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NOTE

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Abstract

The anion exchange behavior of a negatively charged complex of thorium is studied on Dowex-21 K. Various eluants were tried. Hydrochloric, sulfuric, and nitric acid, as well as chlorides, nitrates, and acetates of sodium and ammonium, were tested as eluants. The efficiency of various eluants was determined. Novel methods were developed for the separation of thorium from a large number of elements by the processes of selective sorption, selective elution, and gradient elution. The method was found to be applicable for the separation of thorium from fission product elements.

The separation of thorium from various elements associated with it in fission products has been carried out by anion exchange chromatography in mineral acid media (*1*), but information on anion exchange separation in organic acid media is unknown.

An attempt was made to separate it from uranium, etc. in acetic acid media (*1*), but the method suffered from the disadvantage that phosphate showed strong interference and uranium was separable in only small amounts. It was separated in ascorbate media (*2*, *3*) on Amberlite-IRA-400 or Dowex-1 resin from a large number of elements, but the separation of uranium and thorium was not possible without resort to cation exchange chromatography. The method was further modified (*4*) by using a methanol nitric acid mixture. The separation of uranium, zirconium, thorium,

etc. was carried out in oxalate media (5). Thorium, which was strongly adsorbed, was finally eluted with 4 *M* hydrochloric acid. The adsorption behavior of uranium was carried out in such di- and tricarboxylic acids (6) as malonic, succinic, glutaric, adipic, tartaric, and citric. However, systematic studies of thorium on the anion exchange behavior in organic acid media have been lacking.

This paper presents such studies. Thorium forms an anionic complex with 5% malonic acid at pH 4.3, which can be explored for its separation on Dowex-21 K (1.4 × 18 cm). The proposed method is simple, rapid, and reproducible.

EXPERIMENTAL

Apparatus and Reagents

The ion exchange column (1.4 × 18 cm) was similar to the one described earlier (7) with an automatic fraction collector fitted with a 10-ml siphon. A Cambridge pH meter with a glass electrode and calomel as the reference electrode were used.

A stock solution of thorium was prepared by dissolving 3.20 g of thorium nitrate tetrahydrate (B.D.H., AnalaR) in 250 ml of distilled water containing 1% of concentrated nitric acid. The solution was standardized volumetrically (8) with EDTA using Alizarin-S as the indicator. It was found to contain 4.848 mg/ml of thorium.

Dowex-21 K (Dow Chemical Co., Midland, Michigan) 50 to 100 mesh, Cl form, was used throughout the experiment. For ion exchange runs the resin was converted into the malonate form as described earlier (7).

RESULTS AND DISCUSSION

An aliquot of the solution (2.0 ml) containing ~9.70 mg of thorium was taken. About 0.5 to 1 g of malonic acid was added. The pH of the solution was adjusted to 4.3 with 0.01 *M* malonic acid solution and 0.01 *M* ammonium hydroxide. Then the solution was sorbed on the anion exchange column at a flow rate of 0.5 ml/min. After washing the column with 50 ml of water at a flow rate of 2 ml/min, thorium was eluted with various eluants (Table 1). The effluent was collected in 20 fraction, each of 10 ml. After destroying the organic matter with a mixture of nitric and perchloric acid, thorium from each fraction was determined complexometrically (8) using Alizarin-S as the indicator.

TABLE 1

Anion Exchange Studies of Th(IV) in Malonate Media[a]

No.	Eluant	Conc of eluant (M)	Elution commencing volume V_s (ml)	Peak elution volume V_{max} (ml)	Total elution volume V_t (ml)	Total recovery of Th (%)	Elution constant E	Volume distribution coeff D_v
1	HCl	0.50	20	30	80	90	2.198	0.455
		1.0	20	30	80	100	2.198	0.455
		2.0	20	30	80	100	2.198	0.455
2	HNO_3	0.25	30	40	80	100	1.226	0.815
		0.50	30	30	80	100	2.198	0.455
		0.75	30	40	90	86	1.226	0.815
		1.0	30	40	90	77	1.226	0.815
3	H_2SO_4	0.25	20	40	90	99.5	1.226	0.815
		0.50	20	30	70	95.5	2.198	0.455
		0.75	20	30	50	64	2.198	0.455
4	NH_4Cl	0.5	70	70	140	60	0.526	1.90
		1.0	40	70	100	56	0.526	1.90
		2.0	20	30	100	66	2.198	0.455
5	NH_4NO_3	1.0	30	40	90	88.4	1.226	0.815
		3.0	20	30	90	75	2.198	0.456
6	$NaNO_3$	1.0	30	40	90	50	—	—
7	NaCl	3.0	—	—	—	—	—	—
8	CH_3COONH_4	1.0	50	80	150	50	—	—
9	Malonic acid	5%	20	50	90	73	0.849	1.177

[a]Th, 9.696 mg; wt of resin, 9.0 g.

Various mineral acids and their salts in the concentration range of 0.25 to 3.0 M were tested as the eluants. The elution curves with mineral acid are shown in Fig. 1. The elution constant (E) and the volume distribution coefficient (D_v) were computed from peak elution volume (V_{max}) as usual (9). On the basis of these results, the eluants can be arranged in the order of increasing efficiency: $HNO_3 > H_2SO_4 > HCl$. Other eluants, such as chlorides and nitrates of ammonium and sodium, malonic acid, and ammonium acetate, proved to be inefficient eluants for thorium.

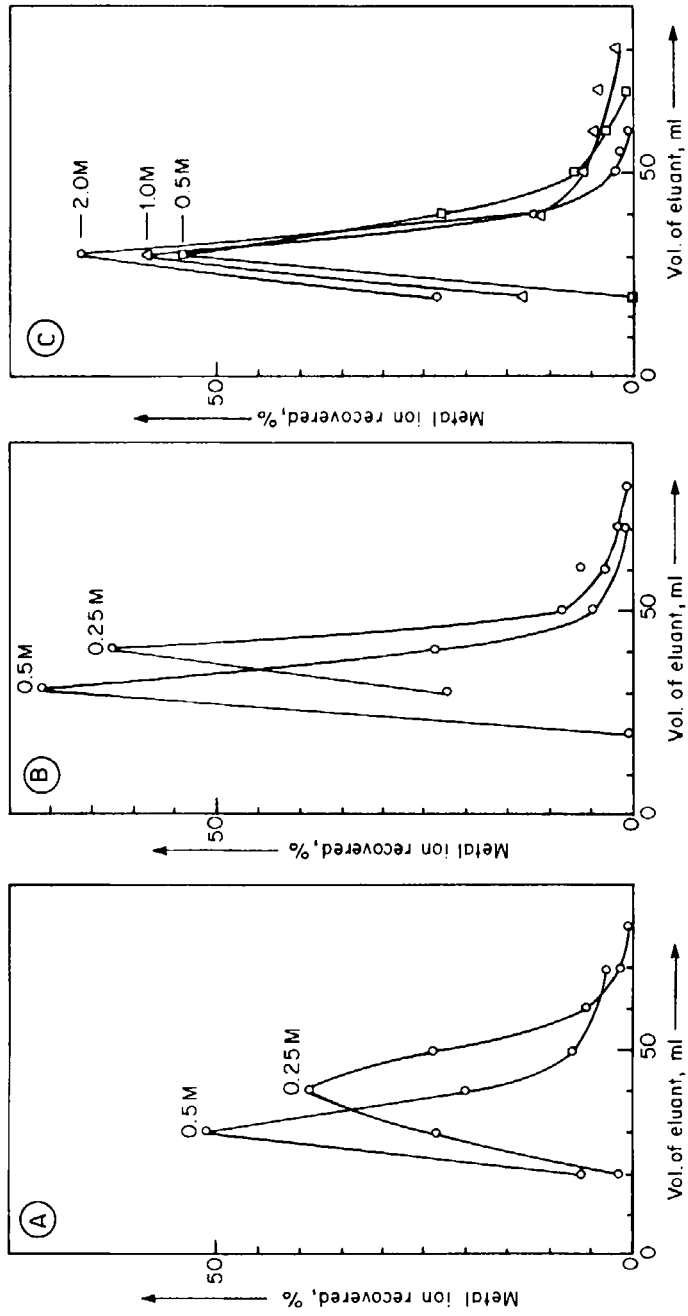

FIG. 1. Elution behavior of Th(IV) in malonate media with (A) sulfuric acid, (B) nitric acid, and (C) hydrochloric acid.

Ion Exchange Separations

Since S-block elements are incapable of forming negatively charged complexes with malonic acid, they could be separated by selective sorption from thorium. Second, some elements form weak complexes with malonic acid as compared to thorium, hence they were eluted with water followed by elution of thorium with 1.0 *M* hydrochloric acid. Finally, in cases where both the elements formed complexes with malonic acid, separation was accomplished by selective elution (Table 2). These separations were devised on the basis of knowledge of the separation factors (α) as given in Table 3. It was observed that the separations were not feasible for separation factor either too large or too small.

TABLE 2

Ion Exchange Separation of Th(IV) in Malonate Media[a]

		Thorium	
Foreign ion	Amount added (mg)	Found (mg)	Recovery (%)
Li	50	4.84	100
Rb	100	4.84	100
Cs	100	4.84	100
Be	100	4.84	100
Mg	100	4.84	100
Ca	100	4.768	98.6
Sr	100	4.84	100
Ba	100	4.74	97.85
Tl(I)	100	4.84	100
Ce(IV)	25	4.84	100
Mn(II)	50	4.826	99.8
Co(II)	50	4.84	100
Ni	50	4.797	99.2
Pd(II)	50	4.84	100
Zn	50	4.84	100
Cd	50	4.773	98.7
Cu(II)	20	4.84	100
Fe(III)	20.2	4.84	100
Sb(III)	19.5	4.84	100
Al	20	4.740	98
Zr(IV)	20.5	4.778	98.8
V(IV)	19.8	4.797	99.2
Pb(II)	20	4.84	100
ScO_3^{2-}	6.3	4.84	100
ReO_4^-	6.0	4.84	100

[a]Th – 4.84 mg.

TABLE 3

Separation Factor for Thorium to Other Ions in Malonate Media

Metal ion	Eluant (M)	V_{max} (ml) (Th)	V_{max} (ml) (M)	E_{Th}	E_M	Separation factor (α), E_{Th}/E_M
Pb(II)	0.25 HNO_3	40	>200	1.226	<0.1	>10
	6.0 HNO_3	30	130	2.198	0.38	5.784
Zr(IV)	0.25 H_2SO_4	40	150	1.226	0.184	6.642
	1.0 H_2SO_4	30	100	2.198	0.33	6.661
V(IV)	0.25 H_2SO_4	40	110	1.226	0.31	3.955
	0.25 H_2SO_4	40	110	1.226	0.31	3.955
Fe(III)	2.0 NaCl	>200	50	<0.1	0.85	<0.2
	1.0 HCl	30	60	2.198	0.65	3.382
Cu(II)	2.0 NaCl	>200	40	<0.1	1.226	<0.1
	1.0 HCl	30	40	2.198	1.226	1.801
Al(III)	0.25 NH_4Cl	90	50	0.307	0.85	0.360
	1.0 HCl	30	50	2.198	0.85	2.586

Separation from Alkali and Alkaline Earths, Thallium(I), and Cerium(IV)

A solution containing thorium and the foreign ion was made, and after formation of the anionic malonate complex of thorium the mixture was sorbed on the column at a flow rate of 0.5 ml/min. The ions which were incapable of forming an anionic complex passed through the column, whereas the malonate complex of thorium was quantitatively retained by the resin. It was subsequently eluted with 200 ml of 1.0 M hydrochloric acid.

Separation from Manganese(II), Cobalt(II), Nickel, Palladium(II), Zinc, and Cadmium

It was observed that these metals formed weak complexes with malonic acid but that thorium formed a relatively strong complex. After sorbing the mixture of these complexes the weakly bound complexes were desorbed by 400 ml of water followed by elution of thorium with 1.0 M hydrochloric acid.

Separation from Copper(II), Iron(III), Antimony(III), and Aluminum

These metals formed weak malonate complex. Therefore they were first eluted with a suitable eluant. Thorium was eluted with a stronger eluant. The separation of copper and iron from thorium was achieved by first eluting copper or iron with 100 ml of 2 *M* sodium chloride followed by the elution of thorium with 1.0 *M* hydrochloric acid (*7*, *9*). Antimony and aluminum were similarly separated from thorium by first eluting antimony with 100 ml of 0.1 *M* ammonium chloride or aluminum with 0.25 *M* ammonium chloride followed by elution of thorium with 1.0 *M* hydrochloric acid.

Separation from Zirconium(IV), Vanadium(IV), and Lead(II)

These metals form strong complexes as compared to that of thorium, hence thorium was first eluted with 0.25 *M* sulfuric acid followed by gradient elution of vanadium or zirconium with 0.25 or 1 *M* sulfuric acid, respectively (Fig. 2). The mixture of the malonate complexes of these ions with that of thorium was sorbed on the column. After elution of thorium with 90 ml of 0.25 *M* sulfuric acid (or nitric acid for lead), zirconium was eluted with 1.0 *M* sulfuric acid, vanadium with 0.25 *M* sulfuric acid, and lead with 6 *M* nitric acid.

Separation from Selenite and Rhenate

A mixture of anionic malonate complexes of thorium with oxyanions such as selenite and rhenate was sorbed on the column. Selenite was eluted with 100 ml of 2 *M* sodium chloride, while rhenate was eluted with 100 ml of 1 *M* potassium chloride solution followed by elution of thorium with 1.0 *M* hydrochloric acid.

An attempt to separate thorium from uranium, indium, and phosphate was unsuccessful. However, it is possible to separate thorium from uranium by cation exchange chromatography (*10*). The method was extended for the separation of thorium from fission product elements.

Separation of Thorium from Fission Product Elements

A synthetic mixture containing rubidium, caesium, strontium, barium, cadmium, palladium, zinc, antimony, and certium was made. After the

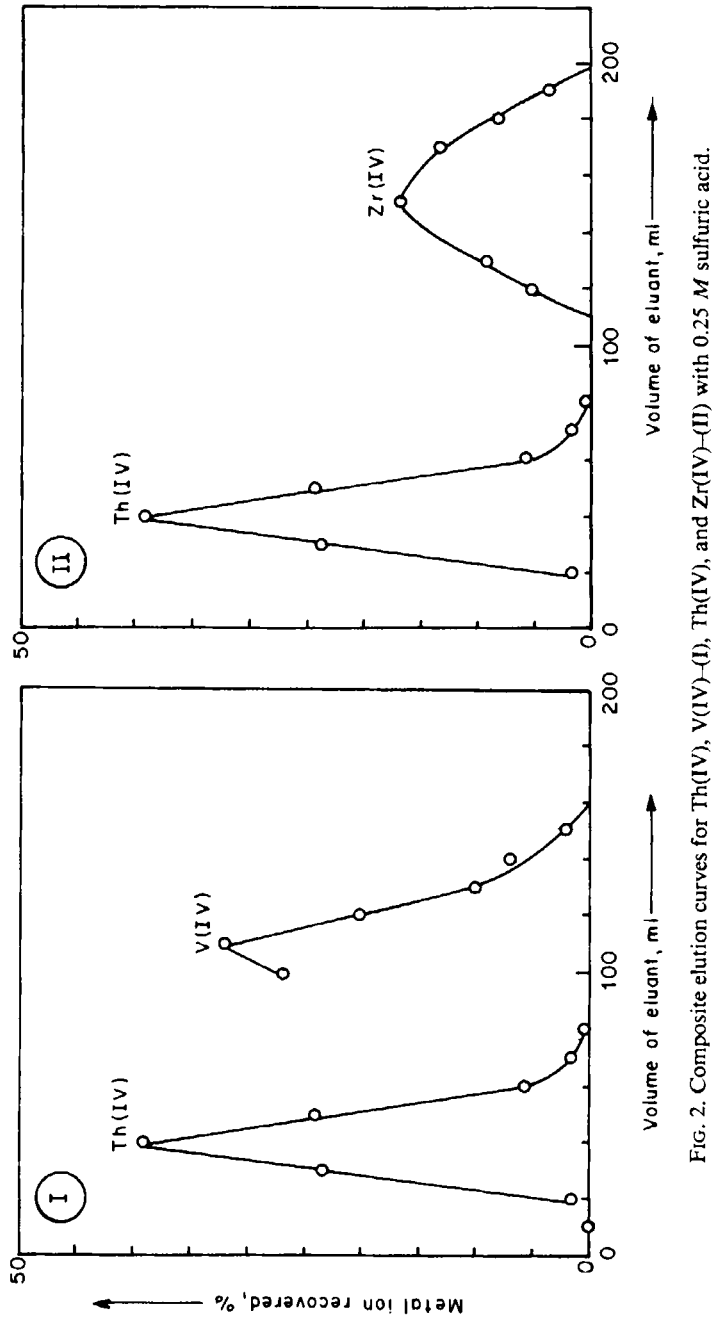

FIG. 2. Composite elution curves for Th(IV), V(IV)–(I), Th(IV), and Zr(IV)–(II) with 0.25 *M* sulfuric acid.

formation of a malonate complex, it was sorbed on the column at a flow rate of 0.5 ml/min. Such elements as barium, strontium, caesium, rubidium, and cerium, which do not form malonate complexes, were not retained by the resin but were separated by selective sorption. Then the column was washed with water to remove weakly bound elements such as antimony, lead, cadmium, and zinc. Thorium was then eluted with 0.25 *M* sulfuric acid followed by elution of zirconium with 1.0 *M* sulfuric acid.

The method is simple, sensitive, and needs less than 2 hr for the complete separation and determination of thorium. The average recovery of thorium was 98.5 $\pm 1.5\%$, with a relative standard deviation of $\pm 1\%$ for 10 runs. The significant feature of this method is that it is possible to separate thorium at milligram concentrations from a large number of elements with which it is associated in minerals and fission product.

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