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Liquid-Liquid Chromatographic Separation of Neodymium, Samarium, and Gadolinium

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Summary

Neodymium, samarium, and gadolinium were separated by a liquid-liquid chromatographic technique. Sulfuric acid was more effective than hydrochloric or nitric acid as an eluent with di(2-ethylhexyl) phosphoric acid (EHPA) as the stationary phase. Recovery of 45% of the neodymium as $>90\%$ Nd_2O_3 , 84% of the samarium as $>99\%$ Sm_2O_3 , and 50% of the gadolinium as $>99\%$ Gd_2O_3 was achieved. The degree of separation and the time required for the separation can be varied by changing the concentration of the eluent and the number of stages in the system. A system comprising a primary amine organic extractant and an aqueous eluent containing diethylenetriaminepentaacetic acid (DTPA) was less effective for separating the rare earths.

INTRODUCTION

Resinous ion-exchange chromatography is capable of separating all of the rare earths in a mixture in a single pass through the resin. However, since the technique is diffusion controlled, it is typically a time-consuming operation. Continuous countercurrent solvent extraction is much faster, but is capable of separating only a limited number of rare earths in a single pass. Also, in countercurrent operation employing end feed, the exiting organic extractant is in contact with the incoming feed solution, thus limiting the efficiency of the process.

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Fischer (1) employed a batch solvent extraction process to separate yttrium-group rare earths by passing methyl isobutyl ketone through successive mixer-settlers. The first stages were loaded with rare-earth nitrates in saturated NH_4SCN solutions, and the remaining stages contained only saturated NH_4SCN .

The present report describes a technique for separating neodymium, samarium, and gadolinium salts by using a stationary organic phase as an ion exchanger for the rare-earth ions and moving an aqueous eluent through the system to effect a chromatographic separation. The investigation was conducted in an attempt to utilize the high-throughput characteristics of solvent extraction and the chromatographic characteristics of resinous ion exchange to yield a rapid technique for separating mixtures into pure fractions in a single pass through the system.

Separation factors of ~ 2.5 for adjacent rare earths in single-stage extractions with di(2-ethylhexyl) phosphoric acid (EHPA) have been reported (2). Tracer quantities of rare earths were separated using reverse-phase partition chromatography with EHPA as the stationary phase (3). Single-stage extractions of cerium-group rare earths were made with a primary amine-chelating agent system, and separation factors as high as 7 were reported (4). The organic-phase extractants studied were EHPA and Primene JM-T,* a commercially available mixture of highly branched primary aliphatic amines, principally $t\text{-C}_{18}\text{H}_{37}\text{NH}_2$ to $t\text{-C}_{22}\text{H}_{45}\text{NH}_2$.

MATERIALS AND PROCEDURE

The organic phase was prepared by dissolving the desired volume of EHPA into an inert solvent, Socal 355L. The charge material consisted of a rare-earth carbonate obtained from Molybdenum Corporation of America. Analysis of a typical charge stock is given in Table 1. Charge solutions were prepared by dissolving the carbonate in a slight excess of the particular mineral acid selected as the aqueous-phase eluent and extracting the rare earths completely into a portion of the organic phase. To avoid polymer formation, the metal-to-EHPA ratio was limited to $<1:6$. The equilibrium pH was 1.5.

The aqueous-phase eluent consisted of mineral acid solutions, ranging in concentration from 0.6 to 1.8 *N*.

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

TABLE 1
Distribution of Rare Earths in Charge Stock

Rare-earth element	Solution analysis, wt-% (oxide basis)
Cerium	1.6
Dysprosium	2.2
Gadolinium	12.2
Lanthanum	0.8
Neodymium	17.2
Praseodymium	2.4
Samarium	52.0
Terbium	1.0
Yttrium	7.0
Zinc	~5.0

The first group of experiments was conducted in a series of six 125-ml separatory funnels, each containing 50 ml of organic phase pregnant with rare earths. The aqueous-phase eluent consisted of 50-ml portions of the appropriate acid solution. A second series of experiments was conducted in eighteen 3-liter mixer-settlers containing 1.5 liters of organic phase; eluting was accomplished with 1-liter portions of mineral acid. Figure 1 illustrates the elution sequence. The charge solution, consisting of the rare earths extracted into the organic phase, was placed in the desired number of stages. Equal volumes of organic phase barren of rare earths were placed in the remainder of the stages. Aqueous-phase eluent was placed in the first stage, and the two phases were mixed for 1.5 min. After the phases separated, the aqueous phase was transferred to the second stage, and fresh aqueous-phase eluent was placed in the first stage. The procedure was repeated with the aqueous phase advancing through each stage. As the elution was conducted, the rare earths were stripped from the loaded organic phase and subsequently redistributed between the aqueous phase and the barren organic phase; the heavier rare earths were extracted into the organic phase while the lighter rare earths remained in the aqueous phase. This resulted in the rare earths being separated into bands in the order of increasing atomic number. The rare earths were continually moved through the series until they were finally washed from the last stage by the aqueous-phase eluent. Periodically, the aqueous phase from the first stage in the series

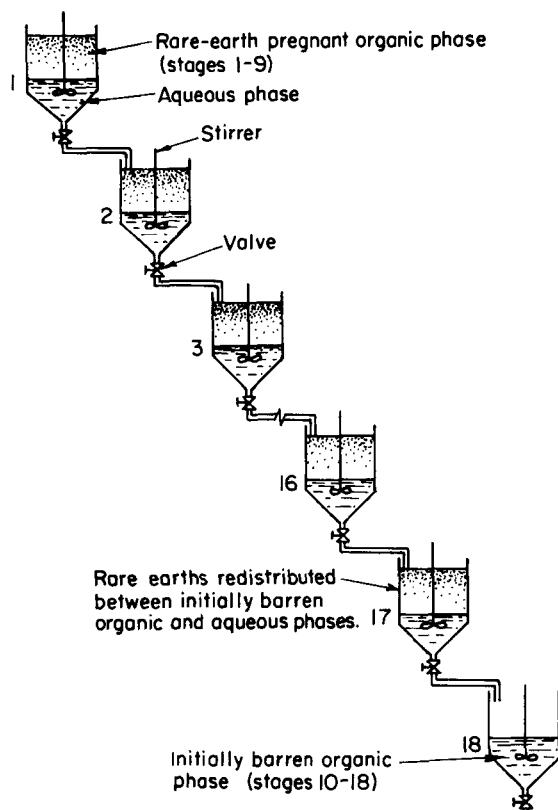


FIG. 1. Mixer-settlers used in liquid-liquid chromatography.

was checked for the presence of rare earths with oxalic acid; each organic phase was removed from the series as it was shown to be barren of rare earths.

The recovered rare earths were precipitated as oxalates and calcined to oxides, which were analyzed by X-ray emission spectroscopy.

Similar experiments were conducted with Primene JM-T. The organic phase was 20% Primene JM-T, 79% kerosene, and 1% hexanol. Rare-earth carbonates were dissolved in H_2SO_4 and extracted into one-third of the organic phase, so that the rare-earth concentration was 12 g/liter (oxide bases). Three aqueous-phase eluents were studied: 25 g/liter NH_4Cl with a pH of 4.5, and 30 and 50 g/liter diethylenetriamine-pentaacetic acid (DTPA) with pH adjusted to 8.5 with ammonia.

Experiments were conducted in a series of thirty 125-ml separatory funnels, the first 10 containing rare-earth pregnant organic phase and the remaining 20 containing initially barren organic phase. Elution was accomplished by passing the aqueous phase through the system as previously described.

RESULTS AND DISCUSSION

Separation Using EHPA

Initial experiments were concerned with the effect of EHPA concentration on the degree of separation achieved and on phase disengagement characteristics. Rare earths were extracted from an aqueous chloride solution into EHPA-Socal 355L solution containing 35, 50, and 75 vol-% EHPA. The resulting pregnant organic solutions contained 15, 25, and 38 g/liter of rare earths (oxide basis), respectively. Elution

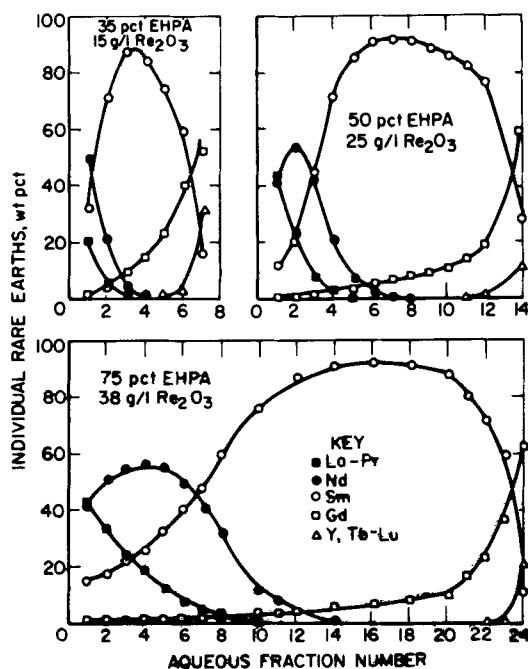


FIG. 2. Effect of EHPA concentration on the elution of rare earth.

TABLE 2

Recovery of Rare-Earth Oxide from Liquid-Liquid Chromatography Separation, %

Eluent	Nd ₂ O ₃ , >90%	Sm ₂ O ₃ , >99%	Gd ₂ O ₃ , >95%
HCl	21	70.5	19.5
HNO ₃	16	71.5	25.5
H ₂ SO ₄	46	83.5	72.0

was accomplished by passing 50-ml portions of 0.6 *M* HCl through six 125-ml separatory funnels, each containing 50 ml of the rare-earth pregnant organic phase. The degree of separation is shown in Fig. 2, in which the percentages of the rare-earth elements present in each fraction of collected effluent are plotted against the aqueous fraction number. Yttrium and terbium through lutetium were not quantitatively stripped from the organic phase. The highest degree of separation was achieved using 75% EHPA. Fractions of >90% Sm₂O₃ were obtained from 75 and 50% EHPA systems with 40 and 35% recovery, respectively. No fractions containing >90% Sm₂O₃ were recovered from the 35% EHPA system. Fifty per cent EHPA was used in the remainder of the investigation because of better phase separation and higher rare-earth concentration in the aqueous phase than when 75% EHPA was used.

The effect of the anionic species in the aqueous-phase eluent on the separation was determined by conducting separate experiments using HCl, HNO₃, and H₂SO₄ in the aqueous phase. A series of 18 mixer-settlers was utilized; the first 9 stages each contained 1.5 liters of rare-earth pregnant EHPA solution, and the second 9 stages each contained 1.5 liters of initially barren EHPA solution which had been scrubbed with aqueous ammonia to an aqueous pH of 3.0. Elution was accomplished by passing 1-liter portions of 0.6 *N* acid through the series of mixer-settlers. Percentages of recovery of individual rare-earth oxides are shown in Table 2. The best separation was achieved with H₂SO₄ as the aqueous phase.

The stabilities of some of the rare-earth complexes with inorganic ligands are discussed by Krumholz (5). These are expressed in terms of consecutive stability constants as defined by

$$K = [\text{LnX}_n]/[\text{LnX}_{n-1}][\text{X}],$$

where Ln stands for any of the rare-earth elements and X for any ligand. He reports that the $\log K$, for the LnSO_4^+ complex ions, decreases from 3.4 for La^{3+} to 2.9 for Nd^{3+} . $\log K$ for rare-earth chloride and nitrate complexes is much lower, and there is doubt as to the formation of complexes with Cl^- ions at concentrations less than 6 N HCl. The greater ability of the sulfate ion to form complexes with the rare earths probably contributed to the better separation achieved with a sulfuric acid aqueous phase.

The rare-earth concentration in the effluent aqueous phase decreased with increasing atomic number; consequently, the acid concentration of the aqueous-phase eluting solution was increased, in stages, in an attempt to maintain a constant rare-earth concentration in the effluent. The concentration of rare-earth elements with visible absorption lines was monitored with a hand spectroscope. When the neodymium absorption lines were no longer observed in the aqueous phase (aqueous fraction No. 42), the acid concentration was increased to 1.2 N . The concentration of rare earths in the aqueous phase began to drop rapidly at fraction No. 80, and the acid concentration was again increased to 1.8 N for the remainder of the experiment. The results of such an elution sequence are presented in Fig. 3. The elution sequence resulted in recovery of 45% of the neodymium in fractions containing $>90\%$ Nd_2O_3 , 84% of the samarium in fractions containing $>99\%$ Sm_2O_3 , and 50% of the gadolinium in fractions containing $>99\%$ Gd_2O_3 .

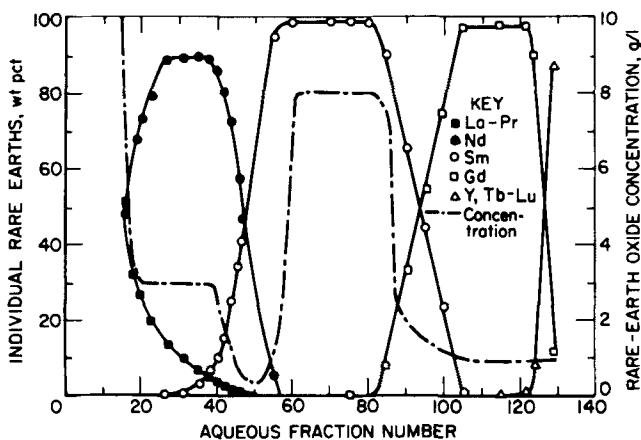


FIG. 3. Separation of Nd, Sm, and Gd using EHPA as stationary phase.

Yttrium and terbium through lutetium were not quantitatively removed from the organic phase. The purity of the products can be varied by changing the ratio of loaded-to-barren stages and by varying the acid concentration in the eluent.

Separation Using Primene JM-T

Primene JM-T was investigated as the stationary phase using aqueous solutions of NH_4Cl and DTPA as eluents. This study was conducted in 30 stages, the first 10 containing rare-earth pregnant organic phases and the remainder containing barren organic phases. Very little separation was achieved when eluting with NH_4Cl , and none of the samarium was recovered in fractions $>85\%$ Sm_2O_3 . DTPA elution was carried out at concentrations of 30 and 50 g/liter, and results of the elution sequence at 30 g/liter DTPA are presented in Fig. 4. Recovery of 54% of the Sm_2O_3 in fractions $>95\%$ Sm_2O_3 was achieved. Elution with 50 g/liter DTPA solution was less effective. Better separation was expected, considering the high separation factors reported by Bauer (4) for single-stage extraction. Another unexpected result was the low concentration of rare earths in the eluent (only 4 g/liter). It was found that as the elution is conducted, the DTPA is extracted by the Primene JM-T, thus lowering its concentration in the aqueous phase and possibly decreasing the separation factors of the rare-earth elements.

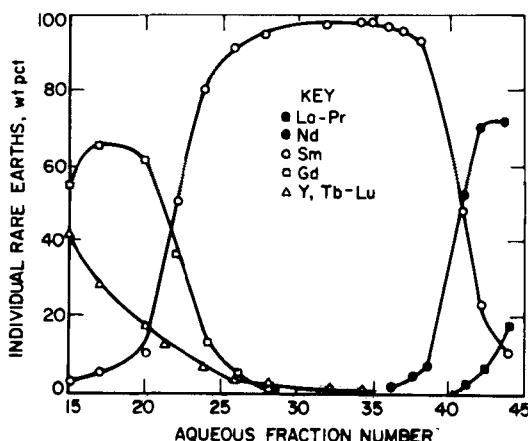


FIG. 4. Separation of Nd, Sm, and Gd using Primene JM-T as stationary phase.

CONCLUSIONS

Liquid-liquid chromatography was shown to be an effective method for separating a mixture of rare-earth elements by a single pass through the system. The use of an organic solution of EHPA as a stationary phase and dilute mineral acid for elution is greatly superior to Primene JM-T stationary phase and DTPA eluent for separating neodymium, samarium, and gadolinium. The purity of the products can be varied by changing the number of stages in the system and the concentration of acid in the eluent.

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