

## PARTITION CHROMATOGRAPHIC STUDIES OF AMERICIUM, YTTRIUM AND THE RARE EARTHS IN THE TRICAPRYLYLMETHYLAMMONIUM THIOCYANATE-AMMONIUM THIOCYANATE SYSTEM\*

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## INTRODUCTION

Column partition chromatography has been shown to have certain advantages over liquid-liquid extraction techniques for analytical applications. The multistage nature of the metal complex-ligand exchange in a mobile system gives rise to favorable separations of elements showing only minor differences in chemical behavior. This technique has been successfully applied to the resolution of adjacent rare earth elements using tri-*n*-butyl phosphate (TBP)<sup>1,2</sup>, di-2-ethylhexyl phosphoric acid (HDEHP)<sup>3-7</sup>, and 2-ethylhexyl phenylphosphonic acid (HEHÖP)<sup>8</sup> as the extracting phase fixed on various inert supports. However, the phosphate systems are not effective for a chromatographic actinide-lanthanide group separation inasmuch as partition coefficients for elements in the two series overlap.

Recently, liquid-liquid extraction data<sup>9,10</sup> were presented which show that this group separation can be accomplished using Aliquat-336 (tricaprylylmethylammonium chloride) as the extractant in an ammonium thiocyanate medium. Because of the greater stability of the actinide thiocyanate complexes, they were preferentially extracted by the quaternary ammonium salt. This investigation was undertaken to learn whether column partition chromatography could be advantageously applied to this and other separations. Of secondary interest was a comparison of the partition data with the reported strong base anion exchange results<sup>11</sup> for the actinide and lanthanide elements, using ammonium thiocyanate as the mobile aqueous phase.

## REAGENTS AND MATERIALS

Plaskon, type CTFE 2300, a trifluorochloroethylene polymer, was obtained from Allied Chemical Corp. as a fine powder and was used without any further treatment.

Aliquat-336 (tricaprylylmethylammonium chloride) has the general formula  $R_3CH_3NCl$ , where R is a mixture of C<sub>8</sub> and C<sub>10</sub> carbon chains, with the C<sub>8</sub> predominating. The reagent grade product is available as a highly viscous liquid from General Mills Inc. with a minimum assay of 88 % in the active ingredient and an average molecular weight of 442. No additional purification was attempted.

\* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

The rare earth standards were prepared at a concentration of 1 mg/ml by the dissolution of high purity oxides in hydrochloric acid. The americium-241 tracer had an assayed concentration of  $1.1 \cdot 10^8$   $\alpha$ -counts  $\text{min}^{-1}\text{ml}^{-1}$ .

All other chemicals were reagent grade. Ammonium thiocyanate was chosen as the aqueous phase, since a minimum inorganic salt content simplified the spectrographic analysis procedure.

Conventional 10 and 25 ml volumetric glass burets were satisfactory as chromatographic tubes. Column packings were supported by polypropylene wool.

## EXPERIMENTAL

Mixtures of Aliquat-336 in xylene were prepared on a weight-percent basis and were stored in glass bottles. The packing for the chromatographic columns was made by manually stirring equal weights of organic extractant and Plaskon polymer support until a uniformly coated mixture was obtained. This preparation was kept at 70° until a constant weight was attained. The weight loss was equivalent to the complete volatilization of the xylene diluent. The resultant product was a homogeneous powder that appeared to be uniformly coated with the amine extractant.

Columns for elution experiments were prepared by slurring a weighed amount of packing with water and pouring it into the chromatographic tubes. The coated particles had a high specific gravity and settled rapidly into a uniform bed free from air bubbles.

For the determination of distribution coefficients, suitable aliquots (50–100  $\mu\text{g}$ ) of several rare earths were combined, taken to dryness, and redissolved in a small volume (0.4 ml or less) of the eluting solution. This mixture was adsorbed at a very slow flow rate onto a previously conditioned column, and the elution was continued at a rate not exceeding 0.5 ml  $\text{cm}^{-2}\text{min}^{-1}$ . Fractions of 1 ml were collected for analysis at the start, and were then increased to larger volumes for higher distribution coefficients. The effluents were acidified with hydrochloric acid and taken to dryness at hot plate temperatures. Any remaining ammonium chloride was removed by sublimation in a flame and the residue was dissolved in 0.5 ml hydrochloric acid. Each fraction was analyzed by the copper spark spectrographic technique<sup>12</sup>, from which the rare earths elution maxima were obtained. A similar procedure was used in the investigation of americium, except that fractions of equal volume were collected throughout a run, and then were  $\gamma$ -counted directly in a NaI (Tl) scintillation counter.

## RESULTS AND DISCUSSION

It is essential that any column packing material to be used in chromatographic separations be prepared in a reproducible form and that columns exhibit a uniform bed density (gram of packing per ml of packing) free from pressure zones and trapped air bubbles. Furthermore, the extracting phase must be held very strongly to the inert support, so that no changes in capacity occur during repeated elutions. These conditions were investigated by preparing columns at different times, from different extractant mixture batches, and in different sizes. In each case reproducible distribution coefficients were obtained within the limits of experimental error. The material showed excellent stability, some columns being used for as many as 15 elutions with no appar-

ent loss in exchange capacity. A check was made on bed densities, containing the 50 wt. % Aliquat-336 packing material. A nearly constant value (0.6 g/ml) was obtained for columns of several different sizes and dimensions, showing that the simple preparative technique resulted in uniform column beds. An additional prerequisite for a sharp separation by elution chromatography requires a fast reaction step between the fixed extractant and the complex in the mobile aqueous phase. MOORE<sup>9</sup> has shown that in liquid-liquid extraction using Aliquat-336, equilibrium was attained in less than one minute. Fig. 1 shows a typical elution curve for americium-241. Its symmetry tends to substantiate favorable ligand-metal exchange kinetics during column operation.

#### *Distribution coefficients and separation factors*

In liquid-liquid extraction the distribution ratio,  $D$ , of an element,  $M$ , is defined as  $D = \text{concentration of } M \text{ in the organic phase} / \text{concentration of } M \text{ in the aqueous phase}$ , irrespective of the organic phase composition. In the present experiments the distribution of an element was likewise related to the amount of the extractant mixture and not to that of the amine retained by the inert support. For example, 0.75 g of the dried column packing, prepared from the 50 wt. % Aliquat-336 in xylene mixture, originally consisted of 0.5 g of the organic phase and 0.5 g of Plaskon. The distribution coefficient for the column experiments is defined as  $K_d = \text{ml of effluent at elution maximum} / \text{g of extractant mixture}$ . Therefore, for the above example, the

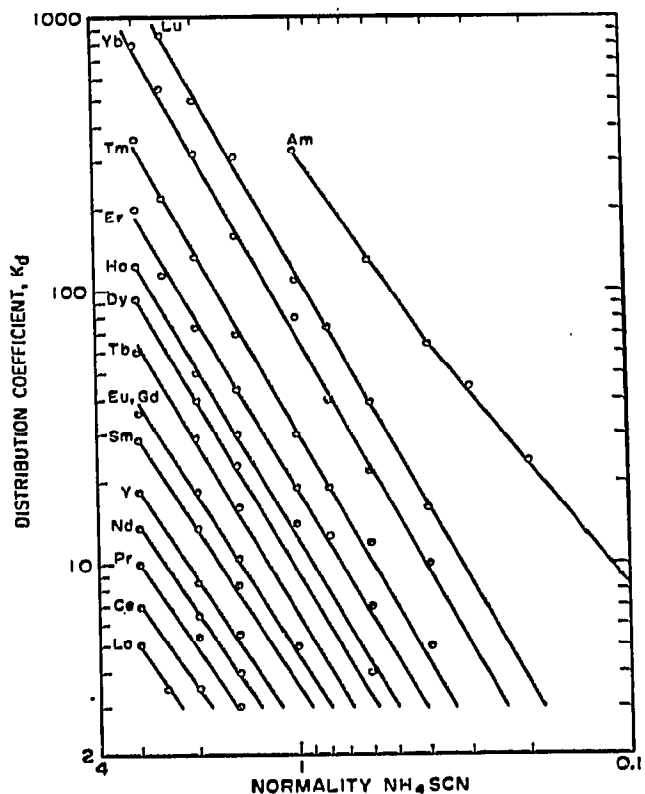
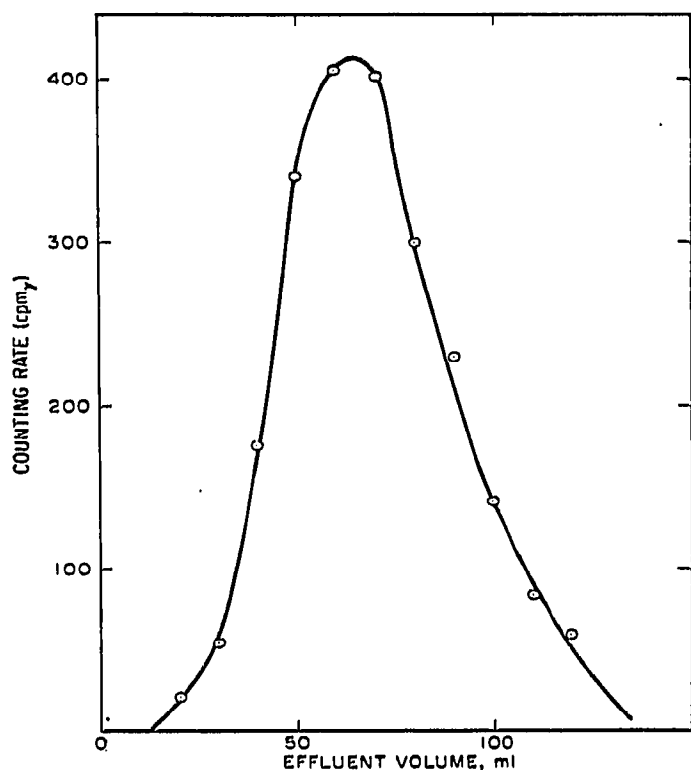


Fig. 1. Elution curve for  $^{211}\text{Am}$  with 0.6  $N$   $\text{NH}_4\text{SCN}$ . Column  $0.34 \text{ cm}^2 \times 3.6 \text{ cm}$ ; flow rate  $0.5 \text{ ml cm}^{-2}\text{min}^{-1}$ .

Fig. 2. Distribution coefficients as a function of  $\text{NH}_4\text{SCN}$  concentration.

$K_d$  was obtained by dividing by 0.5 the volume in ml (corrected for the interstitial liquid, 0.75 ml) at which a metal appeared at a maximum concentration.

The logarithmic relationships between distribution coefficients and ammonium thiocyanate concentrations plotted in Fig. 2 give a family of straight lines with a positive slope of about 2. Europium and gadolinium were found to fall in the same position on this graph. The liquid-liquid extraction data of GERONTOPOULOS *et al.*<sup>10</sup> showed these two adjacent rare earth elements to be reversed, a result not verified by the column elution experiments. The linearity of the discussed logarithmic relationship is consistent with the findings of SURLS AND CHOPPIN<sup>11</sup>, who studied this system using a strong base anion exchanger. The data obtained by partition chromatography are more than an order of magnitude higher than those using an ion exchange resin. This difference might be explained by the fact that, in the present experiments, the active exchange groups are fixed on the surface of an inert carrier and are thus more readily accessible for an exchange reaction with the mobile aqueous phase. A diffusion into the resin matrix network is not necessary, thus leading to a more efficient utilization of available exchange sites. This condition might also be one of the reasons for faster equilibrium rates obtained in these experiments than were generally noted with ion exchangers in a thiocyanate medium.

The  $K_d$ 's generally increase with atomic number, except for the europium-gadolinium pair. In this investigation yttrium was found to fall approximately in the expected promethium position. Promethium was omitted from this study. The separation factors for adjacent elements vary over a very narrow range from 1.3 to 1.6 for lanthanum through erbium. In the region of erbium through lutetium there is a marked increase in separation factors to about 2. Even though the distribution coefficient ratios for adjacent rare earths are higher using acidic phosphates<sup>3-8</sup> as the extracting phase, useful separations within the lanthanide group could be performed using an amine extractant in a thiocyanate aqueous medium. The experimental results further indicate that a separation factor of about 60 can be realized for the 4f and 5f analogs, europium and americium, respectively.

#### *Extractant concentration dependence*

Fig. 3 shows the change in distribution coefficients with Aliquat-336 concentration at constant ammonium thiocyanate for a selected number of rare earth elements. The relationship is linear in the logarithmic representation and the lines have a slope of approximately 1. This result indicates that the metal to ligand ratio is equal to 1. This interpretation is consistent with the liquid-liquid extraction data reported for americium<sup>10</sup>.

Investigators studying the HDEHP (ref. 3) and HEHOP (ref. 8) systems by partition chromatography have shown that the amount of the extracting agent in the stationary phase greatly affects the effective plate height in the column. They showed that at low extractant loadings lower plate heights, and thus better separations, were obtained. It is anticipated that a similar behavior would be noted for the present system. However, no experimental verification was attempted, since high metal capacity of the columns was the primary interest of this investigation.

#### *Acid dependence*

In liquid-liquid extraction studies using Aliquat-336, MOORE<sup>9</sup> reported that

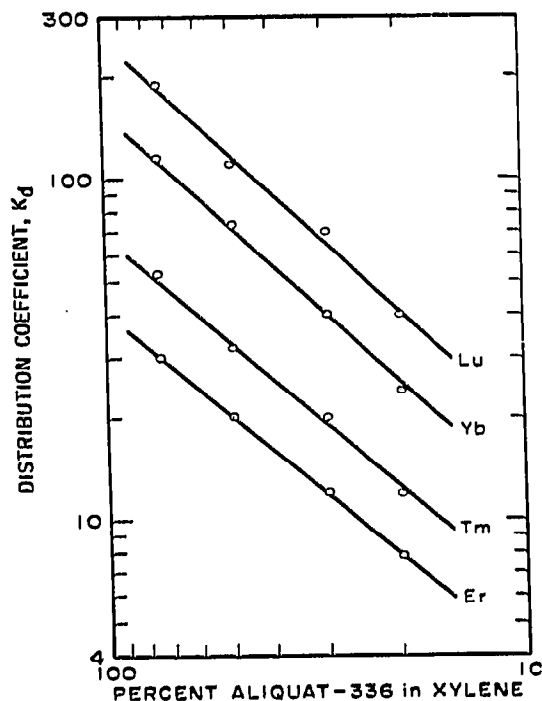


Fig. 3. Distribution coefficients as a function of Aliquat-336 concentration at 1 N  $\text{NH}_4\text{SCN}$ .

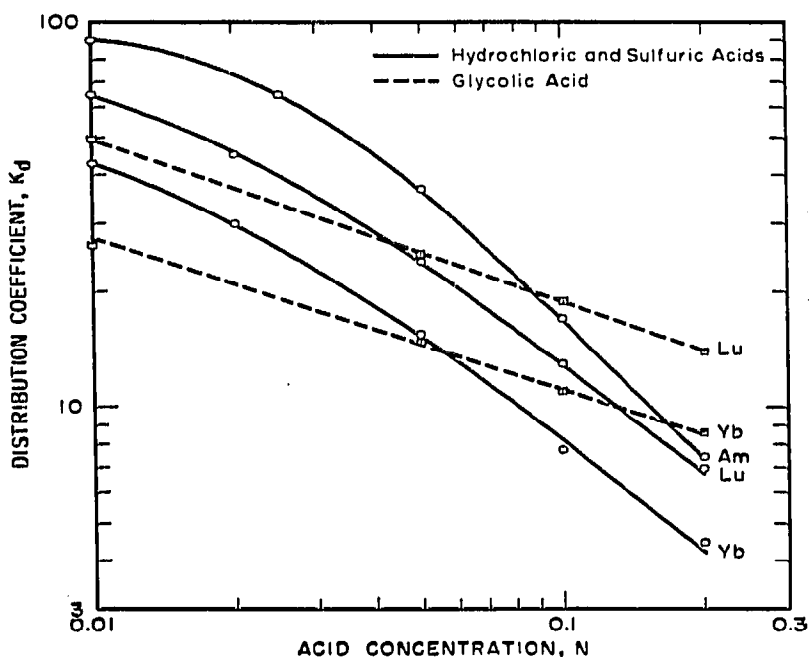


Fig. 4. Distribution coefficients as a function of acid concentration at constant  $\text{NH}_4\text{SCN}$  concentration. 1 N  $\text{NH}_4\text{SCN}$  for Lu, Yb; 0.6 N  $\text{NH}_4\text{SCN}$  for  $^{241}\text{Am}$ .

the addition of mineral acids to the thiocyanate aqueous phase resulted in an enhanced actinide-lanthanide separation. It was of interest to learn whether in column experiments this effect would likewise become apparent. Fig. 4 represents results obtained using glycolic, hydrochloric and sulfuric acids at constant thiocyanate concentrations. The data indicate that in all cases a decrease in distribution coefficients occurred with an increase in acidity. Since hydrochloric and sulfuric acids produce identical curves for representative rare earths, it suggests that the hydrogen ion concentration and not the type of anion produces the observed effect. The relative decrease in  $K_d$  as a function of acid concentration appears to be somewhat greater for americium. However, since the representative actinide element was studied at a lower thiocyanate concentration, no general conclusion can be drawn from this investigation as to the stability of the extractable complexes as a function of acidity within the two groups. Glycolic acid was included in the study as an example of a weak acid and shows a similar effect to the mineral acids, although to a lesser degree. It was anticipated that an increase in distribution coefficients would be noted with this reagent, since HOLM *et al.*<sup>13</sup> have shown that the glycolate ion forms negatively charged chelates in aqueous solutions at controlled pH. The absence of a positive synergism indicates that in the mixed aqueous medium the formation of adsorbable negative complexes was inhibited.

### Separations

Utilizing the experimental distribution coefficient data, several separations were attempted within the lanthanide group. Columns containing the 50 wt. % Aliquat-336 extractant were used for this investigation. Figs. 5 and 6 represent typical elution

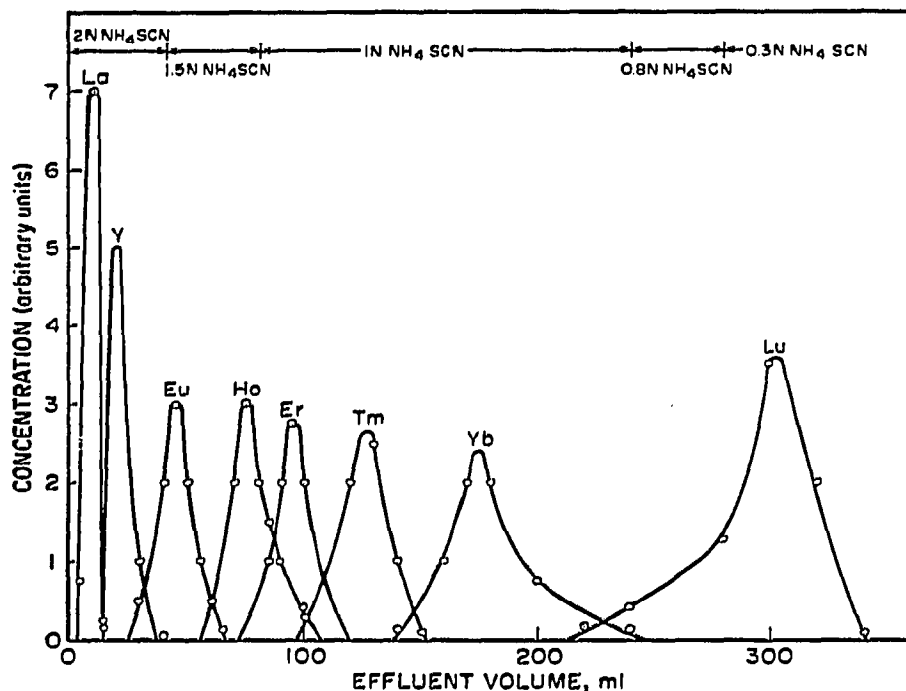


Fig. 5. Separation of rare earths. 1 mg of each element; column  $0.34 \text{ cm}^2 \times 14.7 \text{ cm}$ ; flow rate  $0.5 \text{ ml cm}^{-2} \text{ min}^{-1}$ .

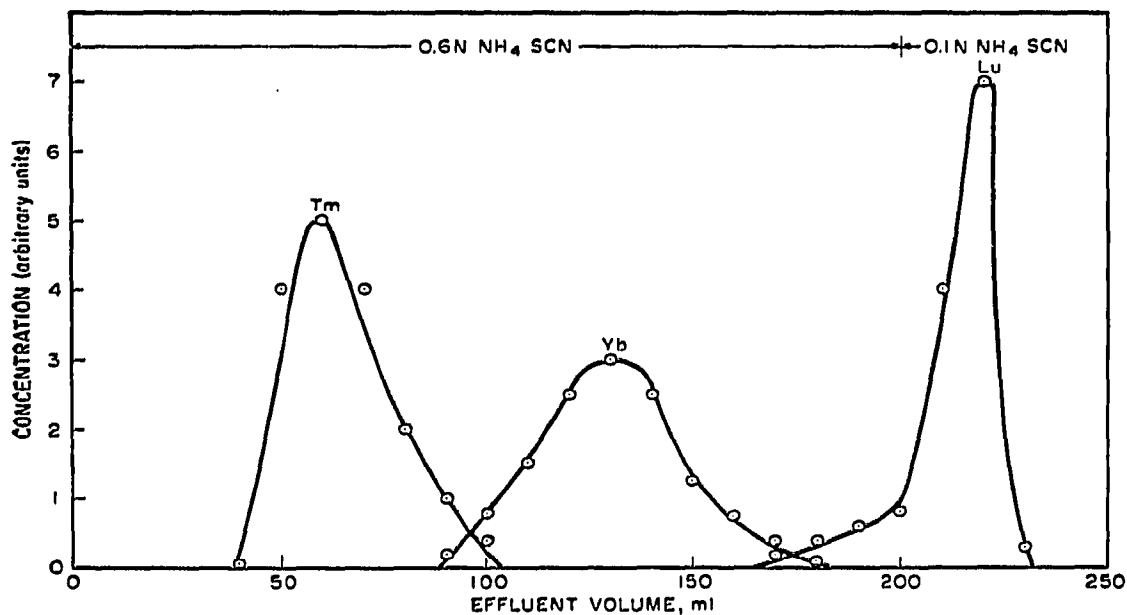


Fig. 6. Separation of rare earths. 2 mg of each element; column  $0.82 \text{ cm}^2 \times 14.5 \text{ cm}$ ; flow rate  $0.4 \text{ ml cm}^{-2} \text{ min}^{-1}$ .

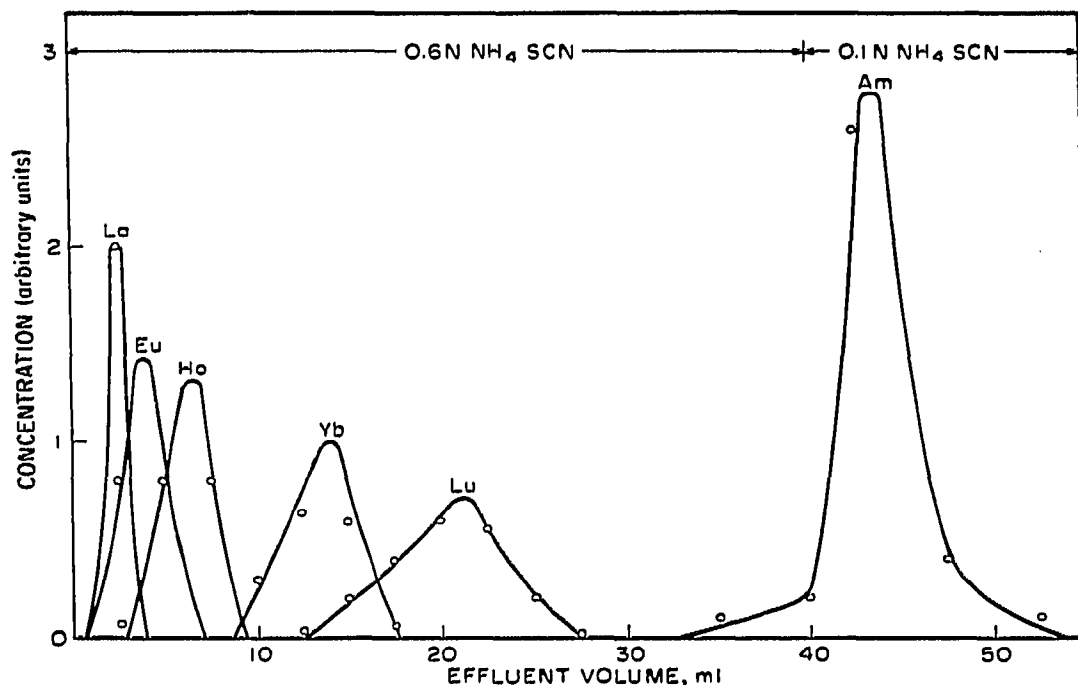


Fig. 7. Separation of rare earths from  $^{241}\text{Am}$ . 0.5 mg of each rare earth;  $1.1 \cdot 10^8$   $\alpha$ -counts/min  $^{241}\text{Am}$ ; column  $0.34 \text{ cm}^2 \times 3.6 \text{ cm}$ ; flow rate  $0.2 \text{ ml cm}^{-2}\text{min}^{-1}$ .

curves obtained for elements within the rare earth group. It is apparent that some cross contamination of adjacent elements occurs under the chosen conditions. However, a more complete separation could be achieved by additional column passes. The system shows its greatest advantage in the resolution of the actinide-lanthanide groups by a one-pass column elution. Fig. 7 shows the isolation of pure americium-241 from a number of selected rare earth elements. Although only americium was studied as a representative actinide, liquid-liquid extraction data<sup>9</sup> and the similarity to the lanthanide group would lead to the prediction that the higher actinide elements should be more strongly adsorbed. The apparent exception is the americium-curium pair for which MOORE<sup>9</sup> found a reversal. This result is to be expected, since the corresponding 4f analogs, europium and gadolinium, were not separated in this system.

The reported results were obtained using element concentrations essentially at the tracer level. The behavior of the systems at macro loadings has not been studied. Therefore, effects pertaining to radiation damage at high actinide content with a subsequent loss in separation efficiency can only be anticipated. KEENAN<sup>14</sup>, in using the anion exchange-thiocyanate system for the purification of americium and curium, found that the high  $\alpha$ -radiation density of curium-244 adversely affected the separation procedure. Americium-241 could be processed in a satisfactory manner. The required lower thiocyanate concentration in the present system might be expected to show greater radiation resistance, resulting in better performance during separations.

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## SUMMARY

The system Aliquat-336 (tricaprylylmethylammonium thiocyanate)-ammonium thiocyanate was investigated by column partition chromatography. The distribution coefficients for americium, yttrium and the rare earths were found to increase with thiocyanate concentration and percentage of Aliquat-336. A decrease in extraction was noted with increased acidity of the aqueous phase. Separation factors for adjacent rare earth elements ranged from 1.3 to 2.0. Some practical separations using this system are indicated.

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