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Note

Reversed-phase extraction chromatographic separation of scandium from the rare earths, uranium and zirconium

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Reversed-phase extraction column chromatography has already been applied for the separation of actinides, lanthanides and light transition metals; however, little information is available on the separation of scandium by this technique. Hisham and El Mohammed[1] used a column of hydrophobic Celite loaded with bis-(2-ethylhexyl) phosphate for separating scandium isotopes from calcium in media of hydrochloric and nitric acids. A cellulose column impregnated with trioctylphosphine oxide was used for the separation of trace amounts of many cations, including scandium, in media of hydrochloric, nitric and phosphoric acids[2]. Scandium, protactinium, zirconium, hafnium, zinc and cadmium were retained on the column from 8 *N* hydrochloric acid, but aluminium, lanthanum, lutetium, nickel, chromium, manganese and arsenic were not. Scandium together with zirconium and hafnium was eluted with 4 *N* phosphoric acid.

Brinkman and De Vries[3] have investigated the thin-layer chromatographic behaviour of 25 ions, including scandium, on silica gel impregnated with high-molecular-weight amines in media of sulphuric acid and ammonium sulphate. A column impregnated with a weakly basic liquid anion-exchanger of the amine type, however, has seldom been used for the separation of scandium. In this paper, the reversed-phase extraction column chromatographic behaviour of scandium and the other rare earth metals on silica gel impregnated with Amberlite LA-2 (Rohm & Haas, Philadelphia, Pa., U.S.A.) in sulphate media is described, and a procedure is developed for the separation of scandium from the other rare earth metals, uranium and zirconium.

EXPERIMENTAL

Stock solutions of scandium(III), lanthanum(III), europium(III), erbium(III) and yttrium(III) were prepared by dissolving appropriate amounts of the respective oxides in small amounts of 2 *M* sulphuric acid, evaporating to dryness and dissolving the residue in a volume of 0.05 *M* sulphuric acid such as to give 1.09, 1.04, 1.20, 1.03 and 1.23 mg of metal per ml, respectively.

Appropriate amounts of zirconium(IV) and uranium(VI) sulphates were dissolved in 2 *M* and 0.05 *M* sulphuric acid to give 1.34 and 4.05 mg of metal per ml, respectively. The concentrations of the solutions were determined by complexometric titration with EDTA.

Amberlite LA-2, pre-washed with water to remove a water-soluble component, was diluted to 20% (v/v) with distilled xylene and converted into sulphate form as described previously[4]. Pre-coating of the support was accomplished by mixing 120 g of purified silica gel[5] (Fuji-Davison, Tokyo, Japan), 100–200 mesh, with 150 ml of the Amberlite LA-2–xylene solution and evaporating the mixture to dryness under an IR lamp, with occasional stirring; the gel so impregnated was stored in a desiccator containing saturated potassium bromide solution.

The impregnated gel (8 g) was made into a slurry with the eluent to be used and poured into a conventional column (20 cm × 1 cm I.D.); the resulting bed height was usually 15 cm. Before use, the column was washed with several column volumes of the eluent.

The sample solution (20 ml), adjusted to 0.025 *M* in sulphuric acid and 1.0 *M* in ammonium sulphate, was applied to the top of the column, which had previously been treated with the same acid sulphate solution, and the column was washed with 30 ml of 0.025 *M* sulphuric acid–1.0 *M* ammonium sulphate solution to remove tervalent rare earths. The scandium(III) was then stripped from the column with 50 ml of the same solution. Then zirconium(IV) and/or uranium(VI) were eluted with 30 ml of 1 *M* perchloric acid. All elutions were carried out at 1.0 ml/min.

RESULTS AND DISCUSSION

To investigate the elution behaviour of europium(III) and scandium(III) in sulphate medium, *ca.* 1 mg of each cation was applied to the top of the column, and elution was carried out with ammonium sulphate solution at various concentrations, the concentration of free sulphuric acid being kept constant at 0.025 *M*. The cumulative elution curves are shown in Fig. 1, from which it can be seen that the points of both breakthrough and complete elution of the cations occur earlier as the concentration of sulphate increases. The widths of the adsorption bands of europium(III) and scandium(III) on the column decrease with increasing sulphate concentration, and there are also considerable differences in adsorption between europium(III) and scandium(III) over the range of sulphate concentrations tested.

In order to achieve good separation of two metal ions, it is important that the separation factor, which is defined by the ratio of their distribution coefficients, $\alpha_2^1 = K_{d_1}/K_{d_2}$, should be large. The value of the distribution coefficient, K_d, was calculated by the following equation for each cation:

$$K_d = (V_{\text{max.}} - V_0)/M$$

where $V_{\text{max.}}$ is the volume of maximum elution, V_0 is the void volume of the column and M is the mass of adsorbent in the column. The factor $\alpha_{\text{Eu}}^{\text{Sc}}$, calculated from the data on the elution behaviour in 0.025 *M* sulphuric acid–1 *M* ammonium sulphate medium, was 6.2, *i.e.*, large enough for good separation of scandium(III) from europium(III) on the Amberlite LA-2 column. The other tervalent rare earth metals were not adsorbed on the column to any great extent. It has been reported that uranium (VI) and zirconium(IV) are almost completely adsorbed on a silica gel column im-

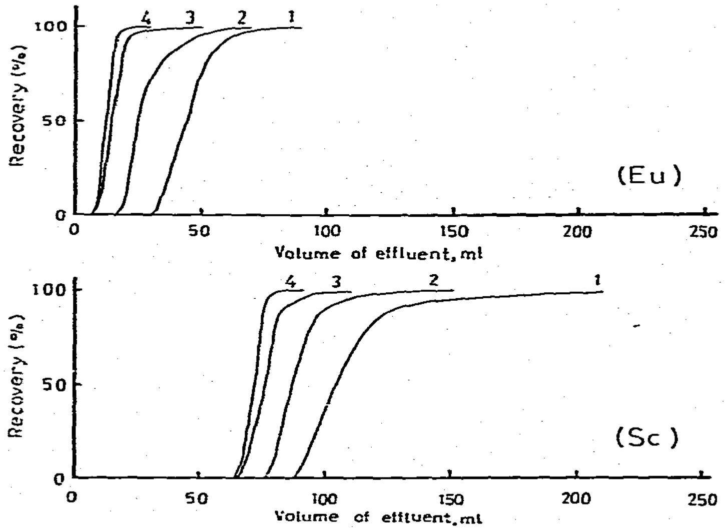

Fig. 1. Cumulative elution curves for europium and scandium with the free acid concentration constant at 0.025 M sulphuric acid. Concentration of ammonium sulphate: 1 = 0.01 M; 2 = 0.1 M; 3 = 0.5 M; 4 = 1.0 M.

TABLE I

SEPARATION OF SCANDIUM FROM LANTHANUM, EUROPIUM, ERBIUM, YTTRIUM, URANIUM AND ZIRCONIUM

Scandium(III)		*Foreign ions*		
Added (mg)	*Found (mg)*		*Added (mg)*	*Found (mg)*
1.09	1.09	La(III)	1.04	1.05
1.09	1.05	La(III)	0.21	0.21
0.22	0.22	La(III)	1.04	1.04
0.22	0.22	La(III)	5.23	5.23
1.09	1.11	Eu(III)	1.20	1.20
1.09	1.09	Eu(III)	0.24	0.24
0.22	0.22	Eu(III)	1.20	1.19
0.22	0.22	Eu(III)	4.78	4.76
0.22	0.22	Eu(III)	9.57	9.48
1.09	1.10	Er(III)	1.03	1.04
1.09	1.11	Er(III)	0.21	0.21
0.22	0.22	Er(III)	1.03	1.08
0.22	0.22	Er(III)	6.19	6.21
1.09	1.08	Y(III)	1.23	1.23
1.09	1.09	Y(III)	0.25	0.26
0.22	0.21	Y(III)	1.23	1.23
0.22	0.21	Y(III)	4.98	4.99
0.22	0.22	Y(III)	9.96	9.95
1.09	1.08	U(VI)	1.01	1.02
1.09	1.09	U(VI)	4.05	3.99
0.22	0.23	U(VI)	4.05	4.07
0.22	0.22	U(VI)	10.1	10.1
1.09	1.11	Zr(IV)	1.34	1.39
1.09	1.11	Zr(IV)	0.27	0.27
0.22	0.22	Zr(IV)	1.34	1.34
0.22	0.22	Zr(IV)	13.4	13.4

pregnated with Amberlite LA-2 from acid sulphate media in the range of concentrations tested and that these metals can be removed from the column by elution with 1 *M* perchloric acid[6,7].

The flow-rate of the eluent does not affect the chromatographic separation over the range 0.7–1.5 ml/min. The results for separations of scandium(III) from other tervalent rare earth metals, uranium(VI) and zirconium(IV) are listed in Table I, from which it can be seen that scandium(III) is separated from large amounts of the other ions. Over-all recoveries (± standard deviations) for scandium(III), lanthanum (III), europium(III), erbium(III), yttrium(III), zirconium(IV) and uranium(VI) are estimated to be 100.2 ± 1.5, 99.3 ± 1.3, 99.6 ± 0.3, 100.3 ± 1.9, 100.8 ± 1.4, 100.9 ± 1.4, and 100.2 ± 0.5%, respectively.

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