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Use of Dowex A-1(H) and ZeoKarb 226(H) for the Sequential Separation of Uranium, Thorium, and Rare Earths in Monazite

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NOTE

Use of Dowex A–1(H$^+$) and ZeoKarb 226(H$^+$) for the Sequential Separation of Uranium, Thorium, and Rare Earths in Monazite

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Abstract

When a mixture of rare earths, thorium, and uranium at pH 1.0 in sulfate medium is passed through a column (1.5 × 12 cm) of Dowex A–1(H$^+$), rare earths pass through. Then thorium is eluted with 6 *N* hydrochloric acid and subsequently the uranium with 2 *N* nitric acid. When the mixture at pH 2.0 in nitrate medium and in the presence of 1,10-phenanthroline is fed to a column of ZeoKarb 226(H$^+$), the rare earths pass through. Then thorium is eluted with 0.05 *M* EDTA at pH 4.5 and subsequently the uranium with 2 *N* hydrochloric acid. These separation schemes are successfully applied to the analysis of monazite samples.

A sequential separation of U, Th, and rare earths is reported using a strong anion exchanger (*1*) and a cation one (*2*). This note describes the use of a chelating exchanger, Dowex A–1(H$^+$), and a carboxylic acid exchanger, ZeoKarb 226(H$^+$), in monazite.

DOWEX A-1

The distribution data in the case of rare earths, thorium, and uranium, reported earlier (*3*), were obtained with nitrate as the anion. To determine the influence of chloride and sulfate, and also that of the kinetics of exchange in column operation, these metal ions were taken in 25 ml at pH 1.0, adjusted with different acids, passed through a column of the exchanger (1.5 × 12 cm) at a flow rate of 1 ml/min, washed with 75 ml of water at pH 1.0 (adjusted with the corresponding acids), and the metal ions in the total effluent determined by conventional methods. Rare earths passed through quantitatively in all the three media, while thorium and uranium were quantitatively retained in chloride and sulfate media only. On continuing washing further, uranium started leaking in chloride but not in sulfate medium. Thorium did not leak in either medium. Only 85% of the rare earths are eluted in 200 ml at pH 2.0 in sulfate medium.

When 2.0 *N* hydrochloric acid was passed through the column, both the elements are quantitatively eluted within 100 ml. Retention of uranium as anionic chlorocomplex is good only with 6.0 *N* acid. Channelling in the column was observed at 8.0 *N* acidity.

Based on the above information, synthetic mixtures and monazite samples were analyzed following the procedure given below. The results are given in Table 1.

Procedure

0.500 g of monazite sample is brought into solution and the phosphate removed employing an alumina column (1.5 × 22.5 cm) (*1*). The pH of the solution (sulfate medium) is adjusted to 1.0 in about 60 ml. This is passed through a column (1.5 × 12 cm) of Dowex A-1(H^+) at a flow rate of 1 ml/min, followed by 100 ml of 0.1 *N* sulfuric acid. The rare earths in the total effluent are determined gravimetrically (*4a*). Thorium is then eluted with 75 ml of 6.0 *N* hydrochloric acid and determined gravimetrically (*4b*). Finally uranium is eluted with 50 ml of 2.0 *N* nitric acid and determined spectrophotometrically with hydrogen peroxide (*4c*).

ZEOKARB 226(H^+)

From the distribution data reported earlier (*5*), thorium and uranium should be held by ZeoKarb 226(H^+) at pH 2.0, while rare earths should not. However, when a solution of rare earths nitrate at pH 2.0 was passed

TABLE 1

Determination of Uranium, Thorium, and Rare Earths

	Amount taken/expected			Amount obtained					
				Dowex A-1			ZeoKarb 226		
Sample	U_3O_8	ThO_2	(Rare earths)$_2$O$_3$[a]	U_3O_8	ThO_2	RE_2O_3	U_3O_8	ThO_2	RE_2O_3
			Milligrams						
Synthetic 1	2.5	37.0	128.0	—	—	—	2.5	37	127
	—	—	—	—	—	—	2.5	37	126
Synthetic 2	10.0	133.0	169.0	9.8	134	171	—	—	—
	—	—	—	10.2	136	167	—	—	—
			Percent						
Indian monazite	0.41	8.7	59.8	0.48	8.5	59.4	0.42	8.9	59.2
				0.48	8.4	59.7	0.41	8.6	58.8
				0.41	8.6	58.7	0.43	8.8	59.0
				0.39	8.5	60.1	0.41	8.7	60.0
				0.42	8.6	60.0	0.40	8.7	59.8
Malaysian monazite	0.33	7.9	60.5	0.39	8.1	60.1	0.38	8.3	59.6
				0.35	8.3	60.1	0.32	7.9	60.7
				0.35	7.8	60.1	0.35	7.7	60.4
				0.33	7.6	60.6	0.33	8.0	60.0
				0.30	7.7	59.6	0.34	7.8	60.0

[a] (Rare earths)$_2$O$_3$ includes higher oxides of Ce and Pr.

through a column of the exchanger, followed by acidified water at the same pH, it was observed that about 5% of rare earths were held by the exchanger rather tenaciously. Since the K_d values of thorium and uranium are also sufficiently high in the presence of phenanthroline, the above experiment was repeated in the presence of phenanthroline. Under these conditions the rare earths pass through the exchanger quantitatively. Under similar conditions, both thorium and uranium were held quantitatively by the exchanger.

Similar experiments were carried in chloride and sulfate media at the same pH. In the case of rare earths, phenanthroline is also added. Uranium and thorium were held by the exchanger in chloride medium, while they leaked through the column in sulfate medium. Rare earths in both the media passed through quantitatively.

Thorium has a higher K_d (1720) than uranium (230), while it is the reverse in presence of phenanthroline (340 and 2770, respectively) at pH 2.0. Hence EDTA was chosen as a selective eluent for thorium. After loading thorium and uranium at pH 2.0, 0.05 *M* EDTA at pH 4.5 was passed through, with the effluent collected in 25 ml fractions. Thorium was eluted quantitatively within two fractions. Uranium was not detected even in the sixth fraction. Then uranium was eluted with 25 ml of 2.0 *N* hydrochloric acid.

Based on the above information, synthetic mixtures and monazite samples were analyzed following the procedure given below. The results are included in Table 1.

Procedure

0.500 g of monazite sample is brought into solution and the phosphate removed as described earlier (*1*) but for the conversion of nitrates to sulfates. pH is adjusted to 2.0 (nitrate medium) in a volume of 400 ml containing 400 mg of phenanthroline. The solution is passed through a column of ZeoKarb 226(H^+) (1.5 × 5 cm) which is preconditioned with phenanthroline solution at pH 2.0 at a flow rate of 1 ml/min. The column is washed with 100 ml of wash solution (1 mg/ml phenanthroline at pH 2.0). The combined effluent is boiled down to 100 ml and the rare earths determined by the oxalate method (*4a*). Thorium is selectively eluted from the column with 50 ml of 0.05 *M* EDTA at pH 4.5 and determined by precipitation with sodium hydroxide and ignition to oxide, after washing with 100 ml of 1% ammonium nitrate. Finally uranium is eluted with 25 ml of 2.0 *N* hydrochloric acid and determined spectrophotometrically with hydrogen peroxide (*4c*).

DISCUSSION

The present studies reveal the significant influence of the anions, chloride, nitrate, and sulfate on the sorption of thorium and uranium by the two exchangers. Retention of uranium from water in the presence of EDTA (*6*) is reported by the iminodiacetic acid exchanger but not from seawater (*7*), probably because of the presence of carbonate or other complexing materials in seawater.

Though distribution data (*5*) do not indicate any sorption of rare earths by ZeoKarb 226(H^+), about 5% of rare earths taken are retained rather tenaciously on the column, in spite of washing. A similar sorption was observed earlier in the case of calcium also (*8*), which was eliminated by mixing calcium with either aluminum or lanthanum solutions. Since the rare earths are eluted quantitatively in the presence of phenanthroline in the present studies, experiments were also carried out with calcium in the presence of phenanthroline (*9*) with a similar quantitative elution. Though it is rather difficult to explain the role of phenanthroline in the quantitative elution of Ca and rare earths, the phenomenon may be compared very qualitatively to surface modified (gas) chromatography (*10*) used to reduce tailing of components.

Uranium is separated from many cations by employing carboxylic acid exchangers, taking advantage of the large differences in the stability constants of metal ions with EDTA (*11–13*). It may be mentioned, however, that such separations will generally be easier on strong cation exchangers. But in the case of separation of thorium from uranium on ZeoKarb 226(H^+), the addition of phenanthroline has decreased the K_d of thorium and enchanced that of uranium(VI), favouring the use of EDTA.

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