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Amino Acids as Retaining Agents in Displacement Chromatography of the Rare-Earth Elements

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Summary

The feasibility of using amino acids as retaining agents with ethylenediaminetetraacetic acid (EDTA) eluents in displacement chromatography of the rare-earth elements was studied at 85° to 90°C. Hydroxyethylethylenediaminetriacetic acid (HEDTA) and diethylenetriaminepentaacetic acid (DTPA) were the most effective retaining agents investigated. Elements of atomic numbers 39 and 57 through 68 were effectively retained, whereas elements of atomic numbers 69 through 71 passed through the retaining-agent band. Utilization of HEDTA or DTPA as retaining agents permits the use of 7 to 10 g/liter EDTA eluting solutions, whereas eluting solution concentrations in the 4–4.5 g/liter range are maximum when using hydrogen or copper as retaining agents. Eighty-five per cent recovery of the EDTA eluent collected before rare-earth breakthrough and during elution of lutetium, ytterbium, and thulium, and essentially complete recovery of the HEDTA or DTPA retaining agents, are possible without extensive processing.

INTRODUCTION

The development of new use patterns for the rare-earth elements has focused attention toward improved separation and purification methods for the elements. Ion-exchange chromatographic techniques have found wide application in rare-earth separation problems, and several processes employing different chelating agents and cationic retaining ions have been developed for rare-earth separation (*1*).

Ethylenediaminetetraacetic acid eluents and copper-retaining ions were used by Spedding (*2*) and Powell (*3*) in a process for separating the rare-earth elements. The maximum concentration of EDTA was approximately 0.015 mole/liter, and close control of the system pH was required to prevent precipitation of insoluble compounds. Copper forms a very stable chelate with EDTA, and recovery of copper and EDTA is difficult. Powell (*4*) and Asher (*5*) reported using hydrogen as a retaining ion with the water-soluble amino acids, HEDTA and DTPA. The effectiveness of hydrogen as a retaining ion with water-insoluble EDTA at 90°C was demonstrated by Lindstrom (*6*). The use of hydrogen as a retaining ion results in adsorption of a zwitterion form of the eluent on that portion of the hydrogen-cycle resin immediately following the rare-earth-cycle resin, and the first portion of effluent from the columns is void of any eluent. As the rare-earth band moves through the system, the adsorbed eluent is eluted in a second portion of column effluent with a concentration 1.5–2.5 times greater than that of the eluting solution entering the columns. Rare-earth ions appear in the column effluent after passage of the adsorbed eluent. The increase in concentration of chelating agent limits the concentration of EDTA that may be used to 4 g/liter without exceeding the solubility of the free acid form of EDTA at 90°C.

The present study was initiated to determine whether the detrimental adsorption of EDTA zwitterions on resin could be prevented by utilizing a water-soluble amino acid zwitterion as a retaining agent, thus maintaining a constant concentration of EDTA in the eluting solution during passage through the columns.

EXPERIMENTAL PROCEDURE

Ion-exchange columns consisted of glass tubes 122 cm long and having an inside diameter of 1.6 cm. The columns were filled to a height of 110 cm with 50- to 100-mesh ammonium-cycle nuclear sulfonic resin, cross-linked with 4% divinylbenzene (Dowex 50 X-4 resin).* The column temperature was maintained at 85° to 90°C with heating tapes and was monitored with a thermistor probe extending about 3 in. into the bottom of the resin bed. A polyethylene displacement pump was used to force the eluent through the resin bed.

Charge solutions were prepared by dissolving mixtures of rare-earth oxides in HCl. Analysis of charge stocks is given in Table 1. The rare-earth mixture was adsorbed on the first of three columns that were

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* Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 1

Analysis of Charge Stocks

Series I		Series II	
Element	Oxide basis, wt. %	Element	Oxide basis, wt. %
Dysprosium	15	Cerium	4
Erbium	30	Lanthanum	19
Holmium	20	Neodymium	48
Lutetium	1	Praseodymium	21
Thulium	8	Samarium	4
Ytterbium	24	Heavier rare-earth elements	4
Yttrium and light rare-earth elements	2		

connected in series. Alanine, DL-aspartic acid, DTPA, glycine, HEDTA, L-lysine, and DL-methionine were investigated as retaining agents. The retaining agent was dissolved in hot water and adsorbed on hydrogen-cycle resin in the second and third columns in the series.

The eluting solution was prepared by dissolving 7, 10, and 15 g/liter EDTA in aqueous ammonia and adjusting to the desired pH. Vacuum-degassed water was used in preparing the eluting solution to minimize subsequent formation of bubbles in the heated columns. Eluting flow through the columns was 5 ml/min/cm^2 of column cross-sectional area and was from top to bottom through each column in the series.

Rare-earth elements in the effluent were precipitated as oxalates, ignited to oxides, and analyzed by X-ray emission spectroscopy.

Concentration of unchelated EDTA in the effluent was determined gravimetrically from the EDTA that precipitated on cooling the column effluents. Concentrations of HEDTA and DTPA were determined by titrating aliquots of the effluent with 0.01 *M* calcium acetate. The concentration of other amino acid-retaining agents was determined by analyzing for nitrogen by the Kjeldahl method.

RESULTS AND DISCUSSION

The initial series of experiments was conducted to determine the degree of rare-earth retention on the resin and the separation efficiency when using an amino acid as a retaining agent and EDTA as an eluent. Rare-earth ions in series I charge stock were eluted through two band lengths of resin on which an amino acid was adsorbed as a retaining agent. Elution was accomplished with a solution of 7 g/liter EDTA and pH 8.5 at 85° to 90°C. Reactions that take place on the resin are represented by the following equations.

Rare-earth ions were adsorbed on ammonium-cycle resin,

$$MCl_3 + 3NH_4R \rightarrow MR_3 + 3NH_4Cl \qquad (1)$$

where M is the rare-earth ion and R represents an exchange site on the resin.

Water-soluble amino acids are adsorbed on hydrogen-cycle resin,

$$Z + nHR \rightarrow Z(HR)_n \qquad (2)$$

where Z represents an amino acid and n the number of amine groups in the amino acid.

The ammoniated EDTA eluent passed through the resin in the rare-earth cycle and then through the resin in the amino acid cycle. As the ammoniated EDTA contacted rare-earth-cycle resin, ammonia was deposited on the resin and rare-earth ions were taken into solution:

$$(NH_4)_3HY + MR_3 \rightarrow MHY + 3NH_4R \qquad (3)$$

where Y represents the $EDTA^{4-}$ anion.

The rare-earth–EDTA chelate subsequently contacts amino acid-cycle resin, whereupon the rare-earth ion is redeposited on the resin and amino acid is taken into solution:

$$nMHY + 3Z(HR)_n \rightarrow nH_4Y + 3Z + nMR_3 \qquad (4)$$

Continued elution results in migration of the most stable chelates to the front of the rare-earth band, and separation is achieved.

The exchange capacity of the ion-exchange resin was approximately 1.5 meq/ml. A total of 660 ml of resin was used—220 ml for loading the rare-earth elements and 440 ml for banding the rare-earth ions on the resin. Based on the reactions in Eqs. (1) through (4) going to completion, 0.22 mole of EDTA will pass through the system before any rare-earth elements appear in the effluent. Elution with 7-g/liter EDTA solution will result in collection of a theoretical volume of 9.2 liters of effluent before appearance of rare-earth ions in the column effluent. The quantity of effluent collected before rare-earth breakthrough is a measure of the relative efficiencies of the retaining ions. Table 2 shows that the volume of effluent collected before rare-earth breakthrough ranged from 11 to 54% of the theoretical volume. HEDTA and DTPA were effective retaining agents for rare-earth

TABLE 2

Effluent Volume Collected before Appearance of Rare-Earth Ions in the Effluent

Retaining agent	Volume, liters	Portion of theoretical volumes, %
Alanine	1.4	15
DL-Aspartic acid	2.0	22
DTPA	4.2	46
Glycine	1.0	11
HEDTA	5.0	54
L-Lysine	1.1	12
DL-Methionine	2.0	22

ions of atomic number 68 or less but did not retain thulium, ytterbium, or lutetium. The three heavier ions were separated from the other rare-earth ions by collecting them simultaneously with the last 45–55% of the retaining agent. The other amino acids investigated had no apparent value as retaining agents.

Separation efficiency achieved with the different retaining agents is summarized in Fig. 1 by plotting the percentage of ytterbium in

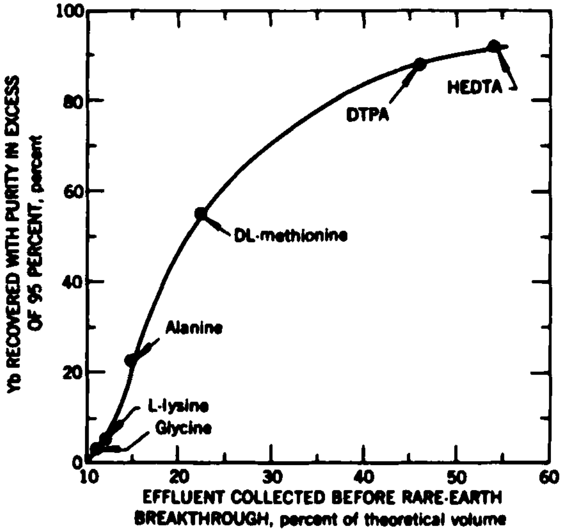

FIG. 1. Effect of effluent volume collected before rare-earth breakthrough on separation. HEDTA—hydroxyethylenediaminetriacetic acid; DTPA—diethylenetriaminepentaacetic acid.

the original charge stock recovered as a column fraction, with a purity greater than 95%, versus per cent of theoretical volume of effluent collected before the first appearance of rare-earth ions in the effluent. Separation efficiency increased rapidly as the percentage of theoretical volume of effluent increased. The use of glycine as a retaining agent resulted in 3% of the ytterbium being recovered with a purity greater than 95%, compared with 92% recovery of 95% pure ytterbium with HEDTA retaining agent.

HEDTA was utilized as a retaining agent to illustrate the separation of cerium-group elements and to study the effect of EDTA eluent concentration. Separation of series II charge stock was accomplished with eluent solutions containing 7, 10, and 15 g/liter EDTA. Use of an ammoniated EDTA eluent at pH 8.5 resulted in precipitation of lanthanum–EDTA chelate, thereby decreasing separation efficiency. However, at pH 9.0, elution with 7- and 10-g/liter EDTA solutions resulted in favorable separation, and no precipitation was observed in the columns. Retention of the cerium-group rare-earth ions by the HEDTA was very effective, and the amount of HEDTA recovered before rare-earth breakthrough closely approached the theoretical value. Data presented in Fig. 2 show the results obtained. The degree of separation of cerium-group elements decreased as the concentration of EDTA in the eluent increased. The percentage of neodymium recovered with a purity greater than 99% decreased from 92 to 86% on increasing the eluent concentration from 7 to 15 g/liter. Figure 2 shows that contamination of the praseodymium and cerium–lanthanum fractions with other rare-earth elements increased as the eluting solution became more concentrated in EDTA. The decrease of rare-earth concentration in the effluent after passage of 1.5 liters of eluting solution with 15 g/liter EDTA was due to precipitation of EDTA, which served to lower the concentration of EDTA in the eluting solution. Precipitation in the column was probably responsible for the increased trailing of neodymium into the praseodymium and lanthanum fractions.

Essentially complete recovery of HEDTA- and DTPA-retaining agents were effected. In addition, 85% recovery was obtained for the EDTA that passed through the system before the appearance of erbium. Precipitation of EDTA from HEDTA or DTPA eluates was accomplished by cooling the solutions. The retaining agent is recovered by passing the EDTA-free filtrate through hydrogen-cycle resin heated to 80°C, thereby adsorbing the HEDTA or DTPA on the

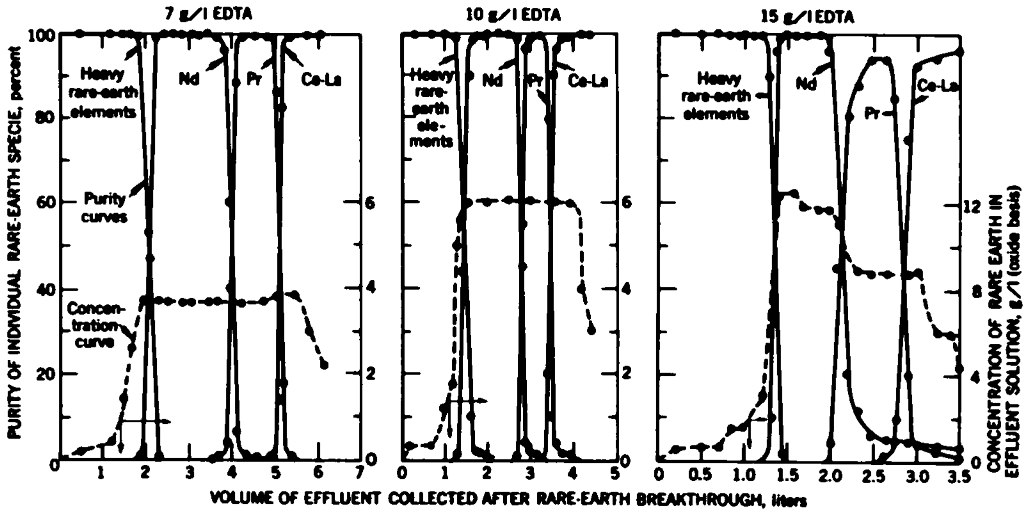

FIG. 2. Effect of ethylenediaminetetraacetic acid (EDTA) eluent concentration on separation of rare-earth elements using hydroxyethylenediaminetriacetic acid as a retaining agent.

resin for reuse as the retaining agent for the next run. The eluent and retaining agent can be recovered from fractions containing small amounts of rare-earth elements by allowing the EDTA to precipitate, filtering, and then precipitating the rare-earth ions with oxalic acid. After filtering the rare-earth oxalates, the filtrate is passed through heated hydrogen-cycle resin to adsorb the HEDTA, whereupon the excess oxalic acid is washed out of the resin.

These studies have shown that HEDTA and DTPA are effective retaining agents for rare-earth elements lanthanum through erbium when eluting with EDTA through ion-exchange resin. High recoveries of >99% major constituent individual rare-earth elements are possible when using either of the two retaining agents. Other advantages of this system are the substantially higher EDTA eluent concentration possible over that obtainable with hydrogen- or copper-retaining ion and ease of recovery of the retaining agent and EDTA collected prior to erbium breakthrough.

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