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## Note

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### Thin-layer chromatographic separation of zirconium, hafnium, thorium, uranium and the rare earths on DEAE-cellulose in sulphate media

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The paper and thin-layer chromatographic (TLC) behaviour of a number of metals on DEAE-cellulose has already been investigated in different binary solvent mixtures consisting of organic solvents and mineral acids such as HCl (refs. 1 and 2), HNO<sub>3</sub> (ref. 3), HSCN (ref. 4) and HN<sub>3</sub> (ref. 5). The chromatographic behaviour of Fe(III), Re(VII), La(III), In(III) and U(VI) on DEAE-cellulose and on aminoethyl-cellulose papers in H<sub>2</sub>SO<sub>4</sub> of varying concentration has been reported by Lederer and Ossicini<sup>6</sup>. Oguma and Kuroda<sup>7</sup> investigated the TLC behaviour of 46 metals on DEAE-cellulose in binary solvent mixtures containing H<sub>2</sub>SO<sub>4</sub>.

Although several paper chromatographic methods<sup>8-11</sup> have been reported for the separation of Zr(IV) and Hf(IV), little is known about the separation of the two metals by TLC. Olsina *et al.*<sup>12</sup> have separated Zr(IV) and Hf(IV) on silica gel G-HR layers with HCl-H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>O as the developing solvent. Kuroda and co-workers<sup>1,7</sup> used a DEAE-cellulose layer to separate multicomponent mixtures involving Zr(IV) and other metals with acid-organic solvent mixtures, but not involving Hf(IV).

The TLC behaviour on DEAE-cellulose in H<sub>2</sub>SO<sub>4</sub>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> media has been investigated in detail for Hf(IV), Zr(IV), U(VI), Th(IV) and the trivalent rare earths and the work is described in this paper. Procedures have been developed for the separation of Zr(IV) and Hf(IV), and for the two-dimensional separation of Zr(IV), Hf(IV), Th(IV), U(VI) and the trivalent rare earths.

## EXPERIMENTAL

### Test solution

Zr(IV) and Hf(IV) solutions of 0.03 M concentration were prepared by dissolving appropriate amounts of respective metals (99.99% purity) in an HNO<sub>3</sub>-HF mixture, evaporating the resulting solution to dryness together with H<sub>2</sub>SO<sub>4</sub> and dissolving the residue in a known volume of 2.0 M H<sub>2</sub>SO<sub>4</sub>. Appropriate amounts of the trivalent rare earths, Sc(III), Y(III), Th(IV) or U(VI) sulphate were dissolved in a known volume of 0.05 M H<sub>2</sub>SO<sub>4</sub> to yield 0.01 M metal solutions.

### Preparation of the thin-layer plates

A cellulose anion exchanger, DEAE-cellulose (diethylaminoethylcellulose for TLC, Serva, Heidelberg, G.F.R.), was used as an adsorbent. A portion of DEAE-

cellulose, about 12 g, was slurried with 80 ml of 0.025 *M* H<sub>2</sub>SO<sub>4</sub>–1.0 *M* (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution and stirred mechanically for 1 h. The DEAE-cellulose was then washed three times with deionized water, each wash solution subsequently being removed by centrifugation. The DEAE-cellulose thus treated was slurried with 35 ml of water and spread to a thickness of 250 μm on five glass plates (200 × 200 × 3 mm). The plates were allowed to dry at 40° for 3 h after air-drying for 24 h and stored in a desiccator over saturated KBr solution.

#### *Application and detection*

A sample or test solution, usually 1 μl, was spotted with a micropipette at a distance of 15 mm from one edge. The plate was air-dried for 30 min and then immediately developed up to 170 mm from the spot by the ascending technique. The developing solvent used was H<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution of varying concentrations. Subsequently, all the metals were detected as green spots on a pink background after spraying with 0.1% aqueous arsenazo III solution and drying the plate under an infrared lamp.

For the separation of Zr(IV), Hf(IV), Th(IV), U(VI) and the trivalent rare earths (or Sc(III)) or Y(III) by the two-dimensional technique, the spot of the sample solution was applied at one corner at 15 mm from the two edges. The plate was developed up to a distance of 170 mm with 0.1 *M* H<sub>2</sub>SO<sub>4</sub>–0.05 *M* (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution, dried in air for 24 h and stored in a desiccator over a saturated KBr solution for a further 24 h. Subsequently, a second development was carried out at right-angles to the first development with 0.1 *M* H<sub>2</sub>SO<sub>4</sub>–1.0 *M* (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution. The metal ions concerned were then all detected with arsenazo III.

*R<sub>F</sub>* values were obtained as averages of triplicate runs.

#### RESULTS AND DISCUSSION

For Hf(IV), Zr(IV), U(VI) and Th(IV), the *R<sub>F</sub>* and *R<sub>M</sub>* (ref. 13) values are tabulated in Table I as a function of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration. The concentration of free H<sub>2</sub>SO<sub>4</sub> was kept constant at 0.1 *M*. It can be seen from Table I that the *R<sub>F</sub>* values of these metal ions increase with increasing concentration of sulphate, and also depend markedly on the free acid concentration. The *R<sub>F</sub>* values of Zr(IV) and Hf(IV) in aqueous H<sub>2</sub>SO<sub>4</sub> also increase with increasing concentration of the acid and then behave in a similar manner to that reported by Oguma and Kuroda<sup>7</sup>. It is difficult to separate Zr(IV) and Hf(IV) on a DEAE-cellulose layer in acid medium.

In order to obtain a good separation of two elements, it is obviously important for the separation factor to be large. The distribution coefficient, *D*, of a metal ion on paper or in thin-layer chromatography was presented by Cerrai and Testa<sup>14</sup> as

$$\log D = \log (1/R_F - 1) + \text{constant}$$

and is related to the *R<sub>M</sub>* value<sup>13</sup> by the equation

$$\log D = R_M + \text{constant}$$

$$D = K \cdot 10^{R_M}$$

TABLE I

$R_F$  AND  $R_M$  VALUES AND SEPARATION FACTORS FOR Hf, Zr, U AND Th AS A FUNCTION OF  $H_2SO_4$  OR  $(NH_4)_2SO_4$  CONCENTRATION

$H_2SO_4$ (M)	$(NH_4)_2SO_4$ (M)	Hf		Zr		U		Th		$\alpha_{Zr}^{Hf}$	$\alpha_U^{Zr}$	$\alpha_{Th}^U$
		$R_F$	$R_M$	$R_F$	$R_M$	$R_F$	$R_M$	$R_F$	$R_M$			
0.10	0.01	0.12	0.87	0.17	0.69	0.37	0.27	0.60	-0.18	1.51	2.89	2.57
0.10	0.05	0.16	0.72	0.22	0.55	0.40	0.18	0.65	-0.27	1.48	2.35	2.82
0.10	0.10	0.17	0.69	0.28	0.41	0.43	0.12	0.69	-0.35	1.91	1.95	2.95
0.10	0.50	0.23	0.52	0.37	0.23	0.61	-0.19	0.73	-0.43	1.95	2.63	1.74
0.10	1.0	0.30	0.36	0.49	0.02	0.67	-0.31	0.75	-0.48	2.19	2.14	1.48
0.10	2.0	0.37	0.23	0.56	-0.10	0.78	-0.37	0.75	-0.48	2.14	1.87	1.29
0.01	0.0	0.09	1.00	0.11	0.91					1.02		
0.05	0.0	0.11	0.91	0.14	0.79					1.48		
0.10	0.0	0.15	0.75	0.24	0.50					1.78		
0.50	0.0	0.78	-0.55	0.72	-0.41					0.74		
1.0	0.0	0.90	-0.96	0.85	-0.75					0.57		
2.0	0.0	0.94	-1.19	0.90	-0.95					0.57		

TABLE II

SEPARATION OF Zr, Hf, U, Th AND THE RARE EARTHS

Solvent	Group	$R_F$ value ( $\times 100$ )
0.1 M $H_2SO_4$ -1.0 M $(NH_4)_2SO_4$	Hf-Zr-Th	Hf (23-33); Zr (35-60); Th (72-78)
	Hf-Zr-U	Hf (21-31); Zr (34-59); U (62-72)
	Hf-Zr-Th-Sc	Hf (18-35); Zr (36-64); Th (71-81); Sc (77-93)
	Hf-Zr-U-Lu	Hf (19-34); Zr (38-60); U (61-74); Lu (77-93)
0.1 M $H_2SO_4$ -0.05 M $(NH_4)_2SO_4$	Zr-U-Th	Zr (12-30); U (34-44); Th (64-72)
	Hf-U-Th	Hf (11-25); U (32-42); Th (64-72)
	Zr-U-Th-Y	Zr (13-30); U (34-44); Th (60-69); Y (76-82)
	Hf-U-Th-La	Hf (10-28); U (34-44); Th (58-66); La (82-92)

The separation factor,  $\alpha_B^A$ , of two elements A and B can be defined as

$$\alpha_B^A = D_A/D_B = 10^{R_{MA} - R_{MB}}$$

Separation factors evaluated on the basis of the  $R_F$  values are also given for Hf(IV)-Zr(IV), Zr(IV)-U(VI) and U(VI)-Th(IV) in Table I. The factor for Hf(IV)-Zr(IV) is large enough to permit a good separation of these two metal ions at sulphate concentrations above 1.0 M. For Zr(IV)-U(VI) and U(VI)-Th(IV), the factors are also large at sulphate concentrations below 1.0 and 0.1 M, respectively. The trivalent rare earths, Sc(III) and Y(III) were not adsorbed to any great extent on

DEAE-cellulose in the acid sulphate media tested, having  $R_F$  values greater than 0.85. A solution adjusted to 0.1  $M$  in  $H_2SO_4$  and to 1.0  $M$  in  $(NH_4)_2SO_4$  is most suitable for use as a developing solvent for the TLC separation of Hf(IV), Zr(IV), trivalent rare earths and U(VI) (or Th(IV)). A 0.1  $M$   $H_2SO_4$ -0.05  $M$   $(NH_4)_2SO_4$  solution will effect the chromatographic separation of U(VI), Th(IV), trivalent rare earths and Zr(IV) (or Hf(IV)); Zr(IV) and Hf(IV) are separated with difficulty, however. Typical separations accomplished are presented in Table II.

The TLC separation of a mixture consisting of Zr(IV), Hf(IV), U(VI), Th(IV) and trivalent rare earths can be accomplished on DEAE-cellulose by a two-dimensional technique, first using 0.1  $M$   $H_2SO_4$ -0.05  $M$   $(NH_4)_2SO_4$  solution and subsequently 0.1  $M$   $H_2SO_4$ -1.0  $M$   $(NH_4)_2SO_4$  solution. A chromatogram obtained in this way is illustrated in Fig. 1. The  $R_F$  value for each metal ion is greater than in single development, because the total concentration of the acid and sulphate in the second development is necessarily higher than 0.1  $M$  in  $H_2SO_4$  and 1.0  $M$  in  $(NH_4)_2SO_4$  owing to the acid and sulphate that remain on the plate after the first development.

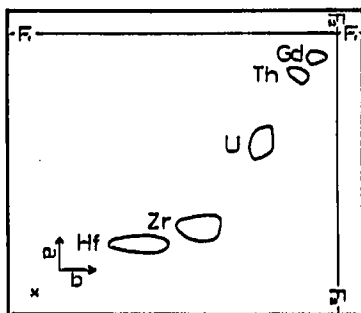


Fig. 1. Chromatogram obtained by the two-dimensional technique. (a) 0.1  $M$   $H_2SO_4$ -0.05  $M$   $(NH_4)_2SO_4$  (first elution); (b) 0.1  $M$   $H_2SO_4$ -1.0  $M$   $(NH_4)_2SO_4$  (second elution).

When the plate that had been eluted with first developing solvent was dried by heating it in an oven or under an infrared lamp, all the metals migrated up to the solvent front in the second development. However, by drying the plate in air for 24 h and subsequently storing it for 24 h in a desiccator over a saturated KBr solution, the metals could be chromatographed satisfactorily and resolved with the second solvent.

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