

CHROM. 18 196

## THIN-LAYER CHROMATOGRAPHIC BEHAVIOUR AND SEPARATION OF RARE EARTHS ON SILICA GEL IN AQUEOUS AMMONIUM NITRATE SOLUTION

KOJI ISHIDA\*

*Department of Chemistry, School of Medicine, Kyorin University, Shinkawa, Mitaka, Tokyo (Japan)*  
and

SHUJI NINOMIYA, YOICHI TAKEDA and KENJU WATANABE

*Department of Chemistry, Faculty of Education, Tokyo Gakuji University, Koganei, Tokyo (Japan)*

(Received September 18th, 1985)

---

### SUMMARY

The thin-layer chromatographic behaviour of all the rare earths except promethium on silica gel in aqueous ammonium nitrate solutions of varying concentration has been investigated. Generally, the  $R_F$  values of the lanthanoids decrease with increase in their atomic number ( $Z$ ), although the variation is not smooth. A cation-exchange mechanism is proposed as the most important factor controlling the adsorbability of the metals in this system. The  $R_F$  values indicate the possibility of good separations of adjacent pairs or groups of lanthanoids from each other by selection of an appropriate concentration of the salt. Typical chromatograms for the separations of binary and multi-component mixtures are presented.

---

### INTRODUCTION

Many papers have been published on the thin-layer chromatographic (TLC) behaviour and separation of the rare earths, and the literature has been reviewed<sup>1,2</sup>. Most of the work has involved the use of the reversed-phase technique<sup>3-7</sup>.

In contrast, there is little information concerning the utilization of normal-phase TLC. Daneels *et al.*<sup>8</sup> achieved the first successful separation of a few lanthanoids by normal-phase TLC using a silica gel layer and bis(2-ethylhexyl) hydrogen phosphate (HDEHP) in carbon tetrachloride as the developing solvent. We<sup>9</sup> also separated several-component mixtures of the lanthanoids ranging from lanthanum to dysprosium on diethylaminoethylcellulose in methanol-nitric acid ( $\text{HNO}_3$ ) media. More recently, Specker and co-workers<sup>10-15</sup> developed excellent TLC systems composed of silanized Kieselgel and *n*-butyl phosphate in isoctane, tetrahydrofuran (THF)-paraldehyde (PA)- $\text{HNO}_3$ , triphenylphosphine oxide in PA- $\text{HNO}_3$ , diisopropyl ether-THF- $\text{HNO}_3$ , diethyl ether (DEE)-HDEHP- $\text{HNO}_3$  and DEE-THF-HDEHP- $\text{HNO}_3$ , and applied their systems to the separation of multi-component mixtures of lanthanoids with adjacent atomic numbers. However, these systems have

usually involved the use of special supports and/or complicated solvents containing organophosphorus compounds. Clearly, widely acceptable systems for normal-phase TLC of the rare earths are not yet available.

This work was undertaken in order to establish further applications of silica gel in inorganic TLC and to develop simpler and more convenient systems for the normal-phase TLC of lanthanoids. The TLC behaviour of all of the rare earths (except promethium) was studied using a system consisting of a silica gel layer and aqueous ammonium nitrate solutions of various concentrations. The nitrate system allowed the separation of several-component mixtures of the lanthanoids with adjacent atomic numbers to be conducted easily and effectively.

## EXPERIMENTAL

### Stock solutions

Most of the stock solutions of the rare earths were prepared by dissolving sufficient nitrate (99.9% or higher purity) in 0.1 mol/dm<sup>3</sup> HNO<sub>3</sub> to give a 0.01 mol/dm<sup>3</sup> metal solution. For other metals, appropriate amounts of the oxides (99.9% or higher purity) were dissolved in 6 mol/dm<sup>3</sup> HNO<sub>3</sub> and evaporated to dryness, followed by dissolution in 0.1 mol/dm<sup>3</sup> HNO<sub>3</sub> to give a 0.01 mol/dm<sup>3</sup> metal solution. When necessary, the stock solutions were diluted with nitric acid of the same concentration. Test and sample solutions were prepared by diluting the stock solutions by mixing some of the stock solutions, respectively, followed by dilution to give a concentration of 0.001 mol/dm<sup>3</sup> with respect to each metal. All the chemicals were of analytical-reagent grade, unless indicated otherwise.

### Preparation of thin-layer plates

A 20-g portion of silica gel without binder (Wakogel B-O; Wako, Japan) was thoroughly blended with 45 cm<sup>3</sup> of a 3% aqueous starch solution. The slurry was spread to a thickness of 250 μm on glass plates (20 × 20 cm) with an applicator. The plates were allowed to stand for 0.5 h at room temperature and then dried in an oven at *ca.* 70°C for 20 min.

In order to remove inorganic impurities from the silica gel used, the plates were thoroughly washed and conditioned by developing up to the upper edge of the plate by the ascending technique with sufficient amounts of a 0.001 mol/dm<sup>3</sup> am-

TABLE I

$R_F$  VALUES ( $\times 100$ ) OF THE RARE EARTHS ON SILICA GEL IN AQUEOUS AMMONIUM NITRATE SOLUTIONS

Concentration of $NH_4NO_3$ (mol/dm <sup>3</sup> )	$R_F \times 100^*$						
	Sc	Y	La	Ce	Pr	Nd	Sm
0.5	–3–3	18–28	78–88	63–72	52–63	51–62	32–43
1.0	–3–3	33–42	85–92	76–84	70–79	70–78	54–63
2.0	–3–4	45–55	91–98	85–93	80–88	81–90	68–78
4.0	–4–4	44–54	92–98	89–95	84–91	84–91	73–81
6.0	0–8	34–44	93–98	88–94	80–90	82–90	66–75

\* The values are averages of two identical runs.

monium nitrate solution for 45 min at room temperature. Subsequently, the plates were dried at *ca.* 70°C for 20 min for activation. After cooling, they were stored in a desiccator containing saturated ammonium nitrate solution until ready for use.

### Procedure

A 0.5- $\mu$ l portion of the test or sample solution was applied to the plate by means of a microcap (Drummond, U.S.A.) at a point 5 or 2.5 cm from one edge, and the spots were dried in air for 10 min. The plate was immediately placed in a chromatographic chamber (22  $\times$  10  $\times$  22 cm), equipped with a tank (21  $\times$  5  $\times$  4 cm) containing 50 cm<sup>3</sup> of developing solvent and developed up to 10 or 15 cm from the starting point by the ascending technique at room temperature. The developing solvents used were ammonium nitrate solutions of varying concentration, with a constant pH (4.9  $\pm$  0.1). The developing time was about 20 and 30 min for the 10- and 15-cm development distances, respectively.

### Detection

After development, the plate was dried thoroughly by blowing warm air and the positions of the metals were revealed by spraying with 0.01% aqueous arsenazo III solution and then aqueous ammonia solution, followed by gentle heating. The lanthanoids (except Pm), Sc and Y were all detected as green spots on a pink background.

## RESULTS AND DISCUSSION

### Adsorption behaviour

*Variation of  $R_F$  values with atomic number.* Table I shows the  $R_F$  values of all the trivalent lanthanoids (except Pm), Sc(III) and Y(III) on a silica gel layer in ammonium nitrate solutions as a function of the concentration of the latter. In general, the  $R_F$  values decrease with increase in their atomic number ( $Z$ ) in all the solutions tested, although the variation is not smooth. A distinct exception is found with Gd, which shows much higher  $R_F$  values than Eu, behaving like Sm. Another feature of this system is that Nd, Ho, and Yb also give  $R_F$  values nearly identical with those of Pr, Dy and Tm, respectively. In addition, Y lies between Tb and Dy, and Sc remains at or near the starting point.

<i>Eu</i>	<i>Gd</i>	<i>Tb</i>	<i>Dy</i>	<i>Ho</i>	<i>Er</i>	<i>Tm</i>	<i>Yb</i>	<i>Lu</i>
26-37	30-42	20-29	16-23	14-24	10-18	4-11	7-14	0-7
47-56	53-63	37-46	30-38	27-36	18-28	9-18	7-17	3-10
64-73	64-77	50-58	41-49	41-50	31-40	17-26	11-21	5-14
67-76	68-78	50-60	40-49	38-48	29-38	17-24	12-21	7-14
59-69	60-72	42-51	30-39	28-37	19-29	10-17	10-18	4-11

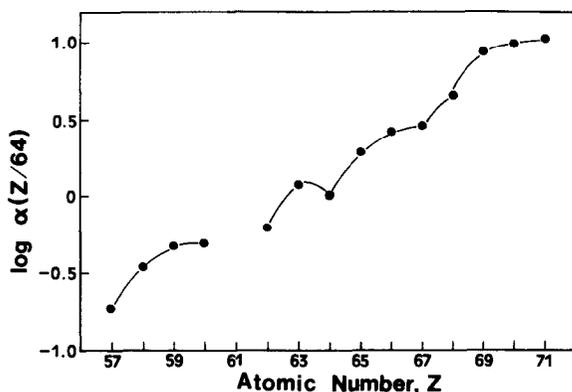


Fig. 1. Variation of separation factors ( $\alpha$ ) [ $\alpha(Z/64)$ ] of lanthanoids with atomic number ( $Z$ ) using a silica gel-1 mol/dm<sup>3</sup> NH<sub>4</sub>NO<sub>3</sub> system.

It is interesting that the sequence of adsorption of the lanthanoids (except Gd) as a function of their atomic numbers is very similar to that in reversed-phase TLC using HDEHP-HCl or HDEHP-HNO<sub>3</sub><sup>3-6</sup>, but is different to those in normal-phase TLC on silica gel with HDEHP in CCl<sub>4</sub><sup>8</sup> and with silanized Kieselgel and organophosphorus compounds in HNO<sub>3</sub><sup>10-15</sup>, and also to that of anion-exchange TLC on DEAE-cellulose with methanol-HNO<sub>3</sub><sup>9</sup>. These facts suggest that cation exchange plays an important role in controlling the adsorbability of the rare earths in our system. This conclusion is also supported by the additional fact<sup>16</sup> that the adsorption of La, Ce, Pr and Tb using a carboxylic cation-exchange resin [Amberlite IRC (La<sup>3+</sup>)] in dilute lanthanum chloride solutions decreased with increase in  $Z$  and that there appeared to be a linear relationship between the selectivity and the ionic radius, although it is well known that cation-exchange systems using various organic complexing agents as eluents usually give the opposite order of adsorption.

Fig. 1 shows the variation of separation factors

$$\left\{ \text{defined as } \left[ \frac{1}{R_{F(Z)}} - 1 \right] / \left( \frac{1}{R_{F(64)}} - 1 \right) \right\}, \alpha(Z/64),$$

for the lanthanoids with  $Z$  on silica gel in 1 mol/dm<sup>3</sup> NH<sub>4</sub>NO<sub>3</sub> solution. This curve is approximately divided into four tetrads, two on either side of Gd ( $Z = 64$ ), as found by Peppard *et al.*<sup>17</sup> for the tetrad effect in liquid-liquid extraction and partition chromatography in the systems composed of HDEHP or 2-ethylhexylphenylphosphonic acid (HEH $\phi$ P) and HCl or HNO<sub>3</sub>. Moreover, the variation of  $\alpha$  with  $Z$  in the present system closely parallels the change with  $Z$  in the number of coordinated nitrate ligands in nitrate complexes of the lanthanoids<sup>18</sup>, and also corresponds to the variation with  $Z$  of the standard free energy changes (relative to that for La) of extraction with the HDEHP-HNO<sub>3</sub><sup>19,20</sup> and TBP-HNO<sub>3</sub><sup>21</sup> systems. From these similarities, it seems reasonable to conclude that the decrease in the  $R_F$  values with increasing  $Z$  in the present system depends principally on the changes in ionic radii due to the lanthanoid contraction and that the uneven variation of the separation

factors with  $Z$  is closely related to the configurations of the  $f$  electrons, which are reflected in the changes with  $Z$  in the coordination numbers<sup>18,22,23</sup> and the thermodynamic and transport properties<sup>19-21</sup>.

*Effect of salt concentration on  $R_F$  values.* The  $R_F$  values of the rare earths (except Sc) first increase with increasing concentration of the  $\text{NH}_4\text{NO}_3$  solutions, pass through a broad maximum in the concentration range 2–4 mol/dm<sup>3</sup> and then decrease gradually with further increase in the salt concentration. The variation of the  $R_F$  values with  $\text{NH}_4\text{NO}_3$  concentration is greater with the middle lanthanoids (Sm to Dy), as can be seen in Table I. With  $\text{NH}_4\text{NO}_3$  solutions of lower salt concentration (less than 2 mol/dm<sup>3</sup>), a plot of

$$R_m \left[ \text{defined as } \log \left( \frac{1}{R_F} - 1 \right) \right]$$

vs.  $\log[\text{NO}_3^-]$  provides approximately a straight line with a slope of  $-1$  for the middle lanthanoids (Ln), so that the cation exchange reaction may be as follows:



Accordingly, the increase in the  $R_F$  values at lower concentrations of the salt can be explained as resulting from the competition of cation-exchange adsorption between  $\text{NH}_4^+$  and  $\text{LnNO}_3^+$ . On the other hand, the decrease in the  $R_F$  values at higher concentrations seems to be primarily responsible for a decrease in the effective concentration of water through hydration of the salt concerned.

### Separation

The most outstanding characteristic of the present TLC system is that the differences in  $R_F$  values of some lanthanoids with adjacent atomic numbers are large enough to resolve them clearly.

The  $R_F$  data in Table I suggest that  $\text{NH}_4\text{NO}_3$  solutions with concentrations lower than 1 mol/dm<sup>3</sup> are more favourable for the separation of lighter lanthanoids (La to Dy), and  $\text{NH}_4\text{NO}_3$  solutions with concentrations higher than 2 mol/dm<sup>3</sup> for

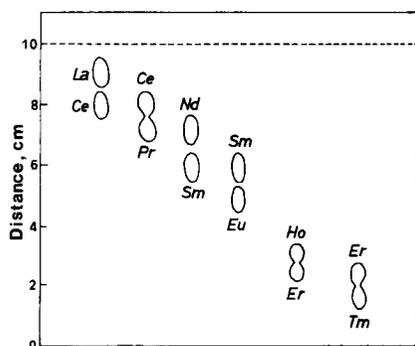


Fig. 2. Separation of adjacent pairs of lanthanoids on silica gel by development with 1 mol/dm<sup>3</sup> ammonium nitrate solution. -----, Solvent front.

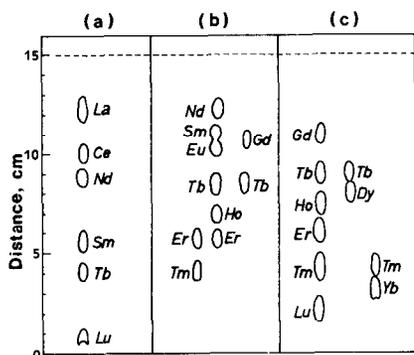


Fig. 3. Separation of binary and multi-component mixtures containing neighbouring lanthanoids. Solvent: (a) 0.5; (b) 2; (c) 4 mol/dm<sup>3</sup> NH<sub>4</sub>NO<sub>3</sub> solution. -----, Solvent front.

that of heavier lanthanoids (Nd to Lu), although the selection of the concentration is rather arbitrary.

Typical thin-layer chromatograms for the separations of binary and multi-component mixtures containing a few adjacent pairs of lanthanoids are given in Figs. 2 and 3. The validity of the separations of each mixture was confirmed by visual comparison with the same amounts of standards chromatographed alongside the sample on the same plate. The  $R_F$  values of the metal ions chromatographed in mixtures were in good agreement with those obtained individually. All the metals gave well defined spots under the experimental conditions used.

Any chromatographic system consisting of silica gel and one of several salt solutions, in addition to the present system, should also provide unusual and effective procedures for separating the rare earths.

## REFERENCES

- 1 U. A. Th. Brinkman, G. de Vries and R. Kuroda, *J. Chromatogr.*, 85 (1973) 187.
- 2 D. Jänchen, *Thin-Layer Chromatography, Cumulative Bibliography, Volume 4, 1973-77*, Camag, Muttenz, 1977, p. 271.
- 3 T. B. Pierce and R. F. Flint, *Anal. Chim. Acta*, 31 (1964) 595.
- 4 T. B. Pierce and R. F. Flint, *J. Chromatogr.*, 24 (1966) 141.
- 5 H. Holzapfel, Le Vief. Lan and G. Werner, *J. Chromatogr.*, 20 (1965) 580.
- 6 H. Holzapfel, Le Vief Lan and G. Werner, *J. Chromatogr.*, 24 (1966) 153.
- 7 T. Shimizu and R. Ishikura, *J. Chromatogr.*, 56 (1971) 95.
- 8 A. Daneels, D. L. Massart and J. Hoste, *J. Chromatogr.*, 18 (1965) 144.
- 9 K. Ishida, *Bunseki Kagaku*, 19 (1970) 1250.
- 10 E. Hohmann, M. Rafizadeh and H. Specker, *Fresenius Z. Anal. Chem.*, 286 (1977) 50.
- 11 K. Jung and H. Specker, *Fresenius Z. Anal. Chem.*, 288 (1977) 28.
- 12 K. Jung, M. Oberscheidt and H. Specker, *Fresenius Z. Anal. Chem.*, 288 (1977) 288.
- 13 K. Jung and H. Specker, *Fresenius Z. Anal. Chem.*, 289 (1978) 48.
- 14 K. Jung, J. Mauer, J. Urlichs and H. Specker, *Fresenius Z. Anal. Chem.*, 291 (1978) 328.
- 15 K. Jung and H. Specker, *Fresenius Z. Anal. Chem.*, 300 (1980) 15.
- 16 R. Arnold and L. B. S. Hing, *J. Chem. Soc. A.*, (1985) 306.
- 17 D. F. Peppard, C. A. A. Bloomquist, E. P. Horwitz, S. Lewey and G. W. Mason, *J. Inorg. Nucl. Chem.*, 32 (1970) 339.
- 18 H. Goebel and H. Specker, *Fresenius Z. Anal. Chem.*, 316 (1983) 253.
- 19 I. Fidelis and S. Siekierski, *J. Inorg. Nucl. Chem.*, 29 (1967) 2629.
- 20 S. Siekierski, *J. Inorg. Nucl. Chem.*, 32 (1970) 519.
- 21 I. Fidelis, *J. Inorg. Nucl. Chem.*, 32 (1970) 997.
- 22 H. Kanno and J. Hiraishi, *Chem Phys. Lett.*, 75 (1980) 553.
- 23 H. Kanno and J. Hiraishi, *J. Phys. Chem.*, 88 (1984) 2787.