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THE REVERSED-PHASE EXTRACTION CHROMATOGRAPHY OF THE RARE EARTHS, THORIUM, URANIUM AND ZIRCONIUM WITH A HIGH-MOLECULAR-WEIGHT AMINE IN SULPHURIC ACID AND AMMONIUM SULPHATE MEDIA

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SUMMARY

The column chromatographic behaviour on silica gel impregnated with a high-molecular-weight amine, Amberlite LA-2 (SO_4^{2-}), of the trivalent rare earths and thorium(IV) in sulphuric acid and acid ammonium sulphate media was investigated. The distribution coefficients of these metal ions decrease with increasing concentration of the acid and sulphate, particularly in the acid system. The separation factor of thorium(IV) to the trivalent rare earths is large enough to separate two metals on the Amberlite LA-2 column in 0.025 *M* sulphuric acid–1.0 *M* ammonium sulphate solution. Thorium(IV), zirconium(IV) and uranium(VI) are adsorbed on the column in the same solution. Thorium(IV) is removed easily from the column by elution with 0.1 *M* sulphuric acid, while uranium(VI) and zirconium(IV) are strongly adsorbed. A separation procedure on the Amberlite LA-2–silica gel column was developed for the trivalent rare earths, thorium(IV), zirconium(IV) and uranium (VI), in which all four of the metal ions can be chromatographically separated by consecutive elution with sulphuric, hydrochloric and perchloric acids.

INTRODUCTION

Reversed-phase extraction chromatography has been used effectively for the separation of many metal ions, although the column packing materials and the column are usually critical. Chromatography with the exchanger-impregnated columns has many advantages, such as well defined elution curves, narrow peaks, high selectivity and higher exchange rates than those achieved with resin exchangers¹. The growth and acceptance of reversed-phase extraction chromatography have been reviewed^{2,3}. Since Cerrai and Testa⁴ used a cellulose column impregnated with tri-*n*-octylamine for separations of thorium–uranium–zirconium and lanthanum–uranium–thorium mixtures in hydrochloric acid or ammonium nitrate media, almost identical procedures with an Aliquat 336–Kel F column have been described for separating thorium from lanthanum⁵ and from uranium⁶ in nitric acid. The Aliquat 336–Kel F column was also used for separating thorium, protactinium and uranium in hydrochloric acid by Mikulski and Stroński⁷. Hayes and Hamlin⁸

demonstrated that uranium was adsorbed in a Kel F column impregnated with Amberlite LA-1 from 0.5 *M* sulphuric acid and removed quantitatively from the column with 1 *M* nitric acid. Using a tri-*n*-octylamine-silica gel column, a procedure was developed for separating the rare earths as a group, together with beryllium, from uranium by elution with 8 *M* hydrochloric acid⁹.

We have investigated the thin-layer chromatographic behaviour of the rare earths, thorium, uranium and zirconium on a high-molecular-weight amine, Amberlite LA-2, as a stationary phase coated on silica gel in sulphuric acid and acid ammonium sulphate media¹⁰. Brinkman and De Vries¹¹ also described the very similar behaviour of these cations on thin-layer plates of silica gel impregnated with amines, including Aliquat 336, Alamine 336, Amberlite LA-1 and Primene JMT in sulphuric acid and ammonium sulphate systems. In this paper, the reversed-phase extraction chromatographic characteristics of several metals on silica gel impregnated with Amberlite LA-2 in acid sulphate media are described. A consecutive chromatographic separation procedure has also been developed for the rare earths, thorium, zirconium and uranium.

EXPERIMENTAL

Stock solutions of metal ions

A solution of zirconium(IV) was prepared by dissolving an appropriate amount of zirconium metal in a mixture of nitric and hydrofluoric acids, converting it into the sulphate with sulphuric acid, evaporating the solution to dryness and dissolving the residue in a calculated volume of 2.0 *M* sulphuric acid so as to give a zirconium(IV) concentration of 1.02 mg/ml. Appropriate amounts of lanthanum(III), samarium(III), ytterbium(III), yttrium(III), thorium(IV) and uranium(VI) sulphates were dissolved in a calculated volume of 0.05 *M* sulphuric acid to give concentrations of 0.92, 1.19, 1.37, 1.23, 1.09 and 1.03 mg/ml, respectively. The strengths of the solutions were determined by titration with EDTA using xylenol orange as the indicator.

Pre-coating of a high-molecular-weight amine on silica gel

A high-molecular-weight amine, Amberlite LA-2 (Rohm & Haas, Philadelphia, Pa., U.S.A.), pre-washed with water so as to remove water-soluble fragments, was diluted to 17% (v/v) with distilled xylene and converted into the sulphate form as described in a previous paper¹². Pre-coating was accomplished by mixing 120 g of silica gel (Fuji-Davison Chem., Tokyo, Japan), 100–200 mesh, purified according to Seiler's method¹³, with 170 ml of the solution of Amberlite LA-2 in xylene and evaporating the mixture to dryness under an infrared lamp with occasional stirring. The impregnated silica gel (0.25 ml/g) was stored in a large desiccator containing saturated potassium bromide solution.

Preparation and pre-treatment of the reversed-phase columns

Two conventional columns, 1.0 cm I.D., 12 and 30 cm long, were used, and 5 and 15 g of the impregnated silica gel were slurried with the eluent and poured into the respective columns. The resulting beds were usually 8.5 and 25 cm high. Before use, the columns were washed with several column volumes of the same eluent.

Determination of distribution coefficients

The distribution coefficients, K_d , of samarium(III) and thorium(IV) were determined by a column method with the shorter column, using the following relationship:

$$K_d = (VEP - V)/m$$

where VEP = volume of elution peak, m = mass of the impregnated silica gel and V = void volume. The flow-rate was usually kept constant at 1.0 ml/min.

Titration with EDTA was used for the determination of metal ions in the effluent fractions.

Column chromatographic separation procedure

A 20-ml volume of the sample solution, adjusted to 0.025 M in sulphuric acid and to 1.0 M in ammonium sulphate, was loaded on to the top of the separation column (25 cm high) that had previously been treated with the same acid sulphate solution as mentioned above. The column was washed with 80 ml of 0.025 M sulphuric acid–1.0 M ammonium sulphate solution and the effluent was collected. This fraction contained the trivalent rare earths and yttrium(III). Thorium(IV) was then stripped from the column by elution with 90 ml of 0.1 M sulphuric acid or 30 ml of 4 M hydrochloric acid.

When uranium(VI) and zirconium(IV) were accompanied by thorium(IV), the column was first washed with 0.025 M sulphuric acid–1.0 M ammonium sulphate solution in order to remove the trivalent rare earths. Thorium(IV) was recovered in a 90-ml fraction of 0.1 M sulphuric acid, while uranium(VI) and zirconium(IV) were strongly adsorbed on the column. Zirconium(IV) and uranium(VI) were removed consecutively from the column by successive elutions with 80 ml of 4 M hydrochloric acid and 30 ml of 1 M perchloric acid.

RESULTS AND DISCUSSION

The distribution coefficients for samarium(III) and thorium(IV) are given in Table I as functions of sulphuric acid and ammonium sulphate concentrations. The K_d values of the two metals decrease rapidly on going to concentrations higher than 0.05 M in sulphuric acid. The ammonium sulphate concentration has a pronounced effect on the K_d values. It appears that the adsorption of these cations on the Amberlite LA-2 column can be improved by the addition of sulphate to sulphuric acid, but the K_d values decrease with increasing sulphate concentration. In order to obtain a good separation of two metal ions, it is obviously important for the separation factor, $\alpha_2^1 = K_{d1}/K_{d2}$, to be large. The factor, $\alpha_{Sm}^{Th} = 5.6$, in 0.025 M sulphuric acid–1.0 M ammonium sulphate medium is large enough for the separation of samarium(III) and thorium(IV) to be achieved on the Amberlite LA-2 column. For lanthanum(III), ytterbium(III) and yttrium(III), the elution characteristics in the long (25 cm) Amberlite LA-2 column with the same eluent are given in Table II. These ions are not absorbed on the column to any great extent. Uranium(VI) and zirconium(IV), as well as thorium(IV), have previously been reported to be almost completely adsorbed on an Amberlite LA-2 thin-layer plate from the acid sulphate solution in the tested range¹⁰. In a similar manner, zirconium(IV) and uranium(VI)

TABLE I

ELUTION CHARACTERISTICS FOR SAMARIUM(III) AND THORIUM(IV) IN SULPHURIC ACID-AMMONIUM SULPHATE SYSTEMS

BTV= breakthrough volume; *VEP*=volume of elution peak; *TEV*=terminal elution volume. Bed height of the column = 8.5 cm.

<i>Metal ion</i>	<i>H</i> ₂ <i>S</i> O ₄ (<i>M</i>)	(<i>NH</i>) ₂ <i>S</i> O ₄ (<i>M</i>)	<i>BTV</i> (<i>ml</i>)	<i>VEP</i> (<i>ml</i>)	<i>TEV</i> (<i>ml</i>)	<i>K_a</i>
Sm(III)	0.01	0	110	130	180	25.4
	0.05	0	10	20	30	3.4
	0.10	0	5	20	30	3.4
	0.50	0	5	20	30	3.4
	1.0	0	10	20	25	3.4
	0.025	0.01	50	70	90	13.4
	0.025	0.10	20	30	70	5.4
	0.025	0.50	10	20	50	3.4
	0.025	1.0	10	15	20	2.4
	Th(IV)	0.01	0	200	230	350
0.05		0	10	20	30	3.4
0.10		0	20	25	50	4.4
0.50		0	10	20	30	3.4
1.0		0	10	20	30	3.4
0.025		0.01	70	160	300	31.4
0.025		0.10	80	110	270	21.4
0.025		0.50	50	70	140	13.4
0.025		1.0	60	70	90	13.4

TABLE II

ELUTION CHARACTERISTICS FOR LANTHANUM(III), YTTERBIUM(III) AND YTTRIUM(III) IN THE 0.025 *M* SULPHURIC ACID-1.0 *M* AMMONIUM SULPHATE SYSTEM

Bed height of the column = 25 cm.

<i>Metal ion</i>	<i>BTV</i> (<i>ml</i>)	<i>VEP</i> (<i>ml</i>)	<i>TEV</i> (<i>ml</i>)	<i>K_a</i>
La(III)	20	30	40	0.7
Yb(III)	30	40	100	2.1
Y(III)	20	30	50	0.7

are strongly absorbed on the column from 0.025 *M* sulphuric acid-1.0 *M* ammonium sulphate solution and 0.1 *M* sulphuric acid, while thorium(IV) can easily be removed by elution with 0.1 *M* sulphuric acid. Hydrochloric acid of concentration 4 *M* effects the quantitative stripping of zirconium(IV) from the Amberlite LA-2 column, leaving uranium(VI), so that the development of the consecutive chromatographic separation of the trivalent rare earths, thorium(IV), zirconium(IV) and uranium(VI) can easily be accomplished in the present system. It was difficult to separate thorium(IV) and scandium(III) because these two metal ions behave in a similar manner in both the acid and acid sulphate systems.

The flow-rate of the eluent does not affect the chromatographic separation over the range 0.5–1.5 ml/min. The results for multicomponent separations are listed in Table III. Overall recoveries (\pm standard deviations) for yttrium(III), lanthanum(III), samarium(III), ytterbium(III), thorium(IV), zirconium(IV) and uranium(VI) are estimated to be 101.2 ± 1.9 , 100.1 ± 1.8 , 102.1 ± 0.6 , 99.7 ± 2.4 , 101.2 ± 2.6 , 100.4 ± 2.4 and $99.7 \pm 2.1\%$, respectively. A typical elution curve is illustrated in Fig. 1.

Silica gel was selected as a suitable support because of its purity, hardness and high capacity for the Amberlite LA-2. The ratio of the impregnant to silica gel (particle size 100–200 mesh) was most favourable at 0.25 ml of the amine per gram

TABLE III
RESULTS FOR MULTICOMPONENT SEPARATIONS

Bed height of the column: 25 cm.

Run	Metal ion	Added (mg)	Found (mg)	Metal ion	Added (mg)	Found (mg)
1	Y(III)	1.23	1.23	Th(IV)	1.09	1.10
2	Y(III)	1.23	1.26	Th(IV)	5.46	5.23
3	Y(III)	4.94	4.85	Th(IV)	1.09	1.07
4	La(III)	0.92	0.92	Th(IV)	1.09	1.15
5	La(III)	0.92	0.90	Th(IV)	5.46	5.56
6	La(III)	3.67	3.79	Th(IV)	1.09	1.12
7	Sm(III)	2.39	2.46	Th(IV)	5.46	5.29
8	Sm(III)	0.48	0.49	Th(IV)	5.46	5.61
9	Sm(III)	3.51	3.55	Th(IV)	1.09	1.12
10	Yb(III)	1.37	1.36	Th(IV)	1.09	1.13
11	Yb(III)	1.37	1.31	Th(IV)	5.46	5.47
12	Yb(III)	5.56	5.61	Th(IV)	1.09	1.14
13	Y(III)	1.23	1.26	Th(IV)	5.46	5.42
	Zr(IV)	1.02	1.05	U(VI)	5.13	5.11
14	Y(III)	2.47	2.55	Th(IV)	2.73	2.77
	Zr(IV)	1.02	1.06	U(VI)	10.26	10.38
15	La(III)	1.83	1.83	Th(IV)	5.46	5.44
	Zr(IV)	0.51	0.52	U(VI)	10.26	10.11
16	La(III)	3.67	3.65	Th(IV)	2.73	2.70
	Zr(IV)	1.02	1.00	U(VI)	5.13	5.31
17	Sm(III)	0.48	0.49	Th(IV)	2.73	2.84
	Zr(IV)	0.20	0.20	U(VI)	5.13	5.13
18	Sm(III)	7.02	7.18	Th(IV)	5.46	5.45
	Zr(IV)	0.51	0.49	U(VI)	10.26	10.04
19	Yb(III)	1.37	1.41	Th(IV)	1.09	1.14
	Zr(IV)	1.02	1.01	U(VI)	5.13	4.93
20	Yb(III)	2.73	2.73	Th(IV)	5.46	5.51
	Zr(IV)	1.02	1.03	U(VI)	2.57	2.58

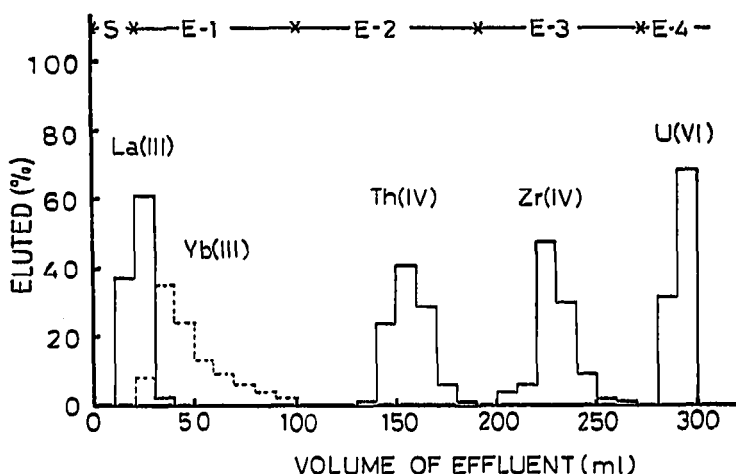


Fig. 1. Chromatographic separation of La(III) [or Yb(III)], Th(IV), Zr(IV) and U(VI). S = Sample solution (0.025 M H_2SO_4 -1.0 M $(\text{NH}_4)_2\text{SO}_4$); E-1 = 0.025 M H_2SO_4 -1.0 M $(\text{NH}_4)_2\text{SO}_4$; E-2 = 0.1 M H_2SO_4 ; E-3 = 4 M HCl ; E-4 = 1 M HClO_4 . La(III): 0.92 mg added, 0.91 mg found; Yb(III): 1.37 mg added, 1.38 mg found; Th(IV): 1.09 mg added, 1.09 mg found; Zr(IV): 1.02 mg added, 1.03 mg found; U(VI): 1.03 mg added, 1.04 mg found.

of the support. When the amine was impregnated on the support in amounts above 0.27 ml/g, the amine was partly stripped from the column throughout the elution process, and the effluents were contaminated with the amine containing metal ions.

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REFERENCES

- 1 E. A. Huff, *J. Chromatogr.*, 27 (1967) 229.
- 2 E. Cerrai and G. Ghersini, *Advan. Chromatogr.*, 9 (1970) 3.
- 3 U. A. Th. Brinkman, *Progr. Separ. Purif.*, 4 (1971) 241.
- 4 E. Cerrai and C. Testa, *J. Chromatogr.*, 6 (1961) 443.
- 5 M. N. Sastri, A. P. Rao and A. R. K. Sharma, *Indian J. Chem.*, 4 (1966) 287.
- 6 C. Testa, *Com. Naz. En. Nucl. Rep., RT/PROT*, 65 (1965) 33.
- 7 J. Mikulski and I. Stroński, *J. Chromatogr.*, 17 (1965) 197.
- 8 T. J. Hayes and A. G. Hamlin, *Analyst (London)*, 87 (1962) 770.
- 9 R. Krefeld, G. Rossi and Z. Hainski, *Mikrochim. Acta*, (1965) 133.
- 10 T. Shimizu and R. Ishikura, *J. Chromatogr.*, 56 (1971) 95.
- 11 U. A. Th. Brinkman and G. de Vries, *J. Chromatogr.*, 56 (1971) 103.
- 12 T. Shimizu, *Bunseki Kagaku (Jap. Anal.)*, 17 (1968) 1187.
- 13 H. Seiler, in E. Stahl (Editor), *Thin-Layer Chromatography*, Academic Press, New York, London, 1965.