

SEPARATION OF THE RARE EARTH ELEMENTS BY ION-EXCHANGE CHROMATOGRAPHY

I. THE USE OF $\text{NH}_4^+ - \text{H}^+$ DEVELOPMENT COLUMNS

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Rare earth cations have similar affinities for ion-exchange materials, and separation methods based on difference in affinity have met with little success^{1,2}. Modern methods of separating these elements depend on the use of complexing agents³. This method was used for separating and identifying tracer quantities of fission product rare earths^{4,5}. The underlying theory of the method was also established. If two rare earth cations, Ln_1^{3+} and Ln_2^{3+} have association constants K_1 and K_2 for a ligand Y^{n-} , then the separation factor between the two elements (K_s) is K_2/K_1 ⁶. Separation is thus dependent on differences in affinity between the individual rare earth cations and the ligand.

To separate the rare earth elements in quantity, it is necessary to use the chromatographic technique of displacement development. This requires large column loadings, in contrast to the trace loadings used for fission product analysis. Two methods have been proposed for establishing development conditions, using amino-carboxylic acids as the complexing agent. Both use two separately loaded ion-exchange columns, which are coupled together in series before elution. The rare earth mixture is loaded to the first column. FITCH and LORIERs both used a second column in the NH_4^+ form⁷⁻⁹, while SPEDDING used metal-loaded columns (*e.g.* Fe^{3+} , Cu^{2+})^{10,11}.

The method used in the present work is similar to the first of the procedures described above, with, however, significant modifications. If ion-exchange columns loaded with Ln^{3+} ions are eluted with solutions of the ammonium salts of nitrilotriacetic acid (TRILO) or ethylenediaminetetraacetic acid (EDTA), lanthanons are eluted from the resin as complexes $\text{Ln}(\text{LnA}_2)$ for TRILO, and $\text{Ln}(\text{LnY})_3$ for EDTA, where $\text{A} = \text{TRILO}$ and $\text{Y} = \text{EDTA}$ (Table I, columns 4 and 5).

The separation obtained under these conditions was poor. Fig. 1 shows an elution curve for the light earth material didymium oxide. This is due to a part of the lanthanon being eluted in cationic form as a counter-ion to the complex anions. It is known that lanthanon cations have similar affinities for ion-exchange materials (see refs. 1, 2 and Table VII).

This difficulty was overcome by using a column loaded with a controlled mixture of ammonium and lanthanon ions. Varying loadings were applied to ion-exchange columns by using the relative affinity data in Table VII, (see experimental section).

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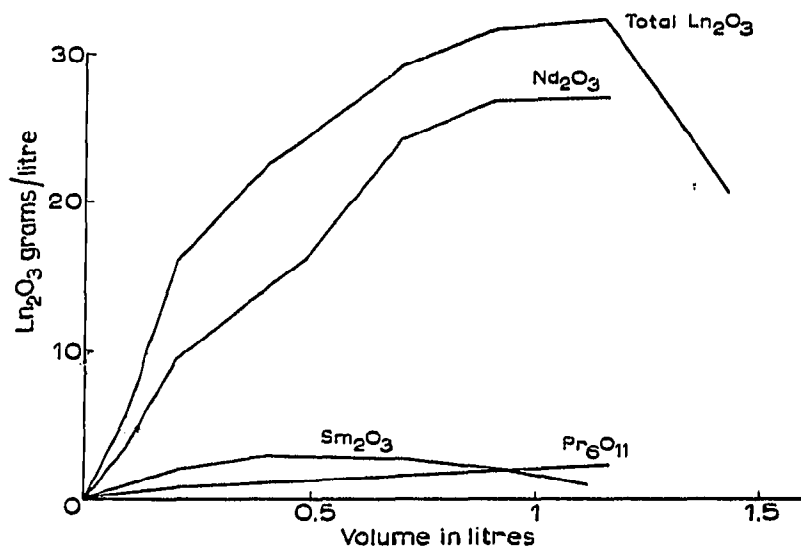


Fig. 1. Elution of 100% lanthanon loaded column. Eluant = 0.2 M TRILO in 0.5 N NH_3 .

The ammonium ion does not form complexes with TRILO or EDTA, hence ammonium salts of the corresponding anionic complexes were formed on elution. The pH of the eluate depended on the lanthanon loading of the cation-exchange column, and, with TRILO, some control could be obtained by varying the eluant ammonium ion concentration. This was not possible with EDTA solutions, where use of less than the stoichiometric quantity of base caused blocking of the column by a precipitate of the acid. Some typical results are shown in Table II.

In all cases, visual indication of separation was obtained, and an elution curve is shown in Fig. 2. This differed considerably from the first case, and is due to the formation of anionic complexes under these conditions. When heavy earth-ammonium ion mixtures were eluted in the same manner, the anionic complexes formed had pH values from 0.2 to 0.4 units lower than in corresponding experiments with the

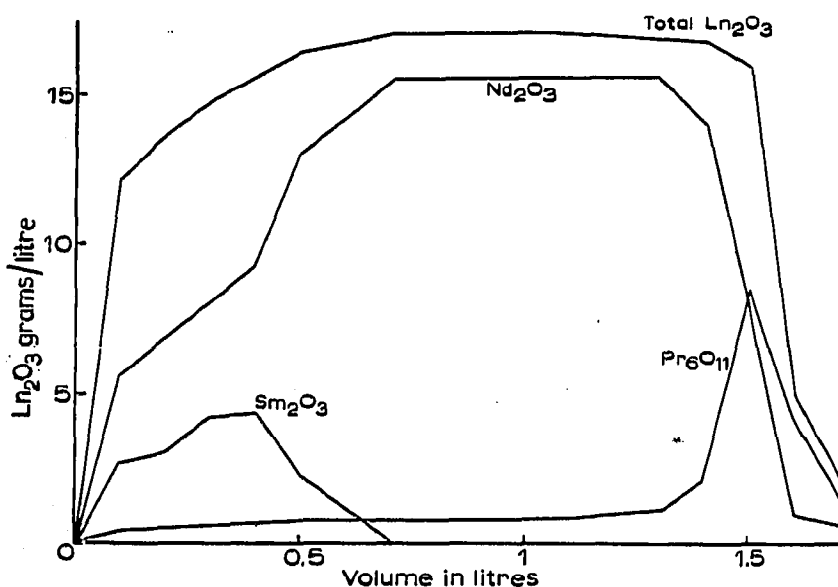


Fig. 2. Elution of $\text{Ln}^{3+}-\text{NH}_4^+$ loaded column (50% equivalents lanthanon). Eluant = 0.2 M TRILO in 0.5 N NH_3 .

TABLE I
ELUTION OF LANTHANON-LOADED CATION EXCHANGE COLUMNS WITH
COMPLEXING AGENT SOLUTIONS

Reagent	Eluant concentration (moles/l)	Eluant (NH ₄ ⁺) (moles/l)	Eluate Ln ₂ O ₃ (moles/l)	Calculated Ln ₂ O ₃ (moles/l)	Eluate pH
TRILO	0.2	0.5	0.193	0.20	2.03
	0.1	0.25	0.093	0.10	2.12
	0.1	0.3	0.108	0.10	3.90
EDTA	0.1	0.4	0.133	0.133	2.40

TABLE II
ELUTION OF Ln³⁺-NH₄⁺ LOADED CATION EXCHANGE COLUMNS
WITH COMPLEXING AGENT SOLUTIONS

Reagent	Lanthanon loading (% equiv.)	Eluant concentration (moles/l)	Eluant (NH ₄ ⁺) (moles/l)	Eluate pH	Eluate (NH ₄ ⁺) (moles/l)	Eluate Ln ₂ O ₃ (moles/l)
TRILO	80	0.2	0.5	2.45	0.134	0.130
	54	0.2	0.5	2.65	0.197	0.107
	38	0.2	0.5	2.80	—	0.094
	54	0.2	0.58	2.90	0.193	0.118
	54	0.2	0.4	2.50	—	0.084
	54	0.1	0.25	2.80	—	0.046
EDTA	54	0.1	0.4	3.0	0.101	0.100

TABLE III
ELUTION OF Ln³⁺-NH₄⁺ (HEAVY EARTH FRACTIONS) WITH 0.1 M EDTA SOLUTIONS

Fraction No.	Yttrium oxide					Xenotime				
	Yb ₂ O ₃ %	Tm ₂ O ₃ %	Er ₂ O ₃ %	Ho ₂ O ₃ %	Dy ₂ O ₃ %	Yb ₂ O ₃ %	Tm ₂ O ₃ %	Er ₂ O ₃ %	Ho ₂ O ₃ %	Dy ₂ O ₃ %
1	3.5	1.5	18	4	20	91	5.6	7.7	—	—
2	0.1	0.1	5	4	20	85	8.2	18.7	tr	3.1
3			0.1	1.5	30	21.5	3.5	33.4	—	4.7
4					35	3	—	4.2		7

light earths. This is due to the formation of stronger complexes between EDTA and the heavy earths. Results obtained by eluting two heavy earth fractions with EDTA solutions are shown in Table III; each eluate was divided into ten equal fractions, and the analysis of the first four is given.

Both of the heavy earth fractions contained a large proportion of yttrium. In each case the heavy earth elements as far as holmium were concentrated with the first third of the eluate.

The lanthanon anionic complexes formed on the first column have a low pH, which varied with the lanthanum-ammonium loading of the column. The NH_4^+/H^+ ratio of these solutions must be determined experimentally, since the relative affinity of the $\text{Ln}^{3+}-\text{NH}_4^+$ ions for the resin does not obey a mass action law. For optimum conditions, it is necessary to condition the development column to the same NH_4^+/H^+ ratio; there is also a lower limit, since if the H^+ loading of the development column is too great the complexing agent is precipitated. Conditions for loading the rare earth column and conditioning the development column in one operation are described in the experimental section.

When the lanthanon complexes pass to the development column, cationic lanthanon is exchanged to the resin phase. At the same pH, weak complexes have a greater cation content than stronger complexes, which tend to the solution phase and are eluted first from the column. The pH of the eluate increased in the development column, owing to the exchange of lanthanon cations for ammonium ions, and the lanthanon content decreased.

When elution was carried out with the stoichiometric salts of TRILO or EDTA, poor separations were obtained and the eluates had pH values from 1 to 2 units greater than those shown in Table II. This difficulty was overcome by buffering the eluant solutions. With TRILO, control was effected by adjusting the $\text{NH}_4^+:\text{com-}$

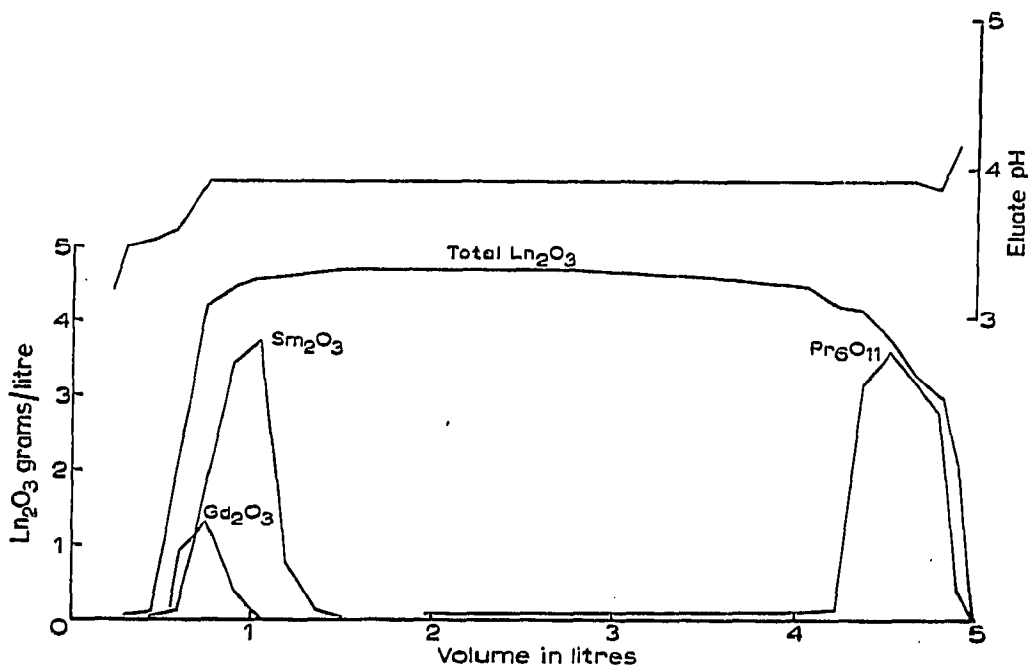


Fig. 3. Elution of light earth oxide through a NH_4^+-H^+ form development column. Eluant = 0.1 M TRILO in 0.25 N NH_3 .

TABLE IV
SEPARATION OF XENOTIME FRACTION WITH 0.05 M EDTA + 0.1 M HCOOH

Fraction No.	Yb ₂ O ₃ %	TmO ₃ %	Er ₂ O ₃ %	Ho ₂ O ₃ %	Dy ₂ O ₃ %	Sm ₂ O ₃ %
1	80.5	5.8	13.8	—	1	
2	58	7.2	26	Tr	5	
3	42.7	14	20	Tr	14.5	
4	4	2	2	—	16	
5					2	
6					0.5	
7					—	1

plexing agent ratio, while formic acid (pK 3.75) was added to the EDTA solutions. The increase in pH of the eluate was then limited to 0.5 unit, and light earth separations of the type shown in Fig. 3 were obtained.

Elution of the rare earth elements rapidly followed "break-through" of the eluate. The major component (Nd₂O₃) was > 99 % pure, and the lanthanon content of the eluate half that required for a stoichiometric anionic complex. A second elution of the neodymium fraction by the same technique gave a > 99.9 % product.

The method was less successful when applied to heavy earth materials. The results obtained by eluting a xenotime fraction with a buffered EDTA solution are shown in Table IV. Satisfactory control of the eluate pH was obtained, but the lanthanon content was 50 % greater than that observed in Fig. 3.

The distribution of lanthanon cations on the development column was examined with a sectioned column apparatus. When the light earth material was eluted, the resin in the development column contained about 5 % equivalents of lanthanon cations; with the heavy earth material, the lanthanon content varied from 2 % to 3 %.

DISCUSSION

The addition of controlled quantities of NH₄⁺ ions to lanthanons on an ion-exchange column forces the rare earths to the anionic form on elution with a complexing agent solution. The partial separations obtained are due to the net reaction $\text{Ln}_1\text{Y}^{1-} + \overline{\text{Ln}_2}^{3+} \rightarrow \text{Ln}_2\text{Y}^{1-} + \overline{\text{Ln}_1}^{3+}$. The concentration of free lanthanon cations under these conditions is very small, so the separations obtained are greater than those obtained with a complete lanthanon loading. The lanthanon band is incompletely developed, and no quantitative estimate of the efficiency of the separation can be made. However, the method is very useful for making preliminary group separations of complex lanthanon mixtures, and in concentrating the less abundant elements¹².

The elution of the light earth elements on an NH₄⁺-H⁺ column with buffered eluates gave results that can be examined quantitatively. The "didymium oxide" contained 74 % Nd₂O₃, while the major fraction of the eluate contained > 99 % Nd₂O₃. (Fig. 3). This gave a 33-fold enrichment, which, taking the Nd-Pr separation factor as 2.5, gave 10 theoretical stages¹³. The equivalent plate height was thus 6 cm; in theory, this should approach the particle size of the resin, but such conditions are rarely approached even in elution experiments.

During elution, the amount of cationic lanthanon found on the development

column was small. A study of the distribution of lanthanon cations between the resin and solutions of rare earth anionic complexes showed the lanthanon content of the resin to vary inversely with solution concentration and pH. Table V shows the equilibrium lanthanon content of resin samples treated with TRILO and EDTA complexes of three lanthanons, adjusted to pH 3.0, the lanthanon content of each solution being 0.05M.

The lanthanon content of the resin decreased from neodymium to erbium, owing to the increased stability of the complexes formed by both reagents in the sequence Nd, Y, Er^{13,14}. They are considerably greater than the amount of lanthanon found in the development column in elution experiments. However, a large excess of reagent was needed to obtain an equilibrium value, and this quantity increased with the stability of the complex. This is due to two effects, the low lanthanon

TABLE V
EQUILIBRIUM LANTHANON CONTENT OF RESIN AFTER TREATMENT WITH
LANTHANON COMPLEXES

Lanthanon	Lanthanon content of resin (% equiv.)	
	TRILO complex	EDTA complex
Nd	55	79
Y	42	56
Er	27	39

cation content of the solutions, and the increase in pH observed when these are exchanged for ammonium ions. Hence smaller quantities of heavy earths are exchanged on the development column, resulting in poor separations.

However, the experimental method described is very convenient for separating the light earth elements, since it is rapid and no metal-rare earth separations are involved. Some advantage would be expected from the use of more dilute eluate solutions, at the expense of prolonging the separation. An examination of weaker complexing agents, which would give an increased reflux on the development column, merits further study.

Materials

EXPERIMENTAL

Three rare earth materials were used in this work. Two of these, "didymium oxide" and "yttrium oxide" were purchased from Thorium Ltd. The third material, xenotime, was extracted from the mineral after fusion with caustic soda. Analysis of these materials is given in Table VI.

TABLE VI
ANALYSIS OF RARE EARTH MATERIALS

Material	CeO ₂	Pr ₂ O ₁₁	Nd ₂ O ₃	Sm ₂ O ₃	Gd ₂ O ₃	Tb ₄ O ₇	Dy ₂ O ₃	Ho ₂ O ₃	Er ₂ O ₃	Tm ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	Y ₂ O ₃
"Didymium"		10.5	74	9.5	6								
"Yttrium"					6.9	1.2	11.9	3.4	6.9	0.3	2.3	0.1	65
Xenotime	0.0	0.1	0.5	1.0	2	1	14.5	2.5	12.5	2	17.2	3	45

Analytical methods for lanthanons

Gravimetric methods were used for the isolation of lanthanon fractions. An excess of oxalic acid was added to the lanthanon solution, the pH adjusted to 2.0, and the precipitate coarsened by heating for 1–2 h. After cooling and filtering the precipitate was ignited in platinum at 800–900° to constant weight. Tests on light and heavy lanthanon fractions showed the recovery to be > 99.9%. If complexing agents were present, the pH of the solution was adjusted to 1.5 and the solution allowed to stand overnight before filtering off the precipitated reagent; lanthanons were determined in the filtrate.

The concentration of lanthanons was determined with a spectrophotometer (Beckman D.U.). Calibration curves were prepared from chloride solutions of "Spec-pure" materials (Johnson Matthey and Co.). Heavy earth fractions from the low-grade "yttrium oxide" were analysed spectrographically using the "iron-flux" method¹⁵.

Complexing agents

EDTA and TRILO were purchased from the Geigy Company and Norman Evans and Rais. The acids were purified by solution in ammonia, treatment with charcoal, and reprecipitation.

The concentration of complexing agent solutions was determined by a modification of SIGGIA's method¹⁶. An aliquot of the solution was boiled with caustic soda to expel ammonia, and pyridine (25 % v/v) was added. After adjusting the pH to 7 with hydrochloric acid, the solution was titrated potentiometrically with a standard copper solution, using a platinum–calomel electrode system. The end-point was indicated by an abrupt change in potential of the order of 100–200 mV.

Relative affinity determinations

A modification of REICHENBERG's method was used¹⁷. Samples (10 ml) of resin were enclosed between two small sinter tubes (porosity 2) joined with a section of P.V.C. tubing. The total exchange capacity of the resin was determined by H⁺ displacement. One column was converted to the NH₄⁺ form and a second to the Ln³⁺ form. Each column was treated with a 10-fold excess of conditioning solution, containing a known

TABLE VII
RELATIVE AFFINITY OF AMMONIUM AND LANTHANON IONS FOR
THE RESIN ZEO-KARB 225

Lanthanon fraction	Solution concentration (Ln ³⁺ + NH ₄) (equiv./l)	Lanthanon concentration (equiv./l)	Lanthanon loading of resin (% equiv.)
"Didymium"	1	0.25	66.3
		0.15	55.5
		0.10	53.3
	2	0.8	71.7
		0.6	63.7
		0.4	49.7
"Yttrium"	1	0.075	46.0
		0.050	45.2
	2	0.4	48.7

ratio of ($\text{Ln}^{3+} + \text{NH}_4^+$) ions. The columns were drained at the pump, and rapidly water-washed to remove excess conditioning solution. They were stripped quantitatively with a potassium-EDTA solution, and ammonia and lanthanon determinations made on the filtrate; in the latter case, two oxalate precipitations were given to minimise potassium occlusion. The ($\text{Ln}^{3+} + \text{NH}_4^+$) content of each column agreed well with the capacity determined by hydrogen displacement, and the ratios in either case were identical, showing that equilibrium had been attained.

Results obtained with two of the lanthanon fractions described in Table VI are summarised in Table VII.

Little difference in affinity was found between the "light" and "heavy" earths. The effect of changing the ionic concentration was qualitatively in agreement with theory, but the results did not fit a mass action law.

Ion-exchange technique

The cation-exchange resin Zeo-Karb 225 (250 μ fraction) was used. It was back-washed to remove fines, and traces of heavy metal were removed by treating the resin, in the ammonium form, with a complexing agent solution.

The elution experiments described in Tables I-III were carried out in columns 60 cm long by 8.5 cm². These were conditioned with an excess of reagents and washed with water before elution. Separation experiments (Fig. 3 and Table IV) were carried out in columns 120 cm long by 8.5 cm². To carry out the loading and conditioning operations together, use was made of the affinity data of Table VII and data obtained by the elution of Ln^{3+} - NH_4^+ columns (Table II). Solution concentrations were selected to give a 50% equivalent lanthanon loading to the first half of the column, and the pH was adjusted to give a suitable $\text{NH}_4^+:\text{H}^+$ ratio. Convenient solution concentrations were 0.1 N $\text{Ln}^{3+} + 0.9$ N NH_4^+ at pH 1.7 or 0.4 N $\text{Ln}^{3+} + 1.6$ N NH_4^+ at pH 1.4. The eluate was sampled with a variable volume fraction collector using a flow rate of 0.5 cm/min.

Distribution of lanthanons on the resin column was examined with a "sectioned column" apparatus. Eight 30 cm \times 8.5 cm² columns were coupled together in series, each column being provided with a 3-way tap for drainage. The columns were loaded and washed in the usual way. Elution was carried out until the complexing agent solution was detected in the eluate. The individual columns were then disconnected, drained at the pump, and the distribution of lanthanon between the two phases was determined.

Preparation of lanthanon anionic complexes

MARSH'S method was used for the preparation of a number of lanthanon anionic complexes¹⁸. The complexing agent and a small excess of lanthanon oxide (1-2%) was refluxed with stirring, and ammonia added dropwise. After heating for 1-2 h a small residue of lanthanon oxide remained undissolved. This was filtered off after boiling off the excess ammonia. Neutral solutions were obtained, analysis agreeing with the composition NH_4LnY for the EDTA complexes, and $(\text{NH}_4)_2\text{H LnA}_2$ for TRILO complexes.

The data of Table V were obtained by the technique used for determining the affinities of $\text{Ln}^{3+}:\text{NH}_4^+$ ions. In these cases, the conditioning solutions were lanthanon anionic complexes.

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SUMMARY

Methods for separating the rare earth elements by ion-exchange chromatography are discussed.

The elution of cation-exchange columns, completely loaded with rare earth ions, with complexing agent solutions gave eluates containing cationic and anionic lanthanon. However, if the ion-exchange column was loaded with a controlled Ln^{3+} - NH_4^+ mixture, elution gave predominantly an anionic lanthanon complex. Partial separations are obtained under these conditions, and this was shown to be a useful method for the preliminary concentration of complex lanthanon mixtures.

Conditions for separating the light earths, using an NH_4^+ - H^+ form development column, were established. This method was not successful for separating the heavy earths, and the reasons for this are discussed.

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