CATION EXCHANGE BEHAVIOR OF METAL IONS IN AMMONIUM SULFATE MEDIA

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(First received February 6th, 1968; revised manuscript received September 30th, 1968)

SUMMARY

The distribution coefficients of 20 metal ions in acid sulfate media with a strong acid type cation exchange resin, Dowex 50W-X8, are presented. The ammonium sulfate concentration varied from 0.10 to 1.0 M at a constant concentration of sulfuric acid (0.025 M). The coefficients of metal ions become significantly lower in acid sulfate media than those in sulfuric acid media, thus allowing many separations to be conducted at lower sulfate concentrations. The distribution coefficient indicates that differences in distribution coefficients between beryllium and a considerable number of metal ions are large enough for good separation. Results of the separation of beryllium from 23 metal ions are given. The acid sulfate system is also suitable for a clear-cut separation of uranium (VI), thorium and the rare earths in widely varying proportions, even permitting a carrier-free separation of ^{234}Th from uranium.

INTRODUCTION

Systematic studies on the behavior and separation of metal ions on anion or cation exchange resin in sulfuric acid or sulfate media are comparatively few. BUNNEY et al.[1] have determined the distribution coefficients for 11 radioactive traces with Dowex 1-X8 in sulfuric acid solutions. DANIELSSON[2] has investigated the anion exchange characteristics of 26 metal ions in sulfuric acid using Dowex 1-X8. Recently, STRELOW AND BOTHMA[3] have presented the anion exchange equilibrium distribution coefficients with Bio-Rad AGI-X8 for as many as 52 elements in sulfuric acid media and shown several elution curves for multicomponent systems like Y(III)–Th(IV)–U(VI)–Mo(VI). Scattered pieces of information on the adsorption and separation of the elements U(VI)[4-10], Th[4-6,11], Zr[12-15], Hf[14,15], Sc[6,16], Fe[17], Mo and W[12,18] and the rare earths[16,19] in aqueous sulfuric acid or sulfate solutions are also available.

Less information has been published concerning cation exchange than anion exchange. Systematic studies on the behavior of uranium (VI) on Amberlite IR 120 with organic and mineral acids, including sulfuric acid, have been described by KHOPKAR AND DE[20]. STRELOW has published distribution coefficient data for 23

cations in nitric acid and 9 cations in sulfuric acid[21]. Recently, STRELOW and collaborators have presented distribution coefficients with Bio-Rad AG 50W X8 for 49 cations in nitric acid and 45 cations in sulfuric acid media[22]. Other scattered information about cation exchange of Hg[23], Zr and Hf[24-26], Mg, Ca and Sr[27] in sulfuric acid or sulfate media is also available.

In the previous paper[28] we have also described the adsorption behavior of scandium on Dowex 50W-X8 in acid sulfate media, establishing a specific separation of scandium from 23 metal ions. The distribution coefficients were given only for scandium and average rare earths. In this work the results of a more extensive survey of distribution coefficients are presented including 20 cations on Dowex 50W-X8 in acid sulfate media. A distinct advantage of sulfate media over sulfuric acid media is a pronounced lowering of coefficients for most cations, so that many separations can be conducted at lower sulfate concentrations without appreciable tailing. Emphasis is particularly placed on a specific separation of beryllium from many other cations and a clear-cut separation of the rare earths, thorium and uranium (VI), from one another, including a carrier-free separation of UXI ([234]Th) from a natural uranium compound.

EXPERIMENTAL

Reagents

The resin used was a strongly acidic cation exchanger, Dowex 50W-X8 of 100–200 mesh in particle size. The resin was purified by washing with 1 M NH$_4$SCN–0.5 M HCl solution and then with deionized water until the thiocyanate test with ferric ion was negative. The resin was converted to the H-form by washing with 3 M HCl and then with deionized water. The resin was finally dried at 60° for 4 h and stored in a desiccator over a saturated KBr solution.

Stock solutions of metal ions were prepared by dissolving appropriate amounts of their salt in mineral acid solution to give usually 1 to 10 mg per ml of the solution. Each stock solution was standardized by a conventional analytical method. Analytical reagent grade chemicals were used whenever possible.

Determination of distribution coefficients

The distribution coefficient was in most cases obtained by a column elution method. 0.05-mmole amounts of each metal ion in 1 ml of dilute mineral acid were percolated through a column of 1 to 2 g of the resin. The metal ion was then eluted using 0.025 M H$_2$SO$_4$ solution of varying (NH$_4$)$_2$SO$_4$ concentrations ranging from 0.2 to 1 M. For a certain sulfate concentration the maximum concentration of metal ion appeared in the effluent after passage of V_{max} ml of eluent. The distribution coefficient was calculated by the following formula:

$$K_d = \frac{V_{max} - i \text{ (ml)}}{\text{amounts of resin (g)}}$$

where i is the interstitial volume of the column.

The distribution coefficients for a few metal ions were obtained by a batch equilibrium method[29] as mmoles metal ion on resin per gram dry resin/mmoles metal ion in solution per ml solution.

PROCEDURES FOR COLUMN SEPARATIONS

1. Separation of beryllium and other metal ions

A sample solution of approximately 10 ml is fed into a column of the resin. Subsequent procedures for individual separations are given in Table I.

TABLE I

PROCEDURES FOR THE SEPARATION OF BERYLLIUM

Column[a]	Eluent	Cation eluted first	Break-through (ml)	Elution complete (ml)	Cation remained on the column[b]
A	$0.20\ M\ (NH_4)_2SO_4$–$0.025\ M\ H_2SO_4$	Zr, Mo		30	Be
	$0.20\ M\ (NH_4)_2SO_4$–$0.025\ M\ H_2SO_4$	Be	70	120	Co(II), Cr(III), Ga
	$0.30\ M\ (NH_4)_2SO_4$–$0.025\ M\ H_2SO_4$	Be	40	80	Al, Ca, RE, Y
B	$0.20\ M\ (NH_4)_2SO_4$–$0.025\ M\ H_2SO_4$	Be	100	160	Cd, Mg, Cu(II), In
	$0.30\ M\ (NH_4)_2SO_4$–$0.025\ M\ H_2SO_4$	Be	50	90	Ni, Zn
C[c]	$0.20\ M\ (NH_4)_2SO_4$–$0.025\ M\ H_2SO_4$	U(VI)	50	70	Be
	$0.20\ M\ (NH_4)_2SO_4$–$0.025\ M\ H_2SO_4$	Sc	50	80	Be
	$0.20\ M\ (NH_4)_2SO_4$–$0.025\ M\ H_2SO_4$	Th	50	100	Be
A	$0.10\ M\ (NH_4)_2SO_4$–$0.50\ M\ H_2SO_4$	Be	40	80	Bi(III)
	$1\%\ H_2O_2$	V(IV)		20	Be
	$2\%\ H_2O_2$–$0.50\ M\ H_2SO_4$	Ti	20	50	Be

[a] Columns: (A) $0.95\ cm^2 \times 10\ cm$ (5.00 g resin contained); (B) $0.95\ cm^2 \times 15\ cm$ (7.50 g resin contained); (C) $0.88\ cm^2 \times 15.5\ cm$ (5.00 g resin contained).
[b] Removal of cations can easily be accomplished by eluting with 0.5 to 1 M $(NH_4)_2SO_4$–$0.025\ M\ H_2SO_4$ solutions.
[c] Placed in a conventional glass jacketed column through which warm water kept at 75° is passed.

2. Separation of uranium (VI), thorium and the rare earths

Four to 10 ml of sample solution containing the three elements is percolated through a column (I.D. 1.1 cm) of 3 g resin at a flow rate of *ca.* 0.5 ml/min. The ions are then eluted using the following elution sequence: 140 ml of 0.1 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 for U(VI), 60 ml of 0.3 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 for Th, and 60 ml of 0.5 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 for the rare earths.

The separation of the rare earths and thorium is conveniently conducted by eluting thorium first with 60 ml of 0.3 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 and then the rare earths with 60 ml of 0.5 M $(NH_4)_2SO_4$–0.025 M H_2SO_4.

3. Separation of zirconium from uranium (VI), thorium, indium and beryllium

A sample of approximately 10 ml solution is percolated through column A (see Table I), the effluent usually being collected. The major fraction of zirconium is then eluted with 10 ml of 0.2 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 and combined with the effluent from the sample solution. When the quantity of zirconium is large (50 mg), the volume for complete elution will extend over to about 70 ml because of its weak

tailing. The other metal ions, which are retained on the column, are recovered with a convenient eluent. When $0.5\ M$ $(NH_4)_2SO_4$–$0.025\ M$ H_2SO_4 is used, 40 ml for uranium (VI), 50 ml for thorium, 30 ml for indium, and 20 ml for beryllium are needed to effect the elution.

4. Separation of carrier-free UX1 from uranyl nitrate solution

One ml of $1\ M$ uranyl nitrate solution is percolated through the column of 3 g resin. Uranium (VI) is eluted down the column as described in section 2 above. UX1 is then removed by elution with 60 ml of $0.3\ M$ $(NH_4)_2SO_4$–$0.025\ M$ H_2SO_4. Twenty milligrams of iron (III) carrier are added to the effluent and precipitated by the dropwise addition of ammonia. The precipitate is filtered through filter paper, washed with 0.1% ammonium nitrate solution, mounted, and subjected to β-activity measurement with a conventional G.M. counter.

Analytical methods used for effluent analyses are summarized in Table II.

TABLE II

ANALYTICAL METHODS USED

Cation	Method
Be	Colorimetrically with 8-hydroxyquinaldine
Cu(II), Ni, Co(II)	Titration with EDTA using murexide as indicator.
Mg, Zn, Cd	Titration with EDTA using eriochrome black T as indicator.
Ca	Titration with EDTA using 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthionic acid as indicator.
Al, Ga, In	Titration with EDTA using Cu-PAN[a] as indicator. Traces of In determined colorimetrically with 8-hydroxyquinoline.
Sc, Y, Rare earths, Zr, Th, Bi(III)	Titration with EDTA using xylenol orange as indicator. Traces of the rare earths, Zr and Th determined colorimetrically with arsenazo III[b]
Ti	Colorimetrically with hydrogen peroxide
U(VI)	Colorimetrically with hydrogen peroxide or arsenazo III
V(IV)	Colorimetrically with sodium tungstate.
Cr(III)	Colorimetrically with diphenylcarbazide.
Mo	Colorimetrically with dithiol.
Fe(III)	Titration with EDTA using variamine blue B as indicator.

    [a] Cu-PAN is a mixture of 1-(2-pyridylazo)-2-naphthol and Cu-EDTA.
    [b] Arsenazo III is a sodium salt of 2,7-bis[(azo-2)-phenylarsono]-1,8-dihydroxy-naphthalene-3,6-disulfonic acid.

RESULTS AND DISCUSSION

The distribution coefficients of 22 metal ions in acid ammonium sulfate media on Dowex 50W-X8 are tabulated in Table III. Distribution coefficients of metal ions in the range from 0.10 to 1.00 M $(NH_4)_2SO_4$ generally decrease with increasing sulfate concentration. It should be emphasized that the values for the distribution coefficient

of most metal ions are significantly lower in sulfate media than in sulfuric acid media, as has been reported by STRELOW et al.[22]. As a measure of comparison, a value

$$\frac{K_d \text{ in } 0.25 \ M \ H_2SO_4}{K_d \text{ in } 0.20 \ M \ (NH_4)_2SO_4 - 0.025 \ M \ H_2SO_4}$$

for each metal ion was calculated, giving 100 for Zr, 28 for Th, 15 for Sc, 12 for In, 7.9 for V(IV), 7.5 for av. rare earths, 6.3 for Al, 4.6 for Cd, 4.1 for Ni, 3.8 for Zn and Be, 3.5 for $UO_2(II)$, 2.7 for Cu(II) and Co(II), 2.6 for Mg, and 1.1 for Mo. It can be stated that the higher the charge of cations, the higher the ratio. The difference in adsorption between media of sulfuric acid and sulfate becomes more pronounced in 0.1 M media, even though only a limited number of data are available. The value

$$\frac{K_d \text{ in } 0.1 \ M \ H_2SO_4}{K_d \text{ in } 0.1 \ M \ (NH_4)_2SO_4 - 0.025 \ M \ H_2SO_4}$$

amounts to 34 for Th, 20 for Sc, 5 for $UO_2(II)$ and 3.3 for Be. Apparently the acid sulfate media serve as good eluting media particularly for polyvalent cations like zirconium and thorium which otherwise are very difficult to remove from the cation

TABLE III

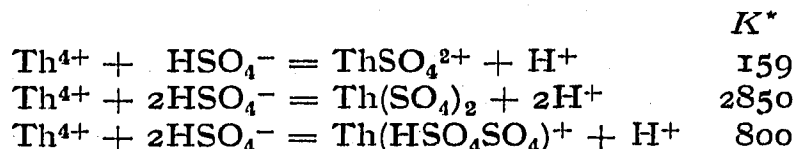DISTRIBUTION COEFFICIENTS OF METAL IONS IN $(NH_4)_2SO_4$ MEDIA ON DOWEX 50W-X8

Ion	Concentration of $(NH_4)_2SO_4$ in 0.025 M H_2SO_4 (M)					
	0.10	0.15	0.20	0.30	0.50	1.0
Be	91	34	20	9.3	4.3	2.2
Be[a]	9.8		6.0	4.6		1.8
Mg			47[b]		6.7	2.5
Ca			75	31	12	2.6
Ni			34	17	5.7	2.4
Zn			35	18	6.0	2.7
Co(II)			47	16	5.5	2.3
Cu(II)			47[b]		6.0	2.5
Cd			31	14	4.5	1.7
Al			85	35	8.0	2.5
Cr(III)			2.7×10^{2b}	77[b]	11[b]	0.2[b]
Ga			64	12	5.3	2.5
In			31	10	4.0	2.5
Fe(III)			23	7.7	3.8	1.8
Bi(III)[a]	32		13	6.3	3.3	1.5
Sc[c]	54	20	9.5		4.5	2.5
av. RE[c]	1×10^3		2×10^2	70	12 (for 0.60 M)	3.2
Ti[a]	5.4		4.5	3.5	2.5	1.5
Zr			<1	<1	<1	<1
Th	1.1×10^2	26	9.2		4.2	2.2
Mo			2.5	1.5	1.0	<1
U(VI)	24	13	8.3		4.0	1.8
V(IV)			18	8.2	4.0	1.9

[a] Obtained keeping the concentration of free acid constant at 0.50 M.
[b] Obtained by the batch equilibrium method.
[c] Coefficients published previously[26] but included to provide complete list. The K_d values for RE in 0.10 and 0.20 M salt solutions were estimated by extrapolation. The K_d values for scandium in lower sulfate concentrations, 0.10 and 0.15 M, were rechecked, and revised values are listed here.

exchange resin column. Differences in cation exchange behavior of many metal ions between sulfuric acid and sulfate media imply that sulfatocomplex formation in sulfuric acid medium may proceed in the following way, as suggested by ZEBROSKI et al.[30] for thorium:

$$
\begin{array}{ll}
 & K^* \\
\mathrm{Th^{4+} +\ HSO_4^- = ThSO_4^{2+} + H^+} & 159 \\
\mathrm{Th^{4+} + 2HSO_4^- = Th(SO_4)_2 + 2H^+} & 2850 \\
\mathrm{Th^{4+} + 2HSO_4^- = Th(HSO_4SO_4)^+ + H^+} & 800
\end{array}
$$

Thus, the presence of free acid prevents the formation of sulfatocomplexes of metal ions. In contrast ammonium sulfate media of low acid concentration greatly favor the stepwise formation of sulfatocomplexes which show low adsorption on cation exchanger.

The information contained in Table III indicates numerous possibilities for separation. Inspection of the relevant K_d values will show that differences in the distribution coefficients are large enough to permit a separation of beryllium from many other metal ions which show a similar analytical behavior, particularly in the

TABLE IV

SEPARATION OF BERYLLIUM FROM FOREIGN METAL IONS

Be		Foreign ions			Column used
Added (mg)	Found (mg)		Added (mg)	Found (mg)	
0.045	0.046	Mo	0.103	0.097	A
0.450	0.440	Co(II)	6.48	6.48	A
0.160	0.165	Cr(III)	9.60	9.70	A
0.045	0.044	Ga	16.0	15.8	A
0.045	0.045	Al	1.83	1.83	A
0.045	0.044	Ca	4.06	4.06	A
0.045	0.046	Y	22.2	22.6	A
0.045	0.047	La	13.4	13.5	A
0.045	0.046	Gd	7.97	7.97	A
0.045	0.046	Lu	17.9	17.8	A
0.045	0.046	Cd	17.2	17.2	B
0.450	0.438	Cu(II)	6.74	6.74	B
0.450	0.438	Mg	3.89	3.83	B
0.045	0.044	In	5.91	6.08	B
0.045	0.045	Ni	3.85	3.87	B
0.045	0.045	Zn	3.36	3.36	B
0.041	0.041	Sc	2.29	2.29	C
0.041	0.045	Th	12.1	12.0	C
0.041	0.043	U(VI)	12.8	12.7	C
0.045	0.046	Bi(III)	6.37	6.27	A
0.045	0.046	V(IV)	25.5	25.9	A
0.450	0.440	V(IV)	5.10	4.96	A
0.045	0.045	Ti	3.30	3.37	A

sulfate concentration range from 0.2 to 0.3 M. Results on quantitative separations are quoted in Table IV. Representative elution profile curves are illustrated in Fig. 1. Because of the strong tendency of scandium, zirconium, molybdenum, thorium and

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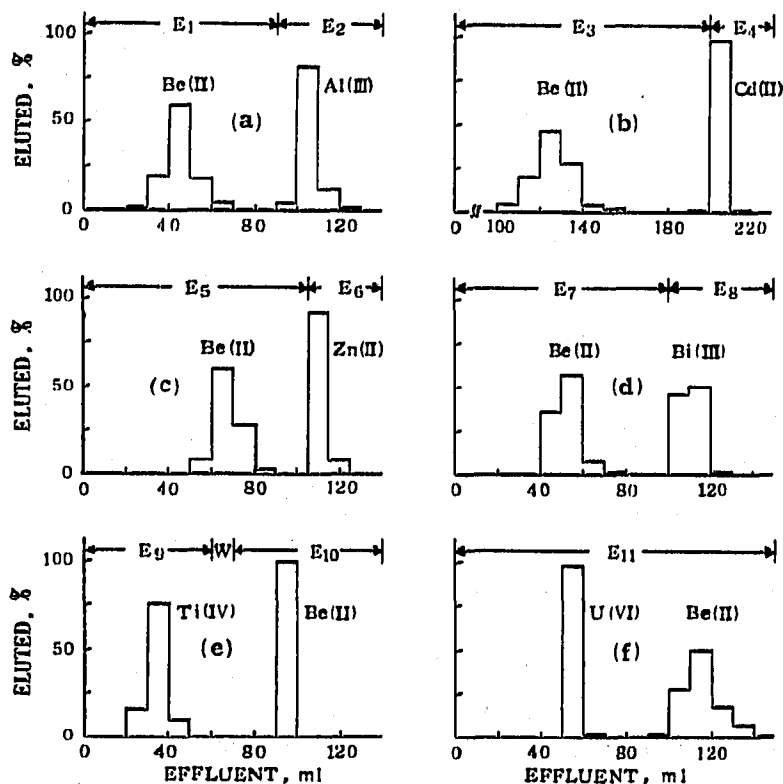* K = Equilibrium constant at 25.0 ± 0.1°.

Fig. 1. Separation of beryllium and other metal ions. Column beds: (a), (d) and (e)—A; (b) and (c)—B, (f)—C. (see footnote to Table I). Eluents: E_1 and E_5—0.30 M $(NH_4)_2SO_4$–0.025 M H_2SO_4; E_2 and E_{10}—0.50 M $(NH_4)_2SO_4$–0.025 M H_2SO_4; E_3 and E_{11}—0.20 M $(NH_4)_2SO_4$–0.025 M H_2SO_4; E_4 and E_6—1.0 M $(NH_4)_2SO_4$–0.025 M H_2SO_4; E_7—0.10 M $(NH_4)_2SO_4$–0.50 M H_2SO_4; E_8—1.0 M $(NH_4)_2SO_4$–0.50 M H_2SO_4; E_9—2% H_2O_2–0.50 M H_2SO_4; W—water.

uranium (VI) to form sulfatocomplexes, these ions are eluted down the column before breakthrough of beryllium. Scandium, thorium and uranium (VI) tend to show a slight tailing by elution with 0.2 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 at room temperature, thus contaminating the eluted fraction of beryllium. However, raising the temperature to 75° reduces tailing so that beryllium can be completely separated from scandium and uranium (VI). A small fraction of thorium (about 1%) still contaminates the eluted fraction of beryllium, even at the elevated temperature.

Some difficulties are encountered in the separation of beryllium and chromium (III). To get reproducible elution behavior of chromium (III) and to obtain a quantitative separation it is necessary to feed both metal ions as nitrate into the column from a nitric acid solution (e.g., 0.5 M) free of chloride and sulfate. Beryllium is best separated by elution with 0.2 M $(NH_4)_2SO_4$–0.025 M H_2SO_4, as indicated in Table I. As little as 0.4% of the chromium (III) present shows a breakthrough in the first 60 ml of the effluent, but this never contaminates the subsequent fraction of beryllium.

Chromatographic separation of rare earths, thorium and uranium (VI) is quite feasible in this ion exchange system because of great differences in distribution coefficients among the three elements. Uranium (VI) can be quantitatively separated from rare earths (abbreviated RE) and thorium in proportions of U:Th = 9000:1; U:RE = 17,000:1 to U:Th = 1:200; U:RE = 1:2,000. Thorium and the rare earths are also separated from each other in proportions of Th:RE = 5,000:1 to 1:400. An
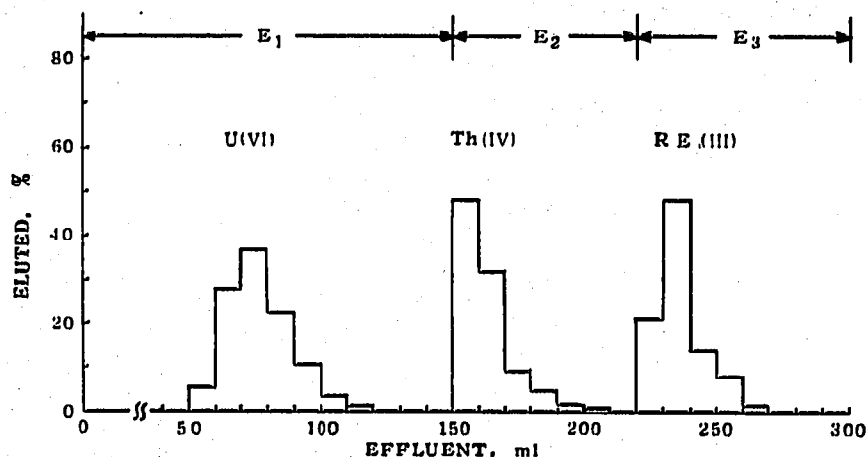
Fig. 2. Separation of uranium(VI), thorium and the rare earths. Column: 0.95 cm^2 × 6 cm. Eluents: E_1—0.10 M (NH$_4$)$_2$SO$_4$–0.025 M H$_2$SO$_4$; E_2—0.30 M (NH$_4$)$_2$SO$_4$–0.025 M H$_2$SO$_4$; E_3—0.50 M (NH$_4$)$_2$SO$_4$–0.025 M H$_2$SO$_4$. The following amounts were added to the column: U(VI), 11.9 mg; Th, 11.2 mg; La, 2.6 mg; Gd, 3.2 mg; and Lu, 3.5 mg.

extreme case is the carrier-free separation of UXI (^{234}Th) from natural uranium. UXI recovered from uranyl nitrate solution decayed away to background activity with a half-life of 24.1 days, exactly as given in the literature. An elution profile curve for the consecutive separation of the rare earths, thorium and uranium (VI) is shown in Fig. 2. The three metal ions are also separated in widely varying proportions, as may be seen in Table V. In general, the system is best suited for the quantitative sepa-

TABLE V

SEPARATION OF URANIUM(VI), THORIUM AND THE RARE EARTHS

U		Th		RE	
Added (mg)	Found (mg)	Added (mg)	Found (mg)	Added (mg)	Found (mg)
11.9	13.0	11.2	11.2	9.3 (La + Gd + Lu)	8.5
11.9	12.7	11.2	11.2	9.3 (La + Gd + Lu)	9.1
11.9	13.0	11.2	11.2	9.3 (La + Gd + Lu)	9.1
11.9	12.2	11.6	11.8	7.9 (La + Sm + Yb)	7.4
11.9	11.9	11.6	11.6	7.9 (La + Sm + Yb)	7.9
11.9	11.9	11.6	11.6	7.9 (La + Sm + Yb)	7.9
500	510	0.034	0.039	0.056 (La + Sm)	0.056
500	508	0.046	0.047	0.056 (La + Sm)	0.060
500	510	0.056	0.058	0.056 (La + Sm)	0.056
0.036	0.037	0.034	0.031	11.0 (Gd)	11.0
0.036	0.030	0.034	0.035	10.8 (La + Sm)	9.4
0.036	0.034	0.034	0.032	10.8 (Sm)	10.4
0.036	0.033	11.6	11.6	0.056 (La + Sm)	0.057
478	478	0.056	0.057	—	—
952	990	—	—	0.056 (La)	0.056
—	—	448	448	0.088 (Y)	0.084
0.060	0.060	11.6	11.6	—	—
0.060	0.060	—	—	114 (La + Yb)	114
—	—	0.056	0.057	22.2 (La)	22.2
0.120	0.124	—	—	139 (La)	139

TABLE VI

SEPARATION OF ZIRCONIUM AND INDIUM FROM OTHER METAL IONS

Ion		Foreign ions		
Added (mg)	Found (mg)		Added (mg)	Found (mg)
Zr 0.0088	0.0087	U(VI)	119	125
0.0088	0.0087	Th	112	111
0.0088	0.0088	In	115	117
45.6	46.3	In	0.057	0.056
45.6	46.4	Be	0.045	0.043
In 0.057	0.057	U(VI)	119	120
0.057	0.058	Mo	51.5	51.0

ration and subsequent determination of small quantities of the rare earths or thorium in uranium.

Many useful separations other than those described above are also possible. Zirconium does not show any marked tendency to adsorb on the resin from sulfate solutions of varying concentrations. This is sharp contrast to its behavior in pure sulfuric acid media[22]. Therefore, the acid sulfate media may provide a simple and specific method for separating zirconium from a number of other metal ions. Several results on quantitative separations are given in Table VI. Microgram quantities of zirconium can be separated with ease from more than ten thousand times as much uranium (VI), thorium and indium. Examples are also given in Table VI for the separation of indium from uranium (VI) and molybdenum in proportions of In:U = 1:2,000 and In:Mo = 1:1,000.

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