantalum, and titanium solutions were prepared by fusing their oxides with previously fused potassium hydrogen sulfate and taken in 7% (m/v) citric acid solution. 0.05% (m/v) arsenazo III was prepared in distilled water.

Distribution Studies: A 250 mg of the air dried anion-exchanger in the nitrate form was equilibrated in 25 ml of the solution (Table 1) containing 250 μg of thorium by shaking it for nearly four hours. The concentration of thorium before and after attaining equilibrium was determined by taking a suitable aliquot from the aqueous phase in a beaker, dried and fumed with a mixture of perchloric acid (0.5 ml) and nitric acid (10 ml) and finally taken in 5% (v/v) hydrochloric acid, diluted to a suitable volume for spectrophotometric measurement with arsenazo III.[16)] Kd values were calculated by the following relationship.

$$K_\mathrm{d} = \frac{\text{Thorium (μg) adsorbed per gram of dried resin}}{\text{Thorium (μg) remaining per ml of solution}}.$$

The results obtained are tabulated in Table 1.

Column Separation: A slurry of ca. 10 g resin (100—200 mesh size) in demineralized water was poured into the column which has a glass wool plug at the bottom. The resin bed was then saturated with a mixture of ice cold 8 M nitric acid in 0.18 M citric acid. Synthetic mixtures of niobium, tantalum, and titanium in different ratios along with known amount of thorium (Table 2) were taken in a beaker and cooled in an ice cold water, and ice cold concentrated nitric acid was added to maintain a final nitric acid acidity ca. 8 M. The solution was passed through the column at the flow rate of 0.5 ml min^{-1}, and it was washed with eight 5 ml portions of 8 M nitric acid. The adsorbed thorium was eluted with ca. 6 M hydrochloric acid (120 ml) at the rate of ca. 1 ml min^{-1}, and collected in a 250 ml beaker. It was concentrated by evaporation, fumed with 0.5 ml $HClO_4$ and 10 ml HNO_3 to remove any traces of organic matter, taken in 5% HCl, and diluted to a fixed volume. Spectrophotometric measurement was carried out as earlier. Results obtained are shown in Table 2.

The presence of, if any, tantalum, niobium, and titanium in the eluted fraction was determined spectrophotometri-

Table 1. Effect of Sulfate and Organic Acid upon the Distribution of Thorium in 8 M Nitric Acid

Solution combination in 8 M HNO_3	K_d	Solution combination in 8 M HNO_3	K_d
8 M Nitric acid alone	330		
1% Citric acid	320	1% $KHSO_4$	285
2% Citric acid	310	2% $KHSO_4$	250
3% Citric acid	300	3% $KHSO_4$	225
4% Citric acid	300	4% $KHSO_4$	190
5% Citric acid	290	5% $KHSO_4$	160
1% Citric acid + 3% $KHSO_4$	210	3% Citric acid + 1% $KHSO_4$	250
2% Citric acid + 3% $KHSO_4$	205	3% Citric acid + 2% $KHSO_4$	230
3% Citric acid + 3% $KHSO_4$	200	3% Citric acid + 3% $KHSO_4$	200
4% Citric acid + 3% $KHSO_4$	200	3% Citric acid + 4% $KHSO_4$	190
5% Citric acid + 3% $KHSO_4$	190	3% Citric acid + 5% $KHSO_4$	150
1% Citric acid + 1% $KHSO_4$	250	1% Tartaric acid + 1% $KHSO_4$	280
2% Citric acid + 2% $KHSO_4$	230	2% Tartaric acid + 2% $KHSO_4$	250
3% Citric acid + 3% $KHSO_4$	200	3% Tartaric acid + 3% $KHSO_4$	210
4% Citric acid + 4% $KHSO_4$	185	4% Tartaric acid + 4% $KHSO_4$	190
5% Citric acid + 5% $KHSO_4$	140	5% Tartaric acid + 5% $KHSO_4$	160
1% Oxalic acid + 1% $KHSO_4$	260	4% Oxalic acid + 4% $KHSO_4$	190
2% Oxalic acid + 2% $KHSO_4$	240	5% Oxalic acid + 5% $KHSO_4$	150
3% Oxalic acid + 3% $KHSO_4$	200		

Table 2. Recovery of Thorium from Synthetic Mixtures of Niobium, Tantalum, and Titanium

Sample number	Synthetic mixtures taken			ThO_2 (μg) added	ThO_2 (μg) recovered
	Nb_2O_5 (mg)	Ta_2O_5 (mg)	TiO_2 (mg)		
1	10	10	25	100	96
				500	490
				1000	1006
2	25	25	50	100	97
				500	495
				1000	980
3	50	25	50	100	95
				500	506
				1000	985
4	50	25	25	100	102
				500	485
				1000	1015
5	25	25	25	100	98
				500	490
				1000	990

cally using malachite green,[17] thiocyanate,[18] and tiron[19] method, respectively.

Separation and Estimation of Thorium in Niobite-Tantalite Samples: Sample (0.500 g) was fused with 7—8 g of previously fused potassium hydrogen sulfate as described above. It was taken in ca. 7% citric acid solution. If any residue left, it was filtered through a Whatman No. 40 filter paper and ignited in a platinum crucible. The residue was fused with a 0.5 g mixture of NaF and KHF_2 (1:3) and heated under low flame with 2 ml of 1:1 H_2SO_4 for the removal of fluoride. It was fumed strongly and taken in original solution, and volume was made upto 100 ml. A suitable aliquot (20 μg to 2 mg Th) was taken in a beaker and cooled in an ice bath, and ice cold concentrated nitric acid was added to a final concentration of ca. 8 M nitric acid. It was passed through the column as mentioned above and thorium was eluted and determined spectrophotometrically as earlier. The results obtained are shown in Table 3.

Results and Discussion

Table 1 shows the K_d values of thorium in 8 M nitric acid in the presence of organic acid, potassium hydrogen sulfate, and the mixture of both. Thorium forms anionic nitrate complex in 5—8 M nitric acid.[11] Distribution studies show a decrease in K_d values in the presence of sulfate, however citric acid upto 5% studied do not have much significant effects upon the K_d values. Increase in concentration of sulfate ion reduces the K_d values probably due to the competition for anionic sites. During the column operation it is observed that even in the presence of 5% (m/v) sulfate quantitative recovery of thorium can be achieved in ca. 8 M nitric acid in the presence of other metal ions. Out of the three organic acids studied, oxalic acid is not selected for column experiment due to its lesser solubility, and also the precipitation chance of thorium oxalate when the thorium content is higher. Among tartaric and citric acids, the hydrolysis tendency in ca. 8 M nitric acid is comparatively more in tartaric acid medium. In citric acid (0.18 M)–nitric acid (8 M) medium under the cold condition the solution remains clear without hydrolysis for at least six hours, which is sufficient to pass the solution through the anion-exchanger column.

Separation of thorium from the synthetic mixtures (Table 2) shows that they are quantitative. Recoveries of thorium in the range of 20 μg to 5 mg studied are also found to be quantitative. Estimation of separated fractions for the presence of niobium, tantalum, and titanium shows that these are less than 10 μg and their

Table 3. Determination of Thorium in Synthetic and Natural Niobite-Tantalite Type Samples by Conventional[a] and Proposed Methods

Sample number	Nature of samples	%Nb_2O_5	%Ta_2O_5	%TiO_2	%MnO	%FeO	%Fe_2O_3	%ThO_2 Conventional method	%ThO_2 Proposed method
1	Tantalite (Synthetic)	10.0	65.0	2.0	5.0	—	18.0	0.190	0.198[b]
2	Niobite (Synthetic)	65.0	10.0	2.0	5.0	—	18.0	0.194	0.203[b]
3	Niobite (Natural)	41.8	36.4	1.3	3.0	11.8	2.5	0.110	0.114
4	Niobite (Natural)	48.4	28.7	1.3	5.3	11.9	1.6	0.164	0.168
5	Tantalite (Natural)	11.8	59.6	2.0	9.5	9.3	3.2	0.061	0.063
6	Tantalite (Natural)	26.0	49.2	1.0	—	—	—	2.30	2.46
7	Tantalite (Natural)	26.6	54.9	1.0	—	—	—	0.060	0.061

a) Sample was fused with Na_2O_2, taken in an excess dilute hydrochloric acid. Boiled to precipitate the hydroxide with aqueous ammonia. Thorium was then subjected to fluoride and iodate precipitation separation and estimated spectrophotometrically with arsenazo III. b) Thorium content taken corresponding to 0.200% ThO_2.

presence did not interfere in the determination of thorium. Elution curve of a column loaded with 200 μg to 500 μg thorium indicates that complete elution takes place within 100 ml of the eluent. By eluting with ca. 6 M hydrochloric acid, co-adsorbed uranium is retained in the column.

The proposed separation method is applied for the separation and photometric estimation of thorium in niobite-tantalite type of samples. Strelow[4] reported the estimation of lead, uranium, and thorium in niobite-tantalite samples, by taking 50 g of sample and treating with HF and HCl. Lead, uranium, and thorium are separated as insoluble fluorides after the reduction of U(VI) with Sn(II). Finally thorium is separated after the multiple anion- and cation-exchange separations.

In the proposed ion-exchange separation method, niobium, tantalum, titanium, zirconium, iron, manganese, rare earth elements, etc., are separated from thorium in a single step without any contamination. Table 3 shows the results obtained for some synthetic and natural niobite-tantalite samples. The result obtained for the synthetic mixtures shows it is accurate and precise and is in good agreement with the tedious and time consuming conventional method. RSD for five independent estimations is 2—3%. This method can also be applied for the estimation of thorium in niobium-tantalum rich minerals like pyrochlore, microlite, euxenite, fergusonite, and samarskite.

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