

CHROM. 5197

THE REVERSED PHASE THIN-LAYER CHROMATOGRAPHIC BEHAVIOR OF THE RARE EARTHS, THORIUM, URANIUM AND ZIRCONIUM WITH A HIGH MOLECULAR WEIGHT AMINE IN SULFURIC ACID AND AMMONIUM SULFATE SYSTEMS

TSUNEO SHIMIZU AND REIKO ISHIKURA

Department of Chemistry, Faculty of Education, Gunma University, Maebashi, Gunma (Japan)

(Received December 9th, 1970)

SUMMARY

Thin-layer plates of silica gel impregnated with a high molecular weight amine, Amberlite LA-2, in the sulfate form, were used to investigate systematically the chromatographic behavior of the rare earths, thorium, uranium(VI) and zirconium in sulfuric acid and acid ammonium sulfate media. The R_F values for these metal ions decrease with increasing concentration of the acid and sulfate, in the acid system particularly. An interesting correlation is revealed between the R_F values of the rare earths and the paramagnetic moment of the trivalent rare earths in the high concentration range of the acid and sulfate. An odd-even fluctuation of the R_F values against atomic number is also found for the heavy lanthanides. Differences in the R_F values of the rare earths in acid sulfate media indicate the possibility of good separations of adjacent pairs or groups of the rare earths from each other by selecting an appropriate concentration of sulfate. The rare earths, thorium, uranium(VI) and zirconium can also be separated chromatographically with either 0.5 or 1.0 *M* sulfuric acid as developing solvent.

INTRODUCTION

Recently, thin-layer chromatography (TLC) has been used effectively for the separation of many metal ions, because of its advantages of rapidity and high capacity. The growth and acceptance of inorganic TLC has been noted in reviews compiled by LEDERER¹ and NICKLESS². Thin-layer chromatographic separations of the rare earths, thorium, uranium and zirconium have been carried out by normal³⁻⁵ and reversed phase chromatography⁶⁻⁸. For the separation of the rare earths from each other, DANEELS *et al.*⁹ used a silica gel layer and a bis-(2-ethylhexyl) hydrogen phosphate (HDEHP)-carbon tetrachloride mixture as developing solvent. PIERCE AND FLINT^{10,11} separated the rare earths by reversed phase TLC using a layer of polyvinyl chloride impregnated with HDEHP in hydrochloric acid medium. HOLZAPFEL *et al.*¹² proposed a separation procedure for binary mixtures of the rare earths on silica gel precoated with HDEHP with hydrochloric or nitric acid systems, and improved it by using

two-dimensional development¹³. BRINKMAN AND DE VRIES¹⁴ described the use of a secondary amine, Amberlite LA-1, coated on silica gel plates for the separation of many metal ions, but not for the rare earths.

In the present work, the thin-layer chromatographic behavior 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 has been investigated systematically in sulfuric acid and acid ammonium sulfate media. The reversed phase thin-layer chromatographic separations have been accomplished for selected adjacent pairs or groups of the rare earths in acid ammonium sulfate media. The separation procedure has also been developed for the rare earths, thorium, uranium and zirconium in sulfuric acid medium.

EXPERIMENTAL

Test solutions of metals

Test solutions of the rare earths were prepared by dissolving the appropriate amounts of the respective oxides in small amounts of 2 *M* sulfuric acid, evaporating to dryness and dissolving in 0.05 *M* sulfuric acid. Appropriate amounts of sulfates of thorium and uranium were dissolved in 0.05 *M* sulfuric acid. The solution of zirconium was prepared by dissolving an appropriate amount of zirconium metal in a nitric and hydrofluoric acid mixture, converting it to sulfate with sulfuric acid, evaporating to dryness and dissolving in 0.05 *M* sulfuric acid. Each solution contained about 1.5 mg of metal ion per ml of solution. The metal ions studied were thorium, uranium(VI), zirconium and all the rare earths except promethium.

Precoating of Amberlite LA-2 on silica gel

Amberlite LA-2 (Rohm & Haas Co. Ltd.) prewashed with water to remove water-soluble fragments was diluted to 8% (v/v) with distilled xylene and converted to the sulfate form as described in a previous paper¹⁵. Precoating was accomplished by mixing 40 g of silica gel, Wakogel B-O (Wako Pure Chemicals Co. Ltd., Japan) purified according to SEILER's method¹⁶, with 125 ml of the LA-2 xylene solution and evaporating to dryness under an infrared lamp, with occasional stirring.

Preparation of the thin-layer plates

Five grams of the silica gel coated with the LA-2 (0.25 ml/g) was thoroughly mixed with 10 ml of 5% starch solution. The slurry was immediately spread to a thickness of 250 μm on 25 \times 100 mm glass plates with an applicator. The plates were dried in air and then in an oven at 60° for 3 h. The plates prepared thus were used immediately.

Procedure

A sample or test solution, usually 1 μl , was spotted with a micropipette at 15 mm from one end of the plate. The spot was dried in air for 30 min. The plate was immediately developed up to 65 mm by the ascending technique at room temperature. The developing solvent used was a sulfuric acid or acid ammonium sulfate solution of varying concentration. Developing periods of 80 to 90 min yielded adequate solvent front movement (up to 65 mm from the spot). Subsequently, thorium, uranium,

zirconium and the rare earths ions were all detected as purplish red colored spots on a pink background after spraying with 0.5 % arsenazo solution, and drying the plate under an infrared lamp.

R_F values are the average of triplicates and are given for the leading and trailing edges of the spots in the separations.

RESULTS AND DISCUSSION

Adsorption behavior of the rare earths

The R_F values of the rare earths in two developing systems, sulfuric acid and acid ammonium sulfate solutions (free acid concentration was kept constant at 0.025 M), in the concentration range 0.01–2.0 M are plotted against the atomic number, respectively, in Figs. 1 and 2.

As can be seen in Figs. 1 and 2, the R_F values of the rare earths generally increase with increasing sulfuric acid or ammonium sulfate concentration, in the acid system particularly. At a rough estimate the R_F curves of the rare earths show a minimum value in the vicinity of atomic number 63 (europium) in the concentration range 0.01–0.1 M of the acid and sulfate, and a maximum in the same neighborhood in the range 0.5–2.0 M . As can be seen a rather abrupt change in adsorption behavior occurs at some concentration of the acid and sulfate between 0.1 and 0.5 M . Such a change in the trend of the R_F curves with the acid and sulfate concentrations seems to suggest that a sulfato complex of the rare earths contributes to the chromatographic behavior and that different species of the complex are involved according to the concentration range tested. The R_F values of the rare earths are relatively small at low concentrations of the acid and sulfate: the sulfato complex of the rare earths is taken up on the LA-2 stationary phase, where the hydrated ion may predominate and has little tendency to associate with sulfate ion in developing solvent. At a high concentration of sulfate, the sulfato complexes of the rare earths are largely in anionic form so that the R_F values should increase with increasing sulfate concentration,

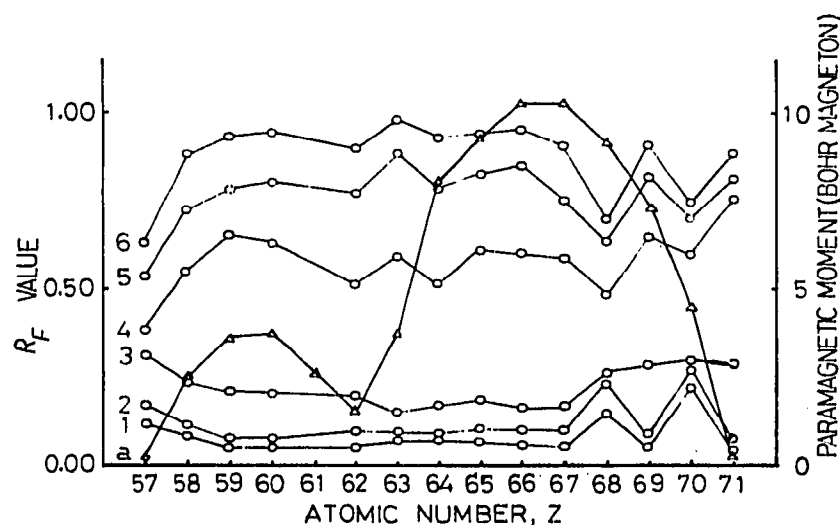


Fig. 1. R_F values of the rare earths at various concentrations of sulfuric acid against atomic number. (1) at 0.01 M ; (2) at 0.05 M ; (3) at 0.10 M ; (4) at 0.50 M ; (5) at 1.0 M ; (6) at 2.0 M . (a) Paramagnetic moment of trivalent rare earths.

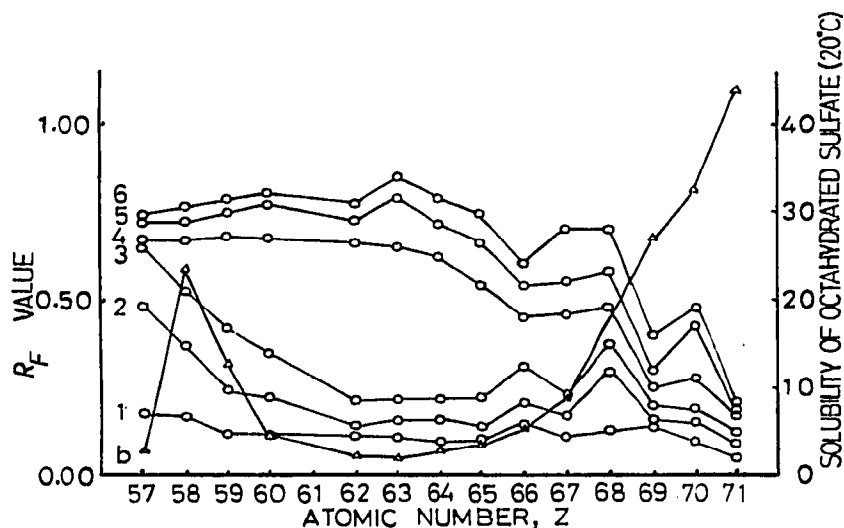


Fig. 2. R_F values of the rare earths in various ammonium sulfate solutions against the atomic number (the free acid concentration was kept constant at 0.025 M). (1) at 0.01 M ; (2) at 0.05 M ; (3) at 0.10 M ; (4) at 0.50 M ; (5) at 1.0 M ; (6) at 2.0 M . (b) Solubility of the salts.

because the higher anionic complexes occupy more fixed ionic groups per LA-2 molecule and are in competition with an increasing number of free sulfate ions. Regarding the extractability of metal sulfates with high molecular weight amines from sulfuric acid solution, MARCUS AND KERTES¹⁷ have reported that irrespective of the class of amine the distribution ratio of the metal sulfates reaches maximum at an acidity lower than 0.1 M , and abruptly decreases as the concentration ratio of bisulfate to sulfate increases. In accordance with their observations, the R_F values of the rare earths on the LA-2 plate in sulfuric acid medium increase markedly when the concentration of the solvent becomes higher than 0.1 M , because the ratio of bisulfate to sulfate in high acid concentrations increases. This suggests that the chromatographic behavior of the rare earths would be affected by the hydrogen ion concentration in an aqueous solvent.

It is of interest to note that there are close correlations between the R_F values for the rare earths, up to around thulium, and the solubility (Fig. 2) of octahydrated sulfates¹⁸. The solubility of a sulfate of the type, $\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, except for that of lanthanum, first diminishes within the lighter groups, reaches a minimum in the vicinity of europium and then increases with increasing atomic number. Over the low concentration range of sulfate ion, the R_F values of the light lanthanides decrease with increasing atomic number and reach a minimum in the vicinity of europium. Thus, it can be seen that the minimum R_F value corresponds to the minimum solubility. Such a correspondance suggests the possibility that the predominance of neutral sulfato complexes in the vicinity of europium is greater relative to other lanthanides in a solution of low sulfate concentration and that this will necessarily result in a greater uptake of europium on the LA-2 through an ion association mechanism. Maximum R_F value of the rare earths corresponds, however, to the minimum solubility in the higher sulfate concentration (0.5–2.0 M), so that the anionic sulfato complex may predominate at the same vicinity. HAMAGUCHI *et al.*¹⁹ reviewed similar corre-

lations between adsorption behavior on anion exchangers and solubility of salts of the rare earths in various solutions.

With a high concentration of sulfuric acid as a developing system, a relationship is found between the R_F values of the rare earths and the paramagnetic moment²⁰ (Fig. 1) of the trivalent rare earths. The curve of the moment against atomic number has two maxima in the vicinity of neodymium and holmium. It can be seen that the minimum affinity of the sulfato complex of the rare earths to the LA-2 in sulfate form on the plate corresponds to the maximum moment. A similar relationship is also observed in the acid ammonium sulfate system but is less marked. Thus, the electronic configuration of inner shell (4f) of trivalent rare earths may be responsible for the adsorption behavior of the sulfato complex on LA-2.

An effect which is responsible for the odd-even fluctuations against atomic number can also be superimposed over the general trend of the thin-layer chromatographic behavior in sulfuric acid and acid ammonium sulfate systems for heavy lanthanides. Similar fluctuations have already been observed by HESFORD *et al.*²¹ in the distribution of the rare earths between nitric acid and tributyl phosphate, and by SURLS²² in the distribution between dilute perchloric acid and Dowex 50 in the sulfate form. MARCUS AND ABRAHAMER²³ also revealed an interesting odd-even atomic number effect in the distribution coefficients of the rare earths in the anion-exchanger, Dowex 1 X8-nitrate system, and in the magnetic susceptibility of the heavy lanthanides extracted into a triisooctyl amine phase from nitrate solution²⁴. Thus, it seems that such an odd-even effect could arise if every second electron paired with the previous electron in building up the inner shell (4f) as suggested by HESFORD *et al.*²¹, and MARCUS AND ABRAHAMER²³.

Adsorption behavior of Th, U(VI) and Zr

The R_F values of thorium, uranium (VI) and zirconium in sulfuric acid and acid ammonium sulfate solutions (0.025 M of free acid) are plotted against the concentration of the acid and sulfate in Fig. 3. The R_F values of these elements increase

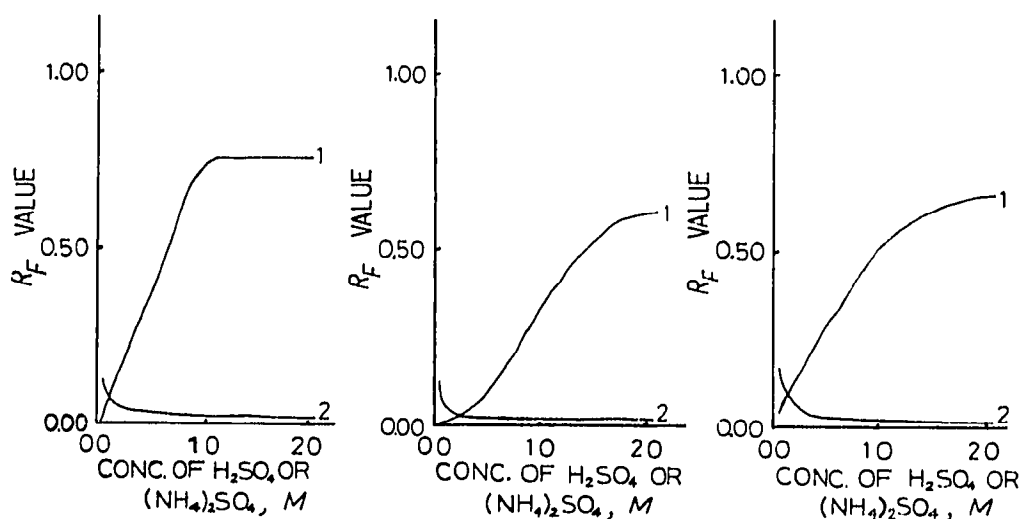


Fig. 3. R_F values of Th, U and Zr against the concentration of sulfuric acid or ammonium sulfate (free acid concentration was kept constant at 0.025 M). (1) In sulfuric acid; (2) in acid ammonium sulfate solution.

TABLE I
SEPARATION OF THE RARE EARTHS, Th, U AND Zr

Solvent	Pair or group	R_F value ($\times 100$)
0.5 M H ₂ SO ₄	U-Zr	U (06-12); Zr (26-32)
	U-Th	U (06-13); Th (34-46)
	U-Eu	U (09-15); Eu (46-57)
	Zr-Th	Zr (25-35); Th (36-46)
	Zr-Eu	Zr (23-34); Eu (46-57)
	U-Zr-Th	U (05-12); Zr (20-34); Th (37-46)
	U-Zr-Th-Eu	U (05-14); Zr (25-34); Th (35-42); Eu (43-57)
1.0 M H ₂ SO ₄	U-Zr	U (22-34); Zr (46-58)
	Y-Th	U (20-34); Th (65-72)
	U-Eu	U (18-36); Eu (90-96)
	U-Zr-Th	U (22-34); Zr (46-53) Th (60-70)

TABLE II
MUTUAL SEPARATION OF THE RARE EARTHS

Solvent	Pair	R_F value ($\times 100$)
0.025 M H ₂ SO ₄ -0.05 M (NH ₄) ₂ SO ₄	La-Pr	La (38-52); Pr (12-28)
	La-Eu ^a	La (35-51); Eu (06-30)
	La-Er ^a	La (34-54); Er (18-37)
	La-Yb ^a	La (35-48); Yb (06-15)
	Ce-Sm ^a	Ce (30-54); Sm (10-18)
	Er-Tm	Er (22-38); Tm (09-25)
	Ho-Er	Ho (10-23); Er (24-30)
0.025 M H ₂ SO ₄ -0.1 M (NH ₄) ₂ SO ₄	Pr-Sm	Pr (30-47); Sm (11-24)
	Sm-Dy ^a	Sm (12-25); Dy (26-37)
	Eu-Yb ^a	Eu (25-34); Yb (06-25)
	Gd-Dy ^a	Gd (14-22); Dy (23-43)
	Tb-Dy	Tb (13-24); Dy (26-36)
	Tb-Ho	Tb (14-23); Ho (24-34)
0.025 M H ₂ SO ₄ -0.5 M (NH ₄) ₂ SO ₄	Nd-Sm	Nd (61-78); Sm (46-57)
	Nd-Eu	Nd (58-77); Eu (42-61)
	Nd-Gd	Nd (58-80); Gd (37-58)
	Nd-Yb	Nd (59-78); Yb (19-27)
	Sm-Ho	Sm (53-66); Ho (32-48)
	Ho-Tm	Ho (34-57); Tm (19-26)
0.025 M H ₂ SO ₄ -1.0 M (NH ₄) ₂ SO ₄	Er-Yb	Er (38-52); Yb (19-26)
	Pr-Er	Pr (63-80); Er (46-55)
	Nd-Tb	Nd (80-92); Tb (52-65)
	Sm-Yb	Sm (57-86); Yb (32-50)
	Eu-Er	Eu (53-72); Er (42-54)
	Eu-Dy	Eu (64-80); Dy (48-62)
	Eu-Ho	Eu (62-78); Ho (45-65)
	Gd-Ho	Gd (72-87); Ho (46-68)
Tm-Yb	Tm (27-34); Yb (35-43)	
Yb-Lu	Yb (30-46); Lu (18-26)	

^a It was also confirmed that the pairs can be separated chromatographically by use of 0.5 or 1.0 M sulfate solutions as a developing solvent.

markedly with increasing acid concentration but become constant at 1.0 *M* for thorium and at 2.0 *M* for uranium(VI) and zirconium. In contrast, these metal ions are strongly adsorbed on the LA-2 from sulfate solutions with a higher concentration than 0.5 *M*, so that the spots scarcely move from the starting point. Pronounced differences in the chromatographic behavior of these elements between the acid and sulfate systems imply that the presence of a large amount of sulfuric acid prevents the formation of the sulfato complexes of the metal ions, as suggested by KAWABUCHI *et al.*²⁵ on the basis of the adsorption behavior of thorium in the Dowex 50W X8-ammonium sulfate system. Ammonium sulfate in acid solution of low concentration greatly favors the formation of the sulfato complexes possessing small R_F values.

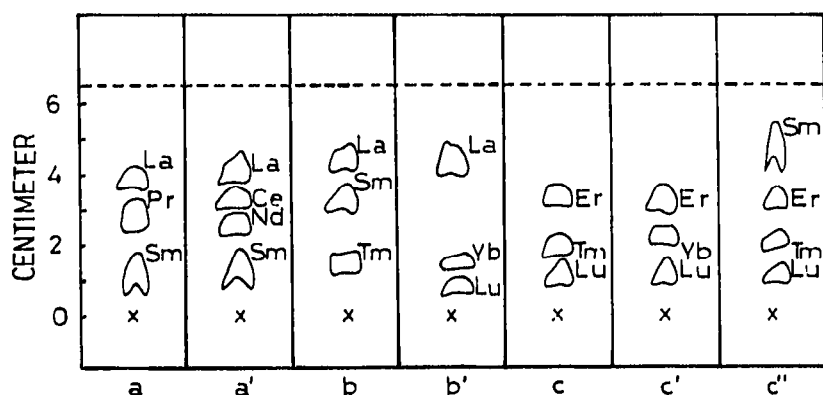


Fig. 4. Chromatograms of the rare earths in acid ammonium sulfate media. (a, a') in 0.025 *M* H_2SO_4 -0.10 *M* $(NH_4)_2SO_4$; (b, b') in 0.025 *M* H_2SO_4 -0.50 *M* $(NH_4)_2SO_4$; (c, c', c'') in 0.025 *M* H_2SO_4 -1.0 *M* $(NH_4)_2SO_4$.

Separation

The R_F values of the rare earths, thorium, uranium(VI) and zirconium in the acid ammonium sulfate system (Figs. 2 and 3) suggest the possibility of a separation of the rare earths from the latter three, but it is difficult to separate all these elements in sulfate medium chromatographically. Thin-layer chromatographic separation of these metal ions can be achieved by choosing either 0.5 or 1.0 *M* sulfuric acid as the solvent. The results are given in Table I.

Inspection of the relevant R_F values in sulfate media (Fig. 2) will show whether a separation of the rare earths from each other is feasible and what the most favorable concentration of sulfate should be. With a sulfate solution higher than 0.05 *M*, some binary mixtures consisting of one in the light group (La to Gd) and one in the heavy (Tb to Lu) can be separated from each other. It is noteworthy that the sulfate system also affords the possibility of separating adjacent pairs of the light or heavy groups. A solution adjusted to 0.025 *M* with respect to sulfuric acid and 0.1 *M* with respect to ammonium sulfate is most favorable as a developing solvent for the chromatographic separation of binary mixtures of the light group. A sulfate concentration higher than 0.5 *M* is effective for the separation of adjacent pairs or groups of the heavy lanthanides. Typical separations accomplished for pairs of rare earths are presented in Table II. Chromatograms involving three or four elements of the rare earths are also illustrated in Fig. 4.

ACKNOWLEDGEMENT

Our sincere thanks are due to Prof. R. KURODA, University of Chiba, for many helpful discussions and suggestions during this study.

REFERENCES

- 1 M. LEDERER, *Chromatogr. Rev.*, 9 (1967) 115.
- 2 G. NICKLESS, *Advan. Chromatogr.*, 5 (1968) 121.
- 3 K. OGUMA, *Talanta*, 15 (1968) 860.
- 4 K. OGUMA, *Talanta*, 16 (1969) 409.
- 5 K. ISHIDA, T. ITO AND R. KURODA, *Jap. Anal.*, 17 (1968) 1122.
- 6 D. MARKLAND AND F. HECHT, *Microchim. Acta*, (1963) 970.
- 7 E. GAGLIARDI AND G. POCORNY, *Microchim. Acta*, (1966) 977.
- 8 T. B. PIERCE AND P. F. PECK, *Analyst (London)*, 89 (1964) 662.
- 9 A. DANEELS, D. L. MASSART AND J. HOSTE, *J. Chromatogr.*, 18 (1965) 141.
- 10 T. B. PIERCE AND R. F. FLINT, *Anal. Chim. Acta*, 31 (1964) 595.
- 11 T. B. PIERCE AND R. F. FLINT, *J. Chromatogr.*, 24 (1966) 141.
- 12 H. HOLZAPFEL, L. V. LAN AND G. WERNER, *J. Chromatogr.*, 20 (1965) 580.
- 13 H. HOLZAPFEL, L. V. LAN AND G. WERNER, *J. Chromatogr.*, 24 (1966) 153.
- 14 U. A. TH. BRINKMAN AND G. DE VRIES, *J. Chromatogr.*, 18 (1963) 142.
- 15 T. SHIMIZU, *Jap. Anal.*, 17 (1968) 1137.
- 16 H. SEIDER, in E. STAHL (Editor), *Thin-layer Chromatography*, Academic Press, New York, 1965.
- 17 Y. MARCUS AND A. S. KERTES, *Ion Exchange and Solvent Extraction of Metal Complexes*, Interscience, London, 1969.
- 18 K. S. JACKSON AND G. RIENACHER, *J. Chem. Soc.*, (1963) 1687.
- 19 H. HAMAGUCHI, A. OHUCHI, N. ONUMA AND R. KURODA, *J. Chromatogr.*, 16 (1964) 396.
- 20 T. MOELLER, *Inorganic Chemistry*, John Wiley, New York, 1952.
- 21 E. HESFORD, E. E. JACKSON AND H. A. MCKEY, *J. Inorg. Nucl. Chem.*, 9 (1959) 279.
- 22 J. P. SURLS, *U.S. At Energy Comm. Rept.*, UCRL-3209 (1956).
- 23 Y. MARCUS AND I. ABRAHAMER, *J. Inorg. Nucl. Chem.*, 22 (1961) 141.
- 24 I. ABRAHAMER, Y. MARCUS AND I. ELIEZER, *Israel At. Energy Comm. Rept.*, IA-1014 (1965).
- 25 K. KAWABUCHI, T. ITO AND R. KURODA, *J. Chromatogr.*, 39 (1969) 61.

J. Chromatogr., 56 (1971) 95-102