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MASTER

ANION EXCHANGE SEPARATION OF THORIUM USING NITRIC ACID*

James S. Fritz and Barbara B. Garralda

Institute for Atomic Research and Department of Chemistry

Iowa State University, Ames, Iowa

Abstract-Thorium is quantitatively retained by an anion exchange column from aqueous 6M nitric acid solution. Most other metal ions are completely eluted from the column with 75 to 100 ml. of 6M nitric acid. Following the separation, thorium is stripped from the column with 0.5M nitric acid and titrated with EDTA

Ion exchange separations of thorium from other metal ions have been carried out using an anion exchange column with HCl eluent (9, 10, 14, 17), anion exchange with H_2SO_4 eluent (7, 11, 12), and ion exchange using organic complexing agents (5, 18). Strelow developed a very selective method for thorium in which other metal ions were eluted from a cation exchange column with 3 to 4M hydrochloric acid leaving thorium on the column (15). Following the separation, it is extremely difficult to remove thorium from the column. Strelow resorted to ashing the resin and weighing the thorium oxide residue.

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Several authors have separated thorium using an anion exchange column and nitric acid. Some of the most comprehensive work is by Korkisch and Tera (8, 16). These authors separated thorium on an anion exchange column in the nitrate form from a solution consisting of 90% methanol and 10% of aqueous 5M nitric acid. They separated thorium from a long list of other elements but reported that barium, lead, bismuth, lanthanum, and rare earths are also taken up by the column. Danon (2, 3) reported distribution coefficients for thorium and certain rare earths using an anion exchange resin at various concentrations of nitric acid. Using a column, he was able to separate quantitatively thorium from lanthanum, neodymium, samarium, europium, and yttrium using 5 to 8M nitric acid. Carswell (1) successfully separated thorium and uranium using an anion exchange resin and aqueous 4M nitric acid as the eluting agent. This separation was carried out at 77°C. Ichikawa (6) reported distribution coefficients of various elements between nitric acid and anion exchange resin. Distribution coefficients reported by Nelson and Kraus (13) showed that thorium, bismuth, and lead are taken up by anion exchange resins from strong aqueous solutions of nitric acid.

The purpose of this paper is to study in a more comprehensive manner the analytical separation and determination of thorium using nitric acid eluent with anion exchange columns. Although the method of Korkisch and Tera is excellent for the separation of thorium from some elements, we found that the method does not work well for mixtures containing macro amounts of thorium and rare earths. Using aqueous 6<u>M</u> nitric acid, we obtained excellent separation of thorium from aluminum, rare earths, iron, zirconium, and other elements.

EXPERIMENTAL

<u>Ion Exchange Columns</u>. Conventional glass columns of 12-mm. i.d. are used. The column is filled with a slurry of resin, in nitric acid of the concentration to be used as the eluent, to a bed height of 16 cm. The eluent is added to the column dropwise from a cylindrical separatory funnel fitted into the column through a one-hole stopper at a flow rate of about 2 ml. per minute.

<u>Ion Exchange Resin</u>. Dowex 1 x 8, 100- to 200-mesh, anion resin in the nitrate form is used. The analyzed reagent grade resin is in the chloride form and must be converted to the nitrate form before use. This is done by placing the resin in a large column and backwashing to remove fine particles. The resin is then washed with 5<u>M</u> nitric acid until the effluent gives a negative chloride test with silver nitrate. The excess nitric acid is rinsed off with distilled water, the water is removed by suction filtration, and the resin is air dried.

<u>Metal Salts</u>. 0.05<u>M</u> solutions of the salts were made using reagent grade nitrate salts of the metals and nitric acid of the concentration to be used as the eluent.

PROCEDURE

Distribution Coefficients. Air-dried anion exchange resin is weighed into a 125-ml. glass-stoppered Erlenmeyer flask. The desired amount of metal ion in nitric acid solution is pipeted into the flask, and nitric acid of the desired concentration is added to bring the total solution volume to 50 ml. The flask is stoppered and shaken for 24 hours. An aliquot is pipeted from the flask and the metal ion content is determined with EDTA titration. The water content of the air-dried resin is determined by oven drying a sample of known weight. The distribution coefficient is then determined on a dry resin basis. The relationship used is:

$$K_d = \frac{\text{mmoles of metal ion on resin/grams dry resin}}{\text{mmoles of metal ion in solution/total volume of solution}}.$$

Column Elutions. For experiments with single metal ions, the column is loaded with 0.25 mmole of metal ion in a solution containing nitric acid of the concentration to be used for elution. The volume of sample solution is indicated in Table I. Nitric acid concentrations greater than about 7M cause decomposition of the resin. The effluent from the sample solution is collected and tested qualitatively for the metal ion present in the sample. The column is then eluted with aqueous nitric acid; 10-ml. fractions are collected and tested qualitatively for the metal ion. The breakthrough volume and the volume required for complete elution are recorded.

For quantitative separation of mixtures containing thorium, a sample containing 0.25 mmole of thorium plus 0.25 mmole of another metal ion is diluted to 15 ml. and the nitric acid concentration is adjusted to 6M. The sample solution is added to a 1.2 x 16 cm. Dowex 1 x 8 column (100- to 200-mesh) which has previously been washed with 6M nitric acid. The other metal ion is then eluted from the column with 75 to 100 ml. of 6M nitric acid at a flow rate of approximately 2 ml. per minute. The effluent is evaporated nearly to dryness, then is diluted, neutralized, and titrated as outlined in Table II. Thorium is stripped from the column by elution with 150 ml. of 0.5M nitric acid at a flow rate of approximately 2 ml. per minute.

The pH of the thorium effluent is adjusted to 2.0 to 3.0 with solid sodium acetate, and the thorium is titrated with 0.05M EDTA using Xylenol Orange indicator.

RESULTS AND DISCUSSION

Preliminary work with methanol-aqueous nitric acid eluents (7) indicated that aqueous nitric acid is preferable for separations of thorium from other metal ions. The nonaqueous nitric acid separations required larger volumes of eluent for quantitative elution, and a slower flow rate had to be employed. Furthermore, 6M aqueous nitric acid solutions caused less deterioration of the resin than methanol-water solutions that were more dilute in nitric acid.

Data for elution of individual metal ions are given in Table I. These elutions are for a 1.2 x 16 cm. anion exchange column (nitrate form) with several different concentrations of nitric acid. The effluent was collected in 10-ml. fractions and each fraction tested for the presence of the metal ion. Most metal ions are completely eluted by 100 ml. of 6M nitric acid. Profile curves for the elutions indicate that there is little tailing of the bands. Since the thorium ion does not breakthrough until more than 300 ml. of effluent have been collected, separation of thorium from most metal ions should be feasible. Cerium(IV), molybdenum(VI), antimony(III), and tungsten(VI) are likely interferences.

Quantitative data for actual separation of mixtures are reported in Table III. Elution of the first metal ion requires 75 to 100 ml. of 6M nitric acid, thus giving a large safety margin before breakthrough of thorium. Although more of the mixtures analyzed contained thorium and another metal ion in approximately equal molar amounts, several samples were analyzed successfully in which thorium was either the major or minor constituent. It thus appears that sample mixtures of widely varying ratios can be separated providing the column is not overloaded.

Although bismuth and lead are quantitatively eluted with 6M nitric acid, bismuth (and to a lesser extent lead) is retained by the column from 2M nitric acid solutions. Elution with 2M nitric acid is a practical method for separating bismuth from other metal ions including lead.

In Fig. 1, the distribution coefficients of several metal ions are plotted as a function of loading using 6M nitric acid. The distribution coefficients show large variations with loading for thorium, but only minor changes for yttrium and lead. In column separations with 10-ml. samples containing 0.25 mmole of thorium plus 0.25 mmole of another metal ion, it was found that breakthrough of the thorium was premature. By increasing the sample volume to 15 ml., this difficulty was avoided. If samples are used which contain more than 0.25 mmole of thorium, the volume of loading solution should be increased accordingly. However, excessive dilution of the sample solution causes tailing of some elements separated from thorium and requires more eluent for their complete elution.

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Table I. Elution of 0.25 mmole of Individual Ions from 1.2 x 16 Cm.

Anion Exchange Columns with HNO_3

Ion	Nitric Acid Conc.	Volume of Sample Solution, Ml.	Breakthrough, Ml.[a]	Elution Complete, Ml.[b]
Al^{+3}	2.0M	100	0	200
	6.0M	10	0	75
	6.0M	100	0	150
Ba^{+2}	2.0M	10	0	20
	6.0M	10	0	30
	6.0M	100	0	150
Bi^{+3}	2.0M	10	100	> 200
	6.0M	10	40	210
Ca^{+2}	2.0M	100	0	50
	6.0M	10	0	25
Cd^{+2}	6.0M	10	0	50
Ce^{+4}	6.0M	10	150	> 200
Co^{+2}	6.0M	10	0	50
Cr^{+4}	6.0M	10	0	50
Cu^{+2}	2.0M	100	0	100
	6.0M	10	0	20
Dy^{+3}	6.0M	10	0	100
Er^{+3}	2.0M	10	0	15
	6.0M	10	0	20
Fe^{+3}	2.0M	100	0	100
	6.0M	10	0	15
Ga^{+3}	6.0M	10	0	25
In^{+3}	6.0M	10	0	50

Table I. (cont.)

Ion	Nitric Acid Conc.	Volume of Sample Solution, Ml.	Breakthrough, Ml.[a]	Elution Complete, Ml.[b]
La^{+3}	6.0M	10	0	25
Lu^{+3}	6.0M	10	0	50
Mg^{+2}	6.0M	10	0	50
Mn^{+2}	6.0M	10	0	50
Mo^{+6}	6.0M	10	150	> 200
Nd^{+3}	6.0M	10	0	75
Ni^{+2}	6.0M	10	0	50
Pb^{+2}	2.0M	10	20	50
	6.0M	10	15	50
Sb^{+3}	6.0M	10	PPT on the column	
Sm^{+3}	6.0M	10	0	50
Sr^{+2}	2.0M	100	0	100
	6.0M	10	0	20
Th^{+4}	2.0M	100	0	300
	4.0M	100	125	> 250
	5.0M	100	375	> 450
	6.0M	10	> 300	---
UO_2^{+2}	6.0M	10	50	100
V^{+4}	6.0M	10	0	50
W^{+6}	6.0M	10	PPT on the column	
Y^{+3}	6.0M	10	0	100

Table I. (cont.)

Ion	Nitric Acid Conc.	Volume of Sample Solution, Ml.	Breakthrough, Ml.[a]	Elution Complete, Ml.[b]
Yb^{+3}	2.0M	100	0	50
	6.0M	10	0	50
Zn^{+2}	6.0M	10	0	25
Zr^{+4}	6.0M	10	0	50

[a] 0 means that breakthrough occurred in effluent from sample solution.

[b] Value given is the eluent required in addition to the sample solution.

Table II. Analytical EDTA Titration Methods

Direct-NAS (4)	B(Cu)-NAS (4)	Other
Pyridine-pH 6	Pyridine-pH 5.5	Eriochrome Black T-Direct-NH_3-10: Ca^{+2}, Mg^{+2}, Mn^{+2}
Cd^{+2}, Ce^{+4}, Co^{+2},	Al^{+3}, Fe^{+3}, Ga^{+3},	Metalphthalein-Direct-NH_3-10: Ba^{+2}, Sr^{+2}
Cu^{+2}, Dy^{+3}, Er^{+3},	In^{+3}, Mo^{+6}	Xylenol Orange-Direct-AC^- - 1 to 3: Bi^{+3}, Th^{+4}, La^{+3}
Lu^{+3}, Nd^{+3}, Ni^{+2},		Xylenol Orange-Back: Cr^{+4}-B(Th)-4.5, Zr^{+4}-B(Bi^{+3})-3
Pb^{+2}, Sm^{+3}, V^{+4},		Redox: UO_2^{+2}
Y^{+3}, Yb^{+3}, Zn^{+2}		Qual. only: Sb^{+3}-Pyrocathechol Violet, W^{+6}-$SnCl_2$

Table III. Quantitative Separations on 1.2 x 16 Cm. Anion Exchange Columns

Ion Pairs	Load in mmoles	Loading Solution	Eluent	EDTA Titrations Theory, Ml.	Actual, Ml.	Diff, Ml.
Al^{+3}	0.25	15 ml. $6.0\underline{M}$ HNO_3	Loading + 75 ml. $6.0\underline{M}$ HNO_3	5.13	5.14	+0.01
Th^{+4}	0.25		150 ml. $0.5\underline{M}$ HNO_3	4.87	4.87	0.00
Ba^{+2}	0.25	10 ml. $2.0\underline{M}$ HNO_3	Loading + 30 ml. $2.0\underline{M}$ HNO_3	4.92	4.93	+0.01
Bi^{+3}	0.25		150 ml. $6.0\underline{M}$ HNO_3	4.92	4.92	±0.00
Bi^{+3}	0.25	15 ml. $6.0\underline{M}$ HNO_3	Loading + 200 ml. $6.0\underline{M}$ HNO_3	5.04	5.06	+0.02
Th^{+4}	0.25		200 ml. $0.5\underline{M}$ HNO_3	5.10	5.10	0.00
Ca^{+2}	0.25	15 ml. $6.0\underline{M}$ HNO_3	Loading + 75 ml. $6.0\underline{M}$ HNO_3	5.02	5.02	±0.00
Th^{+4}	0.25		150 ml. $0.5\underline{M}$ HNO_3	5.01	5.02	+0.01
Cd^{+2}	0.25	15 ml. $6.0\underline{M}$ HNO_3	Loading + 75 ml. $6.0\underline{M}$ HNO_3	5.10	5.10	±0.00
Th^{+4}	0.25		150 ml. $0.5\underline{M}$ HNO_3	5.01	5.01	±0.00
Co^{+2}	0.25	15 ml. $6.0\underline{M}$ HNO_3	Loading + 75 ml. $6.0\underline{M}$ HNO_3	5.05	5.04	-0.01
Th^{+4}	0.25		150 ml. $0.5\underline{M}$ HNO_3	5.01	5.02	+0.01
Cu^{+2}	0.25	15 ml. $6.0\underline{M}$ HNO_3	Loading + 100 ml. $6.0\underline{M}$ HNO_3	6.28	6.28	±0.00
Th^{+4}	0.25		200 ml. $0.5\underline{M}$ HNO_3	4.87	4.88	+0.01
Er^{+3}	0.25	10 ml. $2.0\underline{M}$ HNO_3	Loading + 15 ml. $2.0\underline{M}$ HNO_3	4.38	4.39	+0.01
Pb^{+2}	0.25		150 ml. $6.0\underline{M}$ HNO_3	5.01	5.01	±0.00
Er^{+3}	0.25	15 ml. $6.0\underline{M}$ HNO_3	Loading + 75 ml. $6.0\underline{M}$ HNO_3	4.38	4.39	+0.01
Th^{+4}	0.25		200 ml. $0.5\underline{M}$ HNO_3	5.01	5.02	+0.01

Table III. (cont.)

Ion Pairs	Load in mmoles	Loading Solution	Eluent	EDTA Titrations		
				Theory, Ml.	Actual, Ml.	Diff, Ml.
Fe^{+3}	0.25	15 ml. 6.0M HNO_3	Loading + 75 ml. 6.0M HNO_3	5.06	5.05	-0.01
Th^{+4}	0.25		200 ml. 0.5M HNO_3	4.87	4.86	-0.01
Ga^{+3}	0.25	15 ml. 6.0M HNO_3	Loading + 75 ml. 6.0M HNO_3	5.01	5.02	+0.01
Th^{+4}	0.25		150 ml. 0.5M HNO_3	5.01	5.01	±0.00
La^{+3}	0.25	15 ml. 6.0M HNO_3	Loading + 75 ml. 6.0M HNO_3	4.96	4.98	+0.02
Th^{+4}	0.25		150 ml. 0.5M HNO_3	5.01	5.02	+0.01
Lu^{+3}	0.25	15 ml. 6.0M HNO_3	Loading + 75 ml. 6.0M HNO_3	4.98	4.97	-0.01
Th^{+4}	0.25		150 ml. 0.5M HNO_3	5.09	5.11	+0.02
Mg^{+2}	0.25	15 ml. 6.0M HNO_3	Loading + 75 ml. 6.0M HNO_3	5.02	5.03	+0.01
Th^{+4}	0.25		150 ml. 0.5M HNO_3	5.01	5.01	±0.00
Mn	0.25	15 ml. 6.0M HNO_3	Loading + 75 ml. 6.0M HNO_3	5.02	5.02	±0.00
Th^{+4}	0.25		150 ml. 0.5M HNO_3	5.01	5.03	+0.02
Nd^{+3}	0.25	15 ml. 6.0M HNO_3	Loading + 75 ml. 6.0M HNO_3	5.08	5.07	-0.01
Th^{+4}	0.25		150 ml. 0.5M HNO_3	5.01	5.01	±0.00
Pb^{+2}	0.25	10 ml. 2.0M HNO_3	Load + 50 ml. 2.0M HNO_3	5.01	5.01	±0.00
Bi^{+3}	0.25		150 ml. 6.0M HNO_3	4.92	4.93	+0.01
Pb^{+2}	0.25	15 ml. 6.0M HNO_3	Loading + 100 ml. 6.0M HNO_3	5.31	5.30	-0.01
Th^{+4}	0.25		200 ml. 0.5M HNO_3	4.87	4.87	±0.00
Sr^{+2}	0.25	15 ml. 6.0M HNO_3	Load + 75 ml. 6.0M HNO_3	5.02	5.03	+0.01
Th^{+4}	0.25		150 ml. 0.5M HNO_3	5.01	5.00	-0.01

Table III. (cont.)

Ion Pairs	Load in mmoles	Loading Solution	Eluent	EDTA Titrations Theory, Ml.	Actual, Ml.	Diff, Ml.
UO_2^{+2}	0.25	15 ml. 6.0M HNO_3	Load + 75 ml. 6.0M HNO_3	5.04	5.06	+0.02
Th^{+4}	0.25		150 ml. 0.5M HNO_3	4.87	4.88	+0.01
UO_2^{+2}	0.05	15 ml. 6.0M HNO_3	Loading + 75 ml. 6.0M HNO_3	1.01	1.02	+0.01
Th^{+4}	0.45		200 ml. 0.5M HNO_3	8.78	8.79	+0.01
UO_2^{+2}	0.45	15 ml. 6.0M HNO_3	Loading + 75 ml. 6.0M HNO_3	9.07	9.09	+0.02
Th^{+4}	0.05		200 ml. 0.5M HNO_3	0.98	0.96	-0.02
V^{+4}	0.25	15 ml. 6.0M HNO_3	Load + 75 ml. 6.0M HNO_3	5.22	5.21	-0.01
Th^{+4}	0.25		150 ml. 0.5M HNO_3	5.01	5.01	±0.00
Y^{+3}	0.25	15 ml. 6.0M HNO_3	Load + 100 ml. 6.0M HNO_3	5.01	5.03	+0.02
Th^{+4}	0.25		150 ml. 0.5M HNO_3	4.87	4.88	+0.01
Y^{+3}	0.05	15 ml. 6.0M HNO_3	Loading + 100 ml. 6.0M HNO_3	1.00	1.00	±0.00
Th^{+4}	0.45		200 ml. 0.5M HNO_3	8.78	8.79	+0.01
Y^{+3}	0.45	15 ml. 6.0M HNO_3	Loading + 100 ml. 6.0M HNO_3	9.02	9.01	-0.01
Th^{+4}	0.05		200 ml. 0.5M HNO_3	0.98	0.98	0.00
Yb^{+3}	0.25	15 ml. 6.0M HNO_3	Load + 75 ml. 6.0M HNO_3	4.91	4.90	-0.01
Th^{+4}	0.25		150 ml. 0.5M HNO_3	5.01	5.01	±0.00
Zn^{+2}	0.25	15 ml. 6.0M HNO_3	Load + 75 ml. 6.0M HNO_3	5.04	5.05	+0.01
Th^{+4}	0.25		150 ml. 0.5M HNO_3	5.01	5.02	+0.01
Zr^{+4}	0.25	15 ml. 6.0M HNO_3	Load + 75 ml. 6.0M HNO_3	5.11	5.11	±0.00
Th^{+4}	0.25		150 ml. 0.5M HNO_3	4.88	4.88	±0.00
Zr^{+4}	0.05	15 ml. 6.0M HNO_3	Load + 75 ml. 6.0M HNO_3	1.02	1.03	+0.01
Th^{+4}	0.45		150 ml. 0.5M HNO_3	8.78	8.77	-0.01
Zr^{+4}	0.45	15 ml. 6.0M HNO_3	Loading + 75 ml. 6.0M HNO_3	9.20	9.21	+0.01
Th^{+4}	0.05		200 ml. 0.5M HNO_3	0.98	0.98	±0.00

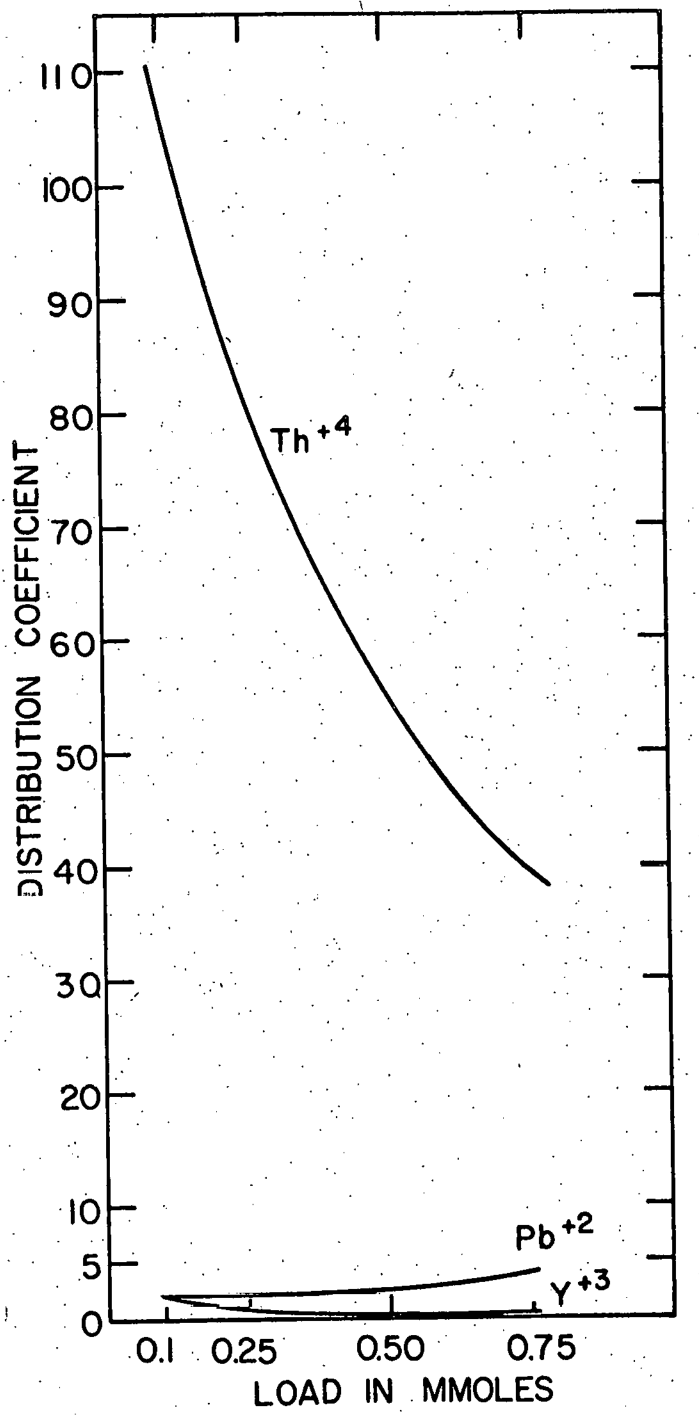

Figure 1. Effect of loading on batch distribution coefficients. Conditions: 1.3 gram of anion exchange resin (nitrate form), metal ion added to the resin in 50 ml. of 6M nitric acid