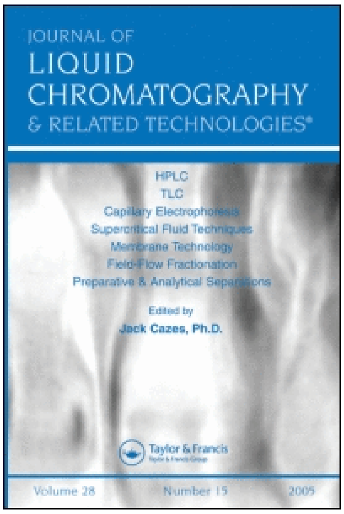

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MUTUAL SEPARATION OF HOLMIUM, ERBIUM, AND YTTRIUM BY HIGH-SPEED COUNTERCURRENT CHROMATOGRAPHY

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ABSTRACT

The separation of yttrium and chemically-similar heavy lanthanoids has been studied by countercurrent chromatography (CCC) equipped with a multilayer coiled column containing a toluene solution of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester as a stationary phase. The retention of the stationary phase in a coiled tubing was enhanced with increasing revolutional speed and with decreasing flow rate of the mobile phase. This high retention of the stationary phase improved the peak resolution. The mutual separation of rare earths with low separation factors was satisfactorily accomplished with good resolution through a single step of CCC.

INTRODUCTION

Lanthanoid series elements remarkably resemble each other in physical and chemical properties. Furthermore, yttrium ion has an ionic radius close to the value for holmium ion owing to lanthanoid contraction. The lanthanoid elements and yttrium are usually classed as rare earths because of their general occurrence in mineral resources and closely similar properties, and multistage processes are required for the mutual separation of individual elements.

Different types of liquid–liquid partition chromatography with support-free stationary phase have been proposed (1–6). This chromatographic method is attractive because it offers the wide choice of two immiscible solvent phases on the basis of liquid–liquid extraction properties. Centrifugal partition chromatography (CPC) has been previously introduced to the separation of a series of lanthanoids, and adjacent elements were isolated with reasonable resolution (7–10). The separation of yttrium and lanthanoids is still so difficult, because the extractability of some heavy lanthanoids is very close to that of yttrium. In a preceding study, the separation of yttrium was performed by two steps of CPC processes (11). Yttrium and accompanying heavy lanthanoids with low separation factors were first fractionated by CPC with a stationary phase containing an acidic organophosphorus compound, and further isolation of yttrium from heavy lanthanoids was accomplished by subsequent CPC treatment through a versatic acid stationary phase.

An alternative high-speed countercurrent chromatography (CCC) using a multilayer coiled column has also afforded great possibility for the separation of chemically-similar materials (1,2). The separation of lanthanoid ions was successfully achieved by passing a mobile phase through a coiled column, yielding excellent peak resolution (12).

An acidic extractant, di(2-ethylhexyl) phosphoric acid (DEHPA) has been most commonly used for the separation of rare earths owing to its high extractability and relatively high separation factor between these elements (13,14). Other acidic extractant, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA) has also excellent properties for the extraction of rare earths (8). Its low extractability compared with DEHPA is rather desirable for a stationary phase component because a mild acidic solution might be available for the mobile phase.

In the present paper, a liquid-liquid extraction process was applied to multistage separation by means of CCC provided with the stationary phase of an organic solution of EHPA having better selectivity for heavy lanthanoids. Chromatographic procedures were performed for the mutual separation of the most difficult separable mixture of yttrium, holmium and erbium.

EXPERIMENTAL

Materials

The extractant, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA; PC-88A, Daihachi Chemical Ind. Co. Ltd.) was washed with a sodium hydroxide solution to remove acidic impurities and diluted with toluene (8). Arsenazo III (Dojindo Lab.) was used as a post column reagent.

Apparatus

A prototype high-speed countercurrent chromatograph apparatus (HCC-1A; Shimadzu Corporation) holds two identical tubing columns symmetrically on the rotary frame. Each column holder undergoes a synchronous planetary motion around own axis and revolution around the central axis of the centrifuge with a 10 cm orbital radius in the same direction. A multilayer coiled column was prepared from a polytetrafluoroethylene (PTFE) tubing with a 1.5 mm inner diameter and ca 150 m length by winding onto two cylindrical column holders with 15 cm diameter and 14 cm length, firming three coiled layers with total about 300 helical turns. The total capacity of the two connected multilayer coil was measured as 265 cm^3. This apparatus was housed in an air-thermostated box regulated at 35°C.

For continuous analysis of elution stream, the detection system consists of a post column-reactor, a photometric detector with a flow cell and a pen recorder (8).

Procedure

In liquid-liquid extraction, a toluene solution (10 cm^3) of 0.02 M (M = mol dm^{-3}) $(EHPA)_2$ was shaken for 1 h at 35°C with an equal volume of an aqueous phase containing 2×10^{-5} M of Dy, Ho, Y and Er. The aqueous pH was adjusted to an appropriate value with 0.1 M $(H,Na)Cl_2CHCOO$. The concentrations of rare earths were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

In CCC experiments, the column was first filled with a toluene solution containing 0.02 M $(EHPA)_2$. The aqueous mobile phase was pre-equilibrated by contacting with the corresponding organic solution, degassed with a on-line degasser and pumped "head to tail" into the column under operating conditions, i.e., a revolutional speed of 800 rpm, a flow rate of 5 cm^3 min^{-1} at 35°C, unless otherwise noted in the text. After an equilibrium had been reached between two phases, a sample solution containing $5 \times 10^{-4} - 1 \times 10^{-3}$ M of Dy, Ho, Er and Y was loaded through a sample loop (1 cm^3). Metal ions were eluted with the mobile phase of an appropriate pH buffered with 0.1 M $(H,Na)Cl_2CHCOO$. The eluted rare earths were monitored by measuring the absorbance at 650 nm for rare earth complexes by a post-column reaction with 0.14%(w/v) Arsenazo III in 50%(v/v) ethanol.

The volume of mobile phase (V_m) was obtained as the elution volume for an unretained component, and that of stationary phase was evaluated by subtracting V_m from the total column volume (V_c). These values were confirmed to be fair agreement with the volumes of column contents expelled by introduction of nitrogen gas after a series of CCC experiments.

RESULTS AND DISCUSSION

Liquid-Liquid Extraction of Rare Earths

Extraction equilibrium of yttrium and lanthanoids having very close extractability with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA) was examined at 35°C in order to select chemical conditions for CCC procedures of the mutual separation of rare earths. As Fig. 1 shows plots of log D against pH gave a series of parallel lines with slopes close to 3 for yttrium and some heavy lanthanoids. Further, the third power dependency of the distribution ratio on the reagent concentration was confirmed. Overall extraction equilibrium for the rare earth ions into the toluene solution of EHPA can be expressed by

$$M^{3+}_{aq} + 3(HA)_{2,org} \rightleftharpoons M(HA_2)_{3,org} + 3H^+_{aq} \qquad (1)$$

$$K_{ex} = \frac{[M(HA_2)_3]_{org}\,[H^+]^3_{aq}}{[M^{3+}]_{aq}\,[(HA)_2]^3_{org}} \qquad (2)$$

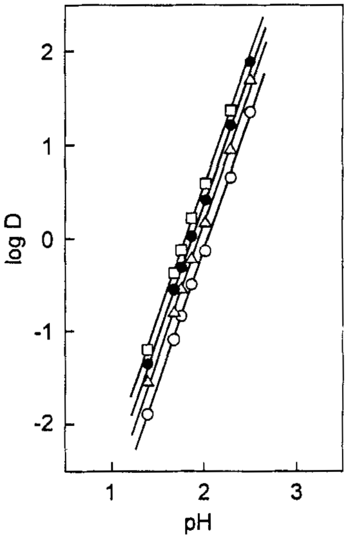

FIGURE 1 Extraction of rare earth elements by EHPA. Organic phase: 0.02 M $(EHPA)_2$ in toluene; aqueous phase: 0.1 M $(H,Na)Cl_2CHCOO$; 35°C. (●) Y, (○) Dy, (△) Ho, (□) Er.

where M denotes the rare earth and $(HA)_2$, the dimer of EHPA. The extraction constant (K_{ex}) and the separation factor (α_D) given by the ratio of their K_{ex} values are summarized in Table 1. The K_{ex} values were in the order Dy < Ho < Y < Er. The separation factors between these ions were small as 1.91 for Ho/Dy, 1.86 for Y/Ho and 1.51 for Er/Y, suggesting particular difficulties in their mutual separation.

Retention of Stationary Phase

In the present CCC process, it is significantly important to provide the satisfactorily stable retention of a suitable organic solution as the stationary phase in the tubing coil. The volume of the stationary phase retained in the column has been found to widely vary depending on operating conditions such as the revolutional speed and the flow rate (15).

TABLE 1

Extraction Constants and Separation Factors

Rare earth	log D at pH 2.0	log K_{ex}	α_D
Er	0.55	-0.35	
			1.51
Y	0.37	-0.53	
			1.86
Ho	0.10	-0.80	
			1.91
Dy	-0.18	-1.08	

Organic phase: 0.02 M $(EHPA)_2$ in toluene.
Aqueous phase: 0.1 M $(H,Na)Cl_2CHCOO$.
Temperature: 35°C.

Figure 2 shows the effect of the revolutional speed on the retention of the toluene solution of EHPA. The retention ratio (V_s/V_c) defined as the ratio of the stationary phase volume (V_s) to the total column volume (V_c) increased along with the revolutional speed ranging from 400 to 800 rpm tested, as indicated by the line (a) in Fig. 2, and no retention was obtained at lower speeds below 400 rpm. After the stationary phase had been retained at a low revolutional speed of 600 rpm, its volume remained almost unchanged even though the revolutional speed further increased up to 800 rpm, as indicated by the line (b) in Fig. 2.

Figure 3 shows the effect of the flow rate of the mobile phase on the retention ratio. As indicated by the line (a) in Fig. 3, the retention ratio was found to decrease with an increase in the flow rate. When the stationary phase had been retained at a high flow rate of 7 $cm^3 min^{-1}$, the retention ratio remained almost constant irrespective of the decreasing flow rate from 7 to 2 $cm^3 min^{-1}$, as indicated by the line (b) in Fig. 3. The retention ratio of the stationary phase thus can be adjusted to an appropriate value by controlling operating conditions; the favorable retention of the stationary phase was obtained with a revolutional speed above 600 rpm and a flow rate below 10 $cm^3 min^{-1}$.

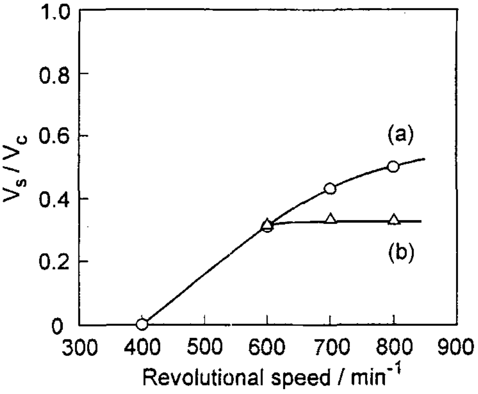

FIGURE 2 Effect of the revolutional speed on the retention of the stationary phase. V_c: column volume; V_s: stationary phase volume; flow rate: 5 cm^3 min^{-1}; 35°C. (a) The stationary phase was retained at different revolutional speeds; (b) the revolutional speed increased after the retention of the stationary phase at 600 rpm.

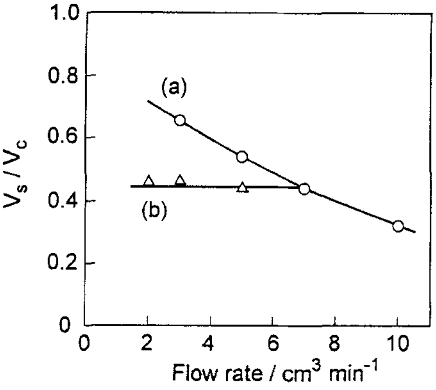

FIGURE 3 Effect of the flow rate of the mobile phase on the retention of the stationary phase. Revolutional speed: 800 rpm; (a) the stationary phase was retained at different flow rate; (b) the flow rate decreased after the retention of the stationary phase at 7 cm^3 min^{-1}.

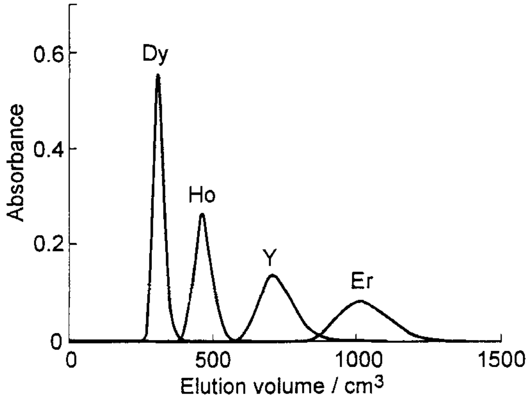

FIGURE 4 Elution peaks of individual rare earth elements. Revolutional speed: 800 rpm; flow rate: 5 cm^3 min^{-1}; V_s/V_c = 0.51; sample: 10^{-3} M RE, 1 cm^3; mobile phase: pH 2.05.

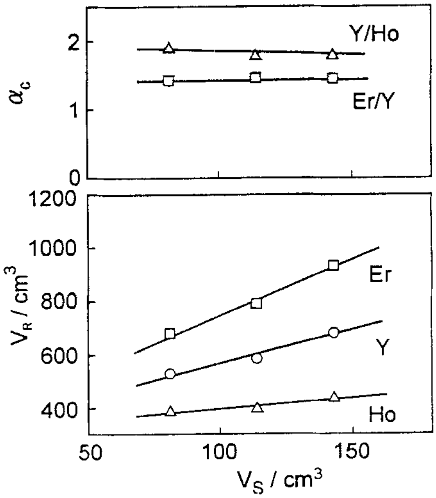

FIGURE 5 Effect of the stationary phase volume on the retention volume and the separation factor. Flow rate: 5 cm^3 min^{-1}; the stationary phase volume was varied by controlling the revolutional speed.

Effect of Stationary Phase Volume on Retention of Rare Earths

The volume of the stationary phase retained in the column would be an important factor governing the retention behavior of desired species and optimizing separating conditions. The elution of each rare earth ion was tested by means of CCC having the stationary phase of EHPA in toluene, and the individual eluted peaks of the rare earth ions are illustrated in Fig. 4. These ions were eluted in the order Dy < Ho < Y < Er in agreement with the order in D values; this implies the possibility of adequate separation of the closely resemble rare earths without any serious overlap of adjacent peaks.

In chromatography, the retention volume (V_R) of a desired component is given by the volumes of the mobile and stationary phases and the distribution ratio (D)

$$V_R = V_m + D\,V_s \qquad (3)$$

where V_m is the mobile phase volume.

Figure 5 shows the V_R value evaluated from individual peaks at different stationary phase volumes produced by varying the revolutional speed. The V_R value increased linearly with the V_s value yielding individual slopes for each rare earth.

The separation factor (α_c) in chromatography is evaluated from the retention volumes of two adjacent peaks ($V_{R,2} > V_{R,1}$)

$$\alpha_c = \frac{V_{R,2} - V_0}{V_{R,1} - V_0} \qquad (4)$$

where V_0 is the elution volume for an unretained component, that is, corresponds to V_m.

The separation factor was almost unaltered independent of variation in the V_s value as shown in Fig. 5, because the V_R value for related rare earths increased linearly with the V_s value.

Retention Volume and Distribution Ratio of Rare Earths

The distribution ratio of the related species is of importance in determining retention volume of the peaks. Figure 6 shows a plot of the V_R value obtained from chromatograms at a constant volume of stationary phase, i.e, V_s = 135 cm^3 at

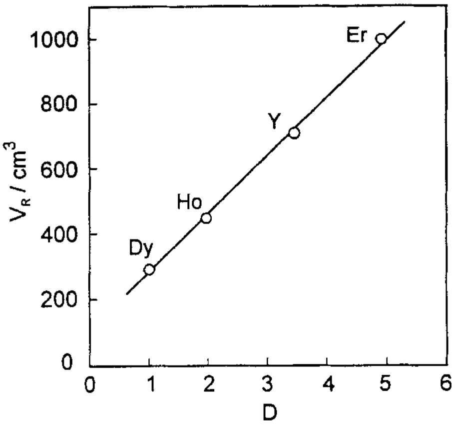

FIGURE 6 Correlation between the retention volume and the distribution ratio. V_s : 135 cm^3; V_m : 130 cm^3; pH 2.05.

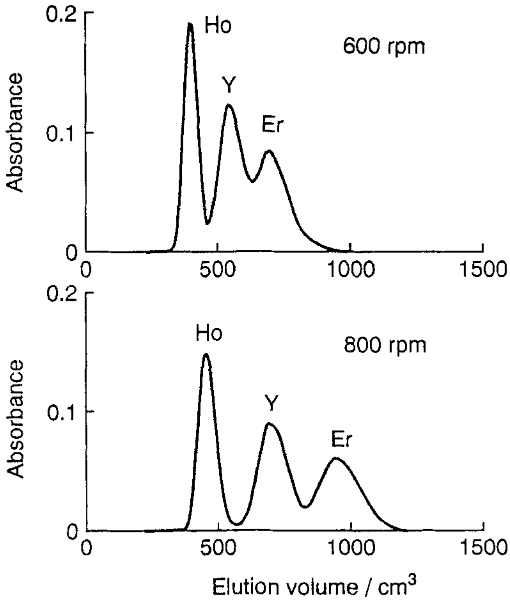

FIGURE 7 Chromatograms at different revolutional speeds. Flow rate: 5 cm^3 min^{-1}; sample: 5x10^{-4} M each RE, 1 cm^3.

800 rpm, against the equilibrium distribution ratio. The retention volumes for individual rare earths were in proportion to their distribution ratios according to Eq.(3). Thus the position of the eluted peak can be predicted from the D value provided the values of V_m and V_s are known.

Separation Parameters

The separation of desired species can be characterized by some chromatographic parameters (16). The number of theoretical plate (N) is related to the retention volume and peakwidth (W):

$$N = 16\,(V_R / W)^2 \tag{5}$$

The resolution (R_s) of adjacent peaks is defined as

$$R_s = 2\,\frac{V_{R,2} - V_{R,1}}{W_1 + W_2} \tag{6}$$

Figure 7 illustrates typical chromatograms obtained for a mixture of Y, Ho and Er, at different revolutional speeds. The elution profiles at a high speed of 800 rpm show good separation of individual peaks. Figure 8 shows the effect of the revolutional speed on the separation parameters. The variation in N was rather minor, though some scatters were observed, and the resolution was appreciably improved along with revolutional speed. This high resolution would be attributable to an increase in the volume of the stationary phase retained from $V_s = 81$ cm^3 at 600 rpm to 143 cm^3 at 800 rpm.

In order to examine the effect of the revolutional speed at a fixed V_s, the subsequent CPC procedure was performed by increasing the revolutional speed after the stationary phase had been previously retained at a low revolutional speed of 600 rpm. Separation parameters evaluated at the constant volume of the stationary phase, V_s = about 85 cm^3, are shown in Fig. 9, as a function of revolutional speed. In this case, the V_R values of given rare earths remained almost unaltered owing a given V_s. The values of N and R_s were also little affected by the revolutional speed provided the stationary phase volume was kept constant. The high retention of the stationary phase resulted from the high speed of revolution would thus contribute to the enhancement of the separation parameters.

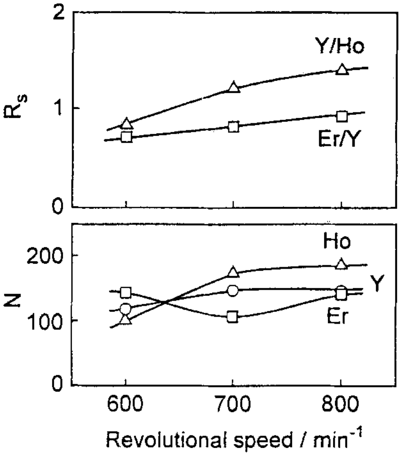

FIGURE 8 Effect of the revolutional speed on the chromatographic parameters. Flow rate: 5cm^3 min^{-1}; pH 2.06.

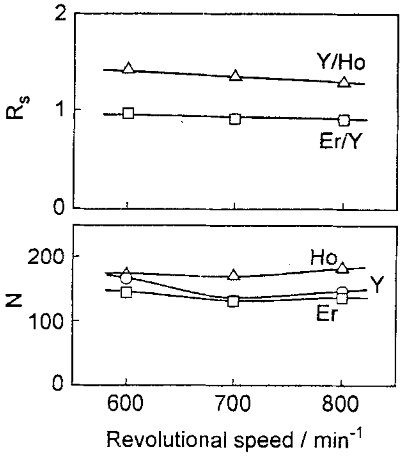

FIGURE 9 Effect of the revolutional speed on the chromatographic parameters at a fixed volume of the stationary phase. The stationary phase was initially retained at 600 rpm. V_s = 85 cm^3; pH 2.17.

Effect of Flow Rate

Further improvement of peak resolution was attempted by varying the flow rate of the mobile phase in the range from 3 to 10 $cm^3\ min^{-1}$ at a constant revolutional speed of 800 rpm. As Fig. 10 shows, the values of N and R_s were found to decrease with an increase in the flow rate. However, these findings also include an effect of a decrease in the stationary phase volume, that is, from V_s = 176 at a flow rate of 3 $cm^3\ min^{-1}$ to V_s = 87 cm^3 at 10 $cm^3\ min^{-1}$.

Variations in separation parameters were examined at a fixed volume of the stationary phase, i.e., V_s = 122 cm^3, by initially retaining the stationary phase at a high flow rate of 7 $cm^3\ min^{-1}$. As Fig. 11 shows, the values of N and R_s were found to be almost independent of the flow rate as long as the V_s value was kept constant.

Thus, the high resolution at the low flow rate noted in Fig. 10 was mainly caused by the high retention ratio of the stationary phase, e.g., V_s/V_c = 0.66 at a flow rate of 3 $cm^3\ min^{-1}$.

Effect of pH of Mobile Phase

Chromatographic separation of Y, Ho and Er was performed by passing the aqueous mobile phases of different pH. The flow rate of mobile phase was adjusted to 3 $cm^3\ min^{-1}$, after two phase equilibration at 5 $cm^3\ min^{-1}$. Figure 12 illustrates resulted chromatograms at different pH. At a lower pH of 1.95, the peaks were not well separated each other. The V_R values increased with increasing pH and the degree of separation of metal ions was much improved. The separation parameters evaluated are summarized in Table 2. The V_R value for each rare earth increased along with pH governing the D value, and the separation factor was almost unchanged as 1.75 for Y/Ho and 1.45 for Er/Y. The higher pH value appreciably led an excellent peak resolution and then the R_s value attained near 1 at pH 2.06 even for the pair of Er/Y with the low separation factor of 1.47.

It is important to control the pH of the mobile phase in order to optimize the distribution ratio of each component for adequate separation. When the D value is low, the resolution will be poor due to low retention on the stationary phase, while at high D value a long time for elution will be required.

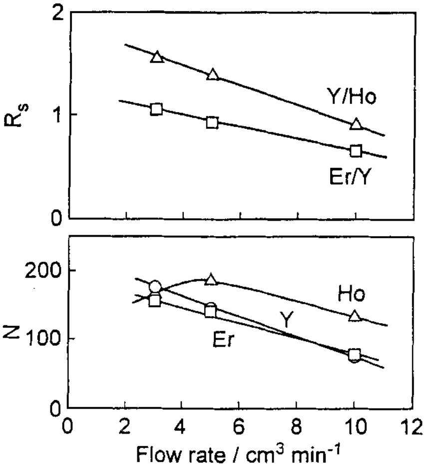

FIGURE 10 Effect of the flow rate on the chromatographic parameters. Revolutional speed: 800 rpm; pH 2.06.

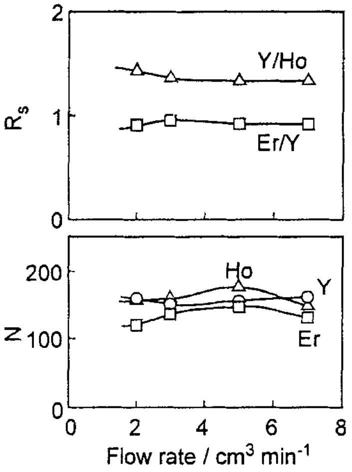

FIGURE 11 Effect of the flow rate on the chromatographic parameters at a fixed volume of the stationary phase. Revolutional speed: 800 rpm; the stationary phase was initially retained at 7 cm^3 min^{-1}; V_s = 122 cm^3, pH 2.09.

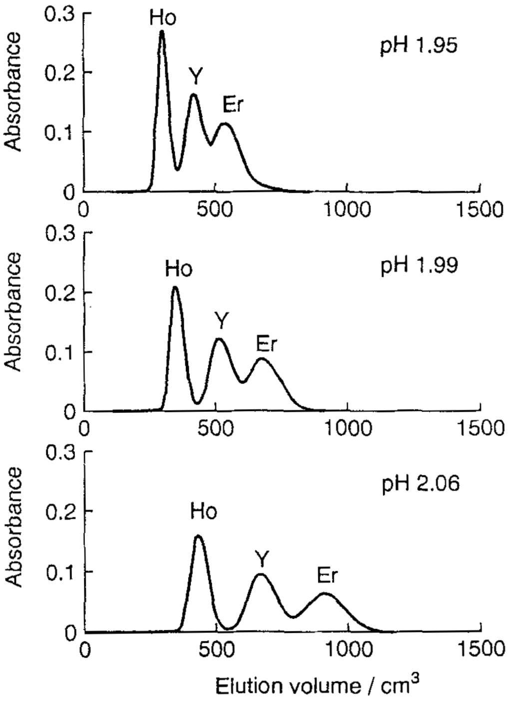

FIGURE 12 Chromatograms at different pH of the mobile phase. Revolutional speed: 800 rpm; flow rate: 3 $cm^3\ min^{-1}$; the stationary phase retained at 5 $cm^3\ min^{-1}$, $V_s = 136\ cm^3$.

Peak Resolution

The resolution of elution peaks usually depends on several chromatographic parameters (17). The resolution between adjacent peaks can be presented with the aid of Eqs. (4)–(6) as

$$R_s = \frac{k'_2(\alpha_c - 1)}{2\,\alpha_c\,(N_1^{-1/2} + N_2^{-1/2}) + 2\,k'_2\,(N_1^{-1/2} + \alpha_c\,N_2^{-1/2})} \tag{7}$$

where k' denotes the capacity factor and is related to V_R or α_c as follows:

$$V_R = V_0(1 + k') \tag{8}$$

$$\alpha_c = k'_2 / k'_1 \tag{9}$$

TABLE 2
Chromatographic Separation of Y,Ho and Er

Rare earth	V_R/cm^3	α_c	N	R_s
pH 1.95				
Ho	290	1.73	182	1.01
Y	407	1.45	124	0.653
Er	532		81	
pH 1.99				
Ho	337	1.78	159	1.18
Y	499	1.45	141	0.815
Er	666		121	
pH 2.06				
Ho	430	1.78	155	1.36
Y	665	1.47	160	0.954
Er	915		133	

Stationary phase: 0.02 M $(EHPA)_2$ in toluene initially retained at 5 cm^3 min^{-1}.
Mobile phase: 0.1 M $(H,Na)Cl_2CHCOO$, 3 cm^3 min^{-1}.
CCC : 800 rpm, 35°C.

Figure 13 shows plots of the R_s values for Y/Ho and Er/Y against the capacity factor for Y. The solid lines (a) and (b) indicate the R_s values calculated from Eq.(7) for Y/Ho and for Er/Y, respectively. Here, the values evaluated at pH 2.06 (Table 2) were used for calculation; $N_{Ho} = 155$, $N_Y = 160$, $N_{Er} = 133$, $\alpha_c(Y/Ho) = 1.78$, and $\alpha_c(Er/Y) = 1.47$. The calculated value of R_s increased with increasing k' and was asymptotic to a plateau. The observed value of R_s varied along the calculated trend. The deviations from the calculated lines are probably due to the variation in the N values which tend to increase with increasing V_s and pH. From Eqs.(3) and (8), k' can be related to D as

$$k' = D\,V_s / V_m \qquad (10)$$

Increases in the stationary phase volume and the distribution ratio bringing about the higher capacity factor are thus desirable for improving mutual separation.

The separation parameters are mainly governed by the stationary phase volume, and hence a high retention volume of the stationary phase would results in the

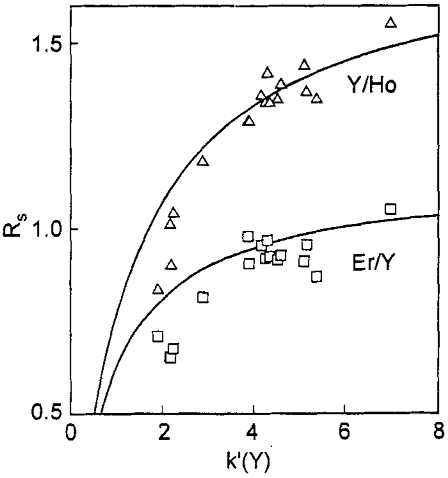

FIGURE 13 Correlation between the resolution and the capacity factor.

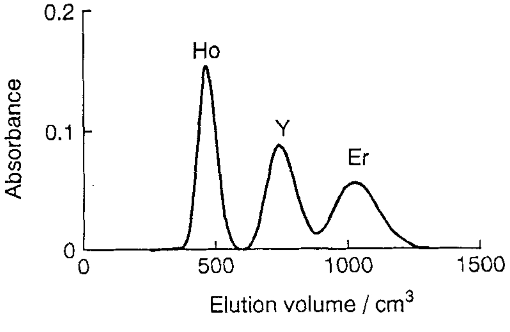

FIGURE 14 Mutual separation of Ho, Y and Er. Revolutional speed: 800 rpm; flow rate: 3 cm^3 min^{-1}; pH 2.05; V_s = 174 cm^3.

good separation of related species. The mutual separation of three rare earths was performed under the optimum conditions of a high revolutional speed of 800 rpm and a low flow rate of 3 cm^3 min^{-1} at pH 2.05. The resulted peaks were sufficiently separated as illustrated in Fig. 14. The R_s value representing the actual separation of elution peaks was found to be above 1 corresponding to a complete peak separation for each pair of Y/Ho (α_c=1.77, R_s=1.55) and Er/Y (α_c=1.45, R_s=1.05).

CONCLUSIONS

The results of the present studies with CCC are summarized as follows:

1. The extractability of yttrium and the heavy lanthanoids, Ho and Er, with EHPA was very close each other giving low separation factors less than 2.0.
2. The retention of the stationary phase in a coiled column increased with increasing revolutional speed and with decreasing flow rate of the mobile phase.
3. The retention volume for each rare earth was found to vary linearly with D and V_s; $V_R = V_m + D\ V_s$.
4. The high retention ratio of the stationary phase improved the mutual separation of the rare earths.
5. The separation parameters, N and R_s, were found to be practically independent of the revolutional speed and flow rate provided the retention ratio of the stationary phase remained constant.
6. The mutual separation of rare earths of low separation factors as α_D=1.86(Y/Ho) and 1.51 (Er/Y) was almost completely separated through a single step of CCC with good resolution, R_s=1.55 for Y/Ho and 1.05 for Er/Y.

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