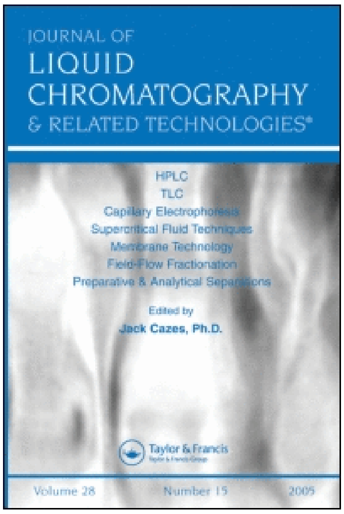

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PURIFICATION OF YTTRIUM BY HIGH-SPEED COUNTERCURRENT CHROMATOGRAPHY

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ABSTRACT

Separation of rare earth elements has been studied by high-speed countercurrent chromatography (CCC) employing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester in toluene as a stationary phase. The CCC method was applied to purification of rare earth elements in a wide range of concentrations. High-purity yttrium was chromatographically isolated by removing micro amounts of similar lanthanoid elements such as holmium and erbium.

INTRODUCTION

Lanthanoid elements and yttrium are ordinarily classified as a rare earth group, and are usually associated with others. Production of various kinds of new advanced materials requires rare earth elements as excellent functional substances, because these elements have unique characteristics as electronic, optical, magnetic, and nuclear materials.[1,2] Their mutual separation and purification have been intensively studied by means of a variety of methods to obtain highly- purified individual elements.

A multistage liquid-liquid extraction technique has been accomplished using high-speed countercurrent chromatography (CCC) with a support-free stationary phase retained in a multilayer coiled column, in which the choice of stationary phase components is possible for desired separation. This looks very effective and promising for separation of chemically similar substances.[3-5]

The principles of this CCC technique are based on liquid-liquid distribution, and we can design not only the compositions of the mobile phase but also those of the stationary phase.

In liquid-liquid extraction of lanthanoids, certain organophosphorus extractants provide fairly high separation factors for adjacent elements.[6-8] These selective extractants make possible separation of lanthanoid elements through CCC acting as a stationary phase component.[9-10]

Lanthanoid elements were successively eluted into individual elements and, further, yttrium was also separated from resemble heavy lanthanoid elements by CCC holding 2-ethylhexylphosphonic acid mono-2-ethylhexylester (EHPA).[11-13]

The CCC procedure using a liquid stationary phase of high capacity is seen as a tool for preparative separation and purification, providing many advantages such as high recovery and high purity.[14-15]

This paper presents an empirical approach to the separation of small quantities of closely related heavy lanthanoid elements, dysprosium, holmium, and erbium, from a large quantity of yttrium; this has been performed by CCC provided with a EHPA stationary phase, for the purification of yttrium, removing a number of most similar impurities.

EXPERIMENTAL

Materials

2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA; PC-88A, Daihachi Chemical Ind. Co. Ltd.) was mixed with a sodium hydroxide solution to remove acidic impurities. Arsenazo III (Dojindo Lab.) was used as a post column reagent for detection of rare earth elements.

CCC Apparatus

A prototype high-speed countercurrent chromatograph apparatus (HCC-1 A; Shimadzu Corporation) holds two horizontal column drams with 15 cm diameter. Multilayer coils consists of about 300 helical turns of polytetrafluoroethylene (PTFE) tubing (15 mm i.d., about 150 m in length).[11] The total capacity of the coiled column was measured as approximately 268 cm^3. The column rotates at radii $R = 10$ cm around its axis and at the same time revolves at radius R = 10 cm around the central axis. The CCC apparatus was housed in a thermostat box at 35°C.

Chromatographic Procedure

The tubing coils were first filled with a toluene solution of 0.02 M (M = mol dm^3) $(EHPA)_2$ in toluene. An aqueous mobile phase buffered with 1 M (H, Na)$CHCl_2COO$ was pre-equilibrated by mixing with toluene. The mobile phase was pumped into the column under revolution; a part of the organic stationary phase was gradually removed by the aqueous phase and then equilibrium between the two phases was established. A sample solution (10^{-3} M HNO_3, 1 cm^3) containing rare earth elements was charged through a sample port. A speed of revolution of 800 rpm and a flow rate of 5 cm^3 min^{-1} for the mobile phase were adopted, and then the stationary phase occupied about 50% of the total capacity of tubing coil.[11]

Rare earth elements eluted with the mobile phase were continuously monitored by UV-vis adsorption detection at 650 nm after a post-column reaction with Arsenazo III (0.04%(w/v) in 50%(v/v) ethanol).[8] In the separation of samples containing high concentration of yttrium, the fractions of effluent were collected. Each fraction in a size of 100 cm^3 was concentrated, by solvent extraction, with 0.02 M $(EHPA)_2$ in toluene at pH 3.0~3.2, stripped with 1 M HNO_3, evaporated to dryness, and dissolved in 0.1 M HNO_3 (10 cm^3), and then the metal contents were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

RESULTS AND DISCUSSION

Chromatographic Behavior of Rare Earth Complexes

Retention of the rare earth species is the basic controlling factor for their mutual separation through the CCC coiled column. The chromatographic elution of rare earth elements is related to the distribution ratio (*D*) between two

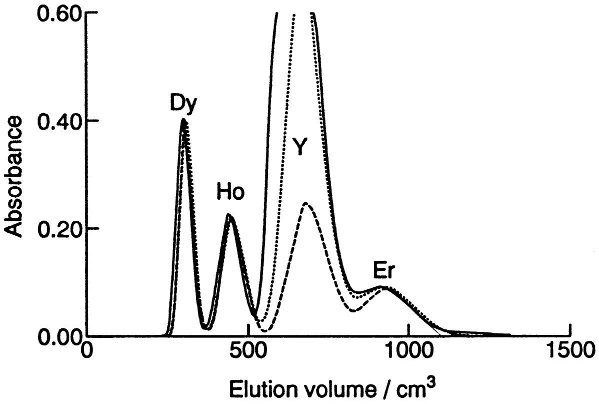

Figure 1. Chromatographic separation of rare earth elements by CCC with a coiled column containing 0.02 M $(EHPA)_2$ in toluene. Sample: (broken line) 10^{-3} M Y, (dotted line) 2.5 x 10^{-3} M Y, (solid line) 5.5 x 10^{-3} M Y, every sample contains 5 x 10^{-4} M each Dy, Ho and Er; mobile phase: 0.1 M $(H,Na)CHCl_2COO$ (pH 2.05).

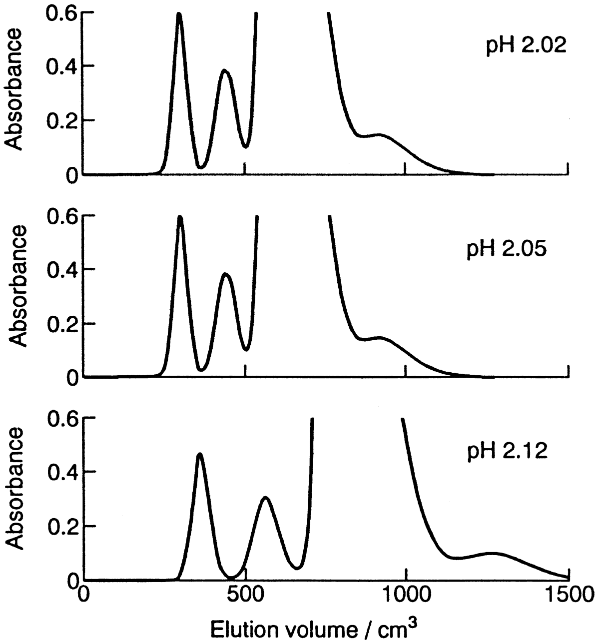

Figure 2. Chromatographic separation of rare earth elements by mobile phases of different pH values. Stationary phase: 0.02 M $(EHPA)_2$; sample: 1.05 x 10^{-2} M Y, 5 x 10^{-4} M each Dy, Ho and Er; mobile phase: 0.1 M $(H, Na)CHCl_2COO$.

phases. The retention volume (V_R) of a desired element is given by the volumes of mobile and stationary phases (V_m and V_s, respectively) and the D value,

$$V_R = V_m + D\,V_s \qquad (1)$$

The chromatographic separation factor (α_c) is obtained from the retention volumes of adjacent peaks ($V_{R,2} > V_{R,1}$),

$$\alpha = \frac{V_{R2} - V_m}{V_{R1} - V_m} \qquad (2)$$

The number of theoretical plates (N) is related to the retention volume and the peak width (W),

$$N = 16\,(V_R / W)^2 \qquad (3)$$

Resolution (R_S) is evaluated from the distance between two adjacent peaks and their widths,

$$R_s = \frac{2(V_{R2} - V_{R1})}{W_1 + W_2} \qquad (4)$$

Chromatographic behavior of rare earth elements was investigated through a coiled column containing 0.02 M $(EHPA)_2$ in toluene as a stationary phase. Figure 1 illustrates typical examples of CCC chromatograms obtained by injection of the solution (1 cm^3) containing yttrium (10^{-3} ~ 5.5 x 10^{-3} M) together with 5 x 10^{-4} M of each lanthanoid element. These elements, dysprosium, holmium, yttrium, and erbium, were chromatographically eluted by passing through the mobile phase of pH 2.05 in the increasing order of their extractability. These elements were separated from the others in a single run, and the most difficult pairs relating to yttrium were also separated. Peak profiles for each rare earth, other than yttrium, were almost same irrespective of yttrium contents, while the peak area for yttrium was found to increase with its concentration.

The retention of rare earth complexes in the CCC column employing acidic extractant is sensitive to pH values of the mobile phase, and their separation, consequently, will be affected by pH values. The chromatographic separation of lanthanoid elements of low concentrations from yttrium of higher concentrations was tested by passing the mobile phases of different pH values. Figure 2 shows an elution chromatogram for 1 cm^3 of the sample solution containing 1.05 x 10^{-2} M yttrium and 5 x 10^{-4} M for each lanthanoid element. Though the elution peak of yttrium was broadened, the peaks were separated from each other.

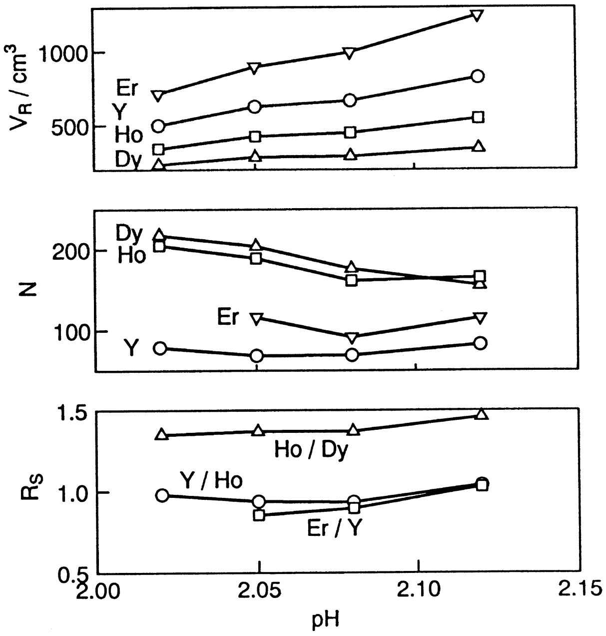

Figure 3. Effect of pH of the mobile phase on the chromatographic parameters. Sample: 1.05 x 10^{-2} M Y, 5 x 10^{-4} M each Dy, Ho and Er; other conditions are the same as those in Fig. 2.

The effect of pH of mobile phase on the chromatographic parameters is illustrated in Figure 3. An increase in the retention volume with rising pH of mobile phase from 2.02 to 2.12 is attributable to an increase in extractability of each element. The number of theoretical plates slightly decreased with rising pH; while variations in resolution were limited to a small extent in the pH region tested. The most difficult separation of the pair of yttrium and erbium was also accomplished, even though rather low resolution ($R_S < 1$), and more excellent peak resolution was achieved for Ho/Dy. The separation of heavy rare earth elements from yttrium is thus possible even with large differences in their concentrations.

Chromatographic parameters obtained for the samples containing different concentrations (5 x 10^{-4} ~ 10^{-2}) of yttrium together with a definite concentration (5 x 10^{-4} M) of each lanthanoid are illustrated as a function of yttrium concentration in Figure 4. It was found that the V_R value is almost constant, irrespective of yttrium concentration, and then, the separation factor α_c for each pair remained unaltered.

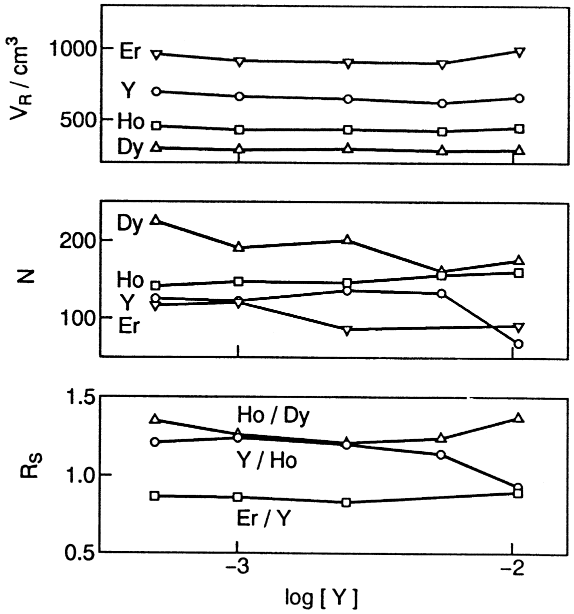

Figure 4. Effect of yttrium concentration on chromatographic parameters. Sample: 5 x 10^{-4} M each Dy, Ho and Er; other conditions are the same as those in Fig. 2.

The N value tends to decrease with an increase in yttrium concentration. Although some scatters were observed, the R_s values for Ho/Dy and Y/Ho, in most cases, were larger than 1, indicating base line separation; however, the R_s value for Er/Y was rather low ($R_s < 1$), implying difficulties in their complete separation.

Isolation of Yttrium

As Figure 5 (a) shows, the chromatographic peak of yttrium of high concentration (1.05 x 10^{-2} M) was considerably broadened and partially overlapped with that of erbium; and the separation of these peaks became uncertain. The contents of each component were confirmed by collecting every fraction; the metal contents determined by ICP-AES in each fraction of 100 cm^3 are illustrated in Figure 5 (b). Most of dysprosium and holmium were present in the 1st and 2nd fractions, respectively, while erbium was detected in the fractions from the 5th to 8th.

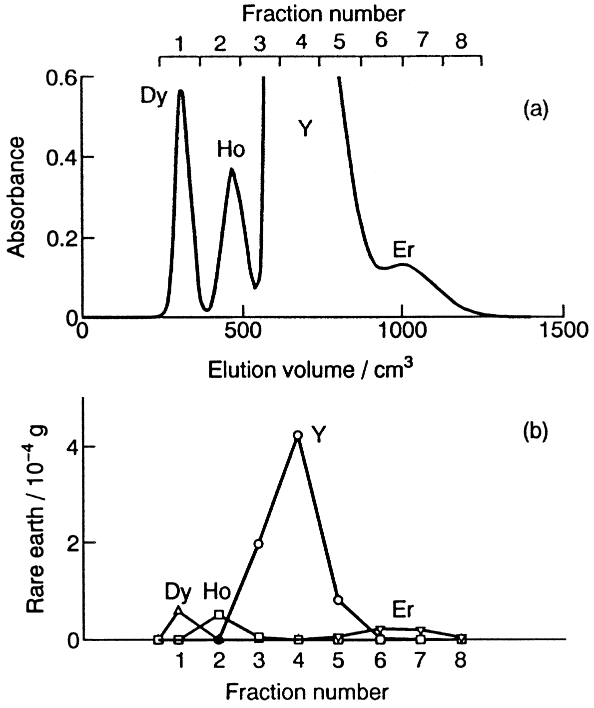

Figure 5. Chromatographic fractionation of rare earth elements. Stationary phase: 0.02 M $(EHPA)_2$; sample: 1.05 x 10^{-2} M Y, 5 x 10^{-4} M each Dy, Ho and Er; mobile phase: 0.1 $(H,Na)CHCl_2COO$ (pH 2.08); (a) chromatogram, (b) rare earth contents in each fraction (100 cm^3).

The yttrium content in the 4th fraction attained 99.95 mol % with respect to rare earth elements, without noticeable contents of accompanying lanthanoid elements. Thus, a crude sample (87.50 mol%) of yttrium was sufficiently purified up to 99.95 mol %.

The CCC procedure was applied to the separation of further increases in yttrium concentration, up to 5.05 x 10^{-2} M, in the presence of lanthanoid elements of low concentrations (5 x 10^{-4} M each). As Figure 6 (a) shows, the resulting chromatographic peaks were poorly resolved. An increase in metal contents shifted the peaks of metal elution curves to the left and the separation became poor; no peak corresponding to erbium appeared because of the overlapping with the yttrium peak. The contents of metals in the fractions of each 100 cm^3 were determined by ICP-AES and the data are illustrated in Figure 6 (b). Dysprosium was eluted in the 1st and 2nd fractions, and holmium was

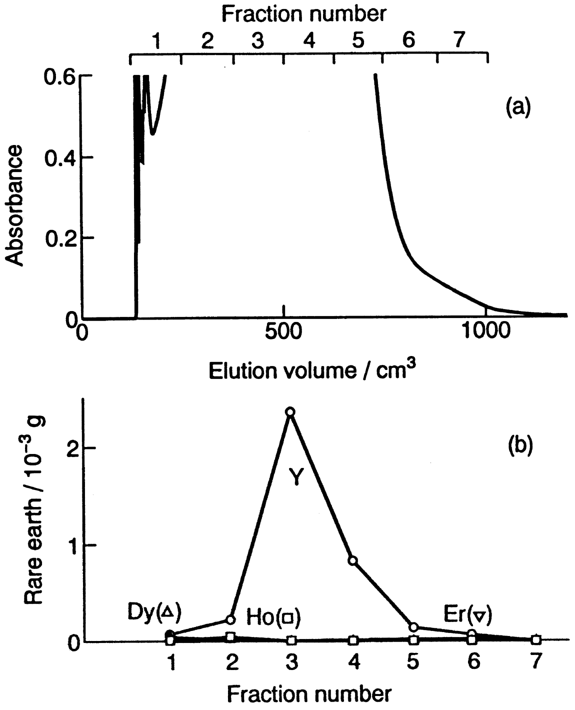

Figure 6. Chromatographic fractionation of rare earth elements. Stationary phase: 0.02 M $(EHPA)_2$; sample: 5.05 x 10^{-2} M Y, 5 x 10^{-4} M each Dy, Ho, and Er; mobile phase: 0.1 M $(H,Na)CHCl_2COO$ (pH 2.05); (a) chromatogram, (b) rare earth contents in each fraction (100 cm^3).

detected in the 1st to 3rd fractions, showing a maximum at the 2nd fraction and no elution after the 4th fraction. Elution of erbium occurred in a wide region yielding a maximum at the 7th fraction. Yttrium was present in a series of fractions, and high purity above 99.8 mol % of yttrium accompanying only trace amounts of lanthanoid elements was obtained in the 3rd and 4th fractions.

A slight decrease in the purity of the yttrium product of high concentration (5.05 x 10^{-2} M yttrium) compared to that for 1.05 x 10^{-2} M yttrium is probably attributable to a decrease in the capacity of the stationary phase free from metal species owing to the high loading of metals. The metal loading in the last case was estimated to be 6% of the EHPA column capacity, assuming that rare earth elements are loaded on the column forming $M(HA_2)_3$ complexes. Further experiments on the application of CCC to purification of rare earth elements are currently in progress.

CONCLUSIONS

The proposed CCC method having a coiled column containing the $(EHPA)_2$ stationary phase provided a complete separation of rare earth elements by elution with the mobile phase. Yttrium and chemically similar lanthanoids were separated each other in wide concentration ranges with adequate resolution. Satisfactory separation of micro amounts of heavy rare earth elements was accomplished in a single step of CCC procedure resulting more than 99.95 mol % of yttrium matrix containing 0.05% impurities of heavy lanthanoid elements.

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