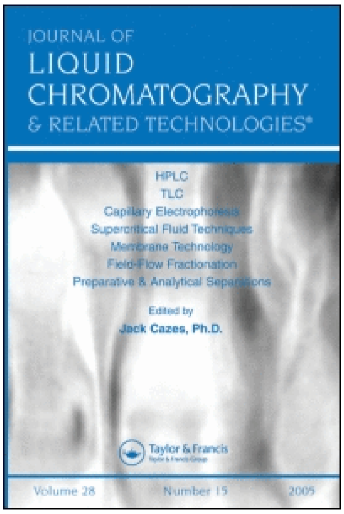

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S. Nakamura[a]; M. Watanabe[a]; K. Akiba[a]
[a] Institute for Advanced Materials Processing Tohoku University, Aoba-ku Sendai, Japan

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SEPARATION OF YTTRIUM FROM LANTHANOID ELEMENTS BY CENTRIFUGAL PARTITION CHROMATOGRAPHY

**SHIGETO NAKAMURA, MINORU WATANABE,
AND KENICHI AKIBA**
*Institute for Advanced Materials Processing
Tohoku University
Katahira-2, Aoba-ku
Sendai 980-77, Japan*

ABSTRACT

Separation of yttrium(III) and heavy lanthanoid elements(III) was performed by centrifugal partition chromatography (CPC) employing different types of stationary phase components, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) and Versatic 10 (VA10). The retention volume (V_R) in CPC provided with the EHEHPA stationary phase increased with the atomic number of lanthanoid elements, and Y was eluted between Ho and Er. Yttrium can be completely separated from most of lanthanoids other than Dy, Ho and Er. As for the VA10 stationary phase, Y was separated from Dy, Ho and Er. Isolation of Y from a lanthanoid mixture was accomplished by means of two steps of CPC fractionation through the EHEHPA stationary phase, followed by treatment through the VA10 stationary phase; the content of each lanthanoid element in the final Y fraction was reduced to less than 0.3% against the content of Y.

INTRODUCTION

Yttrium occurs in natural resources along with lanthanoid elements, and separation and purification of Y require multi-stage processes due to chemical similarities of rare earth elements. Liquid-liquid extraction has provided effective separation methods for rare earth elements (1); industrial separation of Y has been performed by means of series of mixer-settlers employing various types of extractants such as Versatic 911 and tributylphosphate (2). However, it has required a large number of stages and long separation time for complete isolation of high-purity elements.

Centrifugal partition chromatography (CPC) has been developed as an analytical and preparative separation method for chemically-similar materials (3). In this chromatography, an organic solution containing an extracting reagent can be employed as a stationary phase without any solid support, therefore, the stationary and mobile phases can be selected to optimum conditions on the basis of liquid-liquid extraction behavior.

In recent years, the mutual separation of trivalent lanthanoid elements was successfully performed on CPC employing stationary phases containing acidic organophosphorus extractants, such as di(2-ethylhexyl) phosphoric acid (DEHPA) (4-6), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) (7,8) and di(2,4,4-trimethylpentyl)phosphinic acid (DTMPPA) (9,10). A series of lanthanoids were eluted in the increasing order of distribution ratios between the stationary and mobile phases, corresponding to the decreasing order of their ionic radii. The ionic radius of Y(III) is close to those of heavy lanthanoids, and the extractability of Y with DEHPA is placed between Ho and Er, exhibiting the low separation factors of 1.65 for Y and Ho (Y/Ho), and 1.37 for Er/Y (11). Since these separation factors are not sufficiently large, quantitative separation of Y from lanthanoid elements seems to be difficult even by means of CPC provided with acidic organophosphorus extractants. Other kinds of extractants having the desired selectivity are required for the separation of Y from accompanying heavy lanthanoids. Versatic 10 (VA10) is a bulky tertiary alkyl mono-carboxylic acid and has better selectivity for the separation of Y from heavy lanthanoids in contrast with acidic organophosphorus extractants, though the separation factors for neighboring lanthanoids are rather low (12,13).

This study deals with chromatographic separation of Y and some lanthanoid elements by CPC provided with the EHEHPA stationary phase and the VA10 stationary phase. Isolation of Y from lanthanoid elements was performed by fractionation from CPC with EHEHPA, followed by separation on CPC with VA10.

EXPERIMENTAL

Materials

An extractant, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) (PC-88A; Daihachi Chemical Ind. Co. Ltd.), was washed with a sodium hydroxide solution to remove acidic impurities, and its purity was checked to be 96% by potentiometric titration in ethanol with a sodium hydroxide solution. Versatic 10 (VA10) was obtained from Shell Chemical Co., and its purity (97%) was also determined as above. A 50% (v/v) ethanol solution of 0.014% (w/v) Arsenazo III (Dojindo Lab.) was used for a post column reaction. Standard solutions of 1000 ppm of Y, Gd, Tb, Dy, Ho, Er and Tm in 1 M (M = mol dm^{-3}) HNO_3 (Wako Pure Chemical Ind.) were dried up, and diluted with deionized water or pH-buffered solution to the desired concentration.

Apparatus

Chromatographic separation was performed by means of centrifugal partition chromatograph (CPC, Model NMF; Sanki Engineering Ltd.) modified for use at higher temperature up to 70°C. Six partition cartridges (type 250W, total volume 125 cm^3) as separation columns were arranged in a CPC rotor, where one cartridge was composed of 400 microcells. A mobile phase was sent into CPC by a triple plunger pump (LBP-V; Sanki). A part of the eluted solution from CPC was continuously moved to a detection system by a double plunger pump (NP-FX-10U; Nihon Seimitsu Kagaku Co., Ltd). The detection system consisted of a post column-reactor (ICA-3041; Toa Electronics Ltd.), a photometric detector with a flow cell (ICA-3020; Toa) and a pen recorder (FBR-251A; Toa).

Extraction Equilibrium

A toluene solution of 0.02 M $(EHEHPA)_2$ was shaken over 30 min with an equal volume of an aqueous phase containing 2×10^{-5} M of each rare earth ion. The aqueous pH was adjusted to an appropriate value with 0.1 M $(H,Na)CHCl_2COO$. In the extraction with VA10, a kerosene solution of 0.25 M $(VA10)_2$ was contacted with a 0.1 M $NaNO_3$ aqueous solution containing 0.01 M $(H,Na)CH_3COO$ as a buffer. After equilibrium, the concentrations of metals were measured by inductively coupled plasma atomic emission spectrometry (ICP–AES) (SPS 1200A, Seiko Instruments & Electrics Ltd.); the concentration of the extracted element in the organic phase was determined after stripping into 1 M HNO_3.

CPC Process

The toluene solution of 0.02 M $(EHEHPA)_2$ was held in microcells of CPC–cartridges as the stationary phase. The aqueous solution containing 0.1 M $(H,Na)CHCl_2COO$ was chosen for the mobile phase. Further, the kerosene solution of 0.25 M $(VA10)_2$ and the 0.1 M $NaNO_3$ solution buffered with 0.01 M $(H,Na)CH_3COO$ were respectively used as the stationary and mobile phases. The mobile phase was equilibrated with the corresponding organic phase before use. This mobile phase was pumped into the stationary phase through a rotary seal joint at a flow rate of 3 cm^3 min^{-1}. Under the rotation of CPC–rotor at 900 ~ 1100 rpm, the mobile phase flowed through the column as small droplets, replacing a part of the stationary phase in the microcells. At a constant volume ratio of two phases, the sample solution containing $5 \times 10^{-4} \sim 4 \times 10^{-3}$ M of each rare earth ion was charged into the column through a sample loop (1 cm^3). A part of the eluted stream was continuously monitored by measuring the absorbance of lanthanoid–Arsenazo III complexes at 650 nm.

Chromatographic Parameters

Chromatographic parameters were evaluated to clarify elution characteristics of rare earth elements in CPC. The number of theoretical plates (N) is related to the retention volume (V_R) and the peak width (W):

$$N = 16 \left(V_R / W \right)^2 \tag{1}$$

The separation factor (α_c) in chromatography is evaluated from the retention volumes of corresponding components 1 and 2:

$$\alpha_c = \frac{V_{R,2} - V_0}{V_{R,1} - V_0} \tag{2}$$

where V_0 is the elution volume for an unretained component.

The resolution (R_s) is evaluated by the distance between the two peaks and their peak widths.

$$R_s = \frac{2\,(V_{R,2} - V_{R,1})}{W_1 + W_2} \tag{3}$$

RESULTS AND DISCUSSION

Extraction with EHEHPA

Mutual separation of rare earth elements is based on the differences in the distribution ratios between the stationary and mobile phases. Extraction behavior of Y and some heavy lanthanoids with EHEHPA in toluene was examined in order to optimize separation conditions on CPC. Figure 1 represents the distribution ratios (D) of closely resemble rare earths as a function of pH, where the extractant concentration is formally expressed as a dimer $(\mathrm{EHEHPA})_2$, since the acidic organophosphorus extractants are commonly present as dimeric species in nonpolar diluents. The slopes of the log D-pH plots were of 2.7 to 2.9, indicating that the extraction proceeds in the following reaction (7);

$$M^{3+}_{aq} + 3(HA)_{2,org} \rightleftharpoons M(HA_2)_{3,org} + 3H^{+}_{aq} \tag{4}$$

where M denotes the rare earth element and $(HA)_2$ is the dimer of extractant. The extraction constants (K_{ex}) for Eq.(4) are listed in Table 1. The value of K_{ex} increased with atomic number of lanthanoids, and that for Y was situated between Ho and Er. These K_{ex} values for the toluene solution were lower about 2 order of magnitude than those for the kerosene solution (7); the K_{ex} values have been found to decrease in the order hexane > carbon tetrachloride > 1,2-dichloroethane > toluene > benzene for extraction with acidic organophosphorus compounds (14). This lower extractability in toluene may permit to employ the dilute acid as the mobile phase of CPC, and/or the higher concentration of extracting reagent in the stationary phase. The separation factors (α_D) are summarized in Table 1. The values of α_D for Y/Ho and Er/Y were low and the separation of Y from Ho and Er might be rather difficult by CPC with the EHEHPA stationary phase, since the mutual separation has been often insufficient for lanthanoids having low α_D values less than 2 (7).

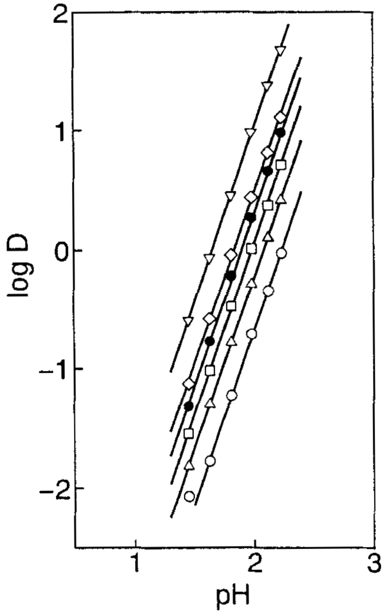

FIGURE 1 Extraction of rare earth elements with 0.02 M $(EHEHPA)_2$ in toluene. 0.1 M (H, Na)$CHCl_2COO$, 25°C, (●) Y, (○) Tb, (△) Dy, (□) Ho, (◇) Er, (▽) Tm.

TABLE 1
Extraction Constants and Separation Factors of Rare Earth Elements in EHEHPA System at 25°C

Element	log K_{ex}	α_D
Tb	−1.65	
		3.1
Dy	−1.15	
		2.0
Ho	−0.85	
		1.9
Y	−0.58	
		1.5
Er	−0.41	
		3.5
Tm	0.14	

Organic phase : 0.02 M $(EHEHPA)_2$ in toluene.
Aqueous phase : 0.1 M (H,Na)$CHCl_2COO$.

Application to CPC

The extraction system with EHEHPA was applied to the CPC procedures for rare earths, Y, Ho and Er, having low separation factors. The sample solution (1 cm^3) containing 1×10^{-3} M Y or a mixture of Ho and Er was introduced into the column containing 0.02 M $(EHEHPA)_2$–toluene. Resulted chromatographic peaks on CPC are presented in Fig. 2. The elution peak of Y was situated between the Ho and Er peaks, in the agreement with corresponding order in the distribution ratios. The retention volume became large with rising pH owing to increase in the distribution ratio. The retention volume can be related to the D value in the ordinary chromatograph as:

$$V_R = V_m + D\,V_s \qquad (5)$$

where V_s and V_m are the volumes of the stationary and mobile phases, respectively. Plots of the V_R values against the D values determined by liquid–liquid extraction are shown in Fig. 3. The solid line indicates the calculated value from Eq.(5) by employing the experimental values of 78 cm^3 for V_m and 47 cm^3 for V_s. The experimental points were in fair agreement with the calculated ones; the retention volumes of rare earths can be predicted from individual extraction data.

As can be seen in Fig. 2, the chromatogram of Er and Ho was considerably overlapped at low pH as 1.98, while this chromatographic separation was improved with an increase in pH. Further, a rise in temperature improved the peak profile; e.g., the N values for Y increased from 17 at 25°C to 30 at 40°C. This enhancement may be attributable to the promotion of extraction rate with the rise of temperature. The separation factors between Ho and Er were evaluated as close values, 2.8 and 2.7 at 25°C and 40°C, respectively. The resolution of 0.77 at 25°C was somewhat enhanced to 0.83 at 40°C owing to the increasing N. At higher temperature of 50°C, no distinct chromatogram was obtained because of gradual losses of the stationary phase along with the mobile phase.

Separation of Y from Lanthanoids on CPC with EHEHPA

Chromatographic separation of Y and lanthanoid elements was examined by using EHEHPA as the CPC stationary phase at 40°C. The

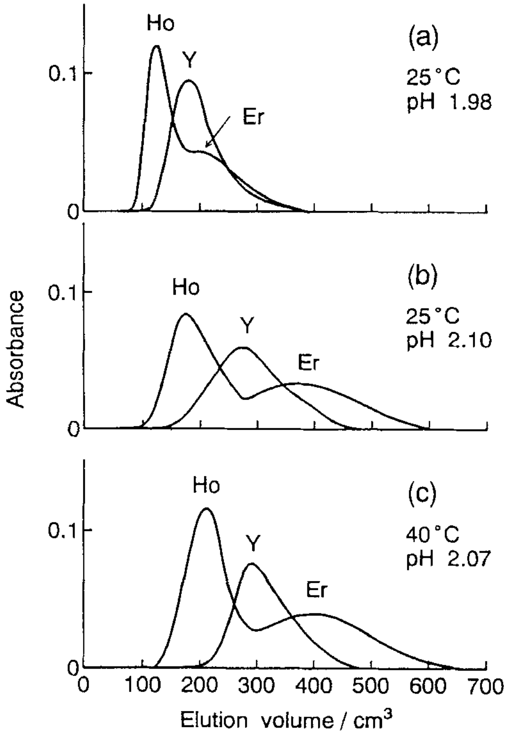

FIGURE 2 Chromatograms of Y and the binary mixture of Ho and Er by CPC with EHEHPA. CPC : 6 cartridges of 250W, 1100 rpm; stationary phase : 0.02 M $(EHEHPA)_2$ in toluene; mobile phase : 0.1 M (H, Na)$CHCl_2COO$; sample : 1 × 10^{-3} M Y, or a mixture containing 1 × 10^{-3} M Ho and Er, 1 cm^3.

chromatogram for a mixture of 4 × 10^{-3} M Y, Tb and Tm is shown in Fig. 4. Yttrium was completely separated from Tb and Tm. The other lanthanoids lighter than Tb will be less retained than Tb due to lower distribution ratios and heavier lanthanoids than Tm having higher distribution ratios will be more retained than Tm.

Under the same conditions, the chromatograms for desired lanthanoids, Dy, Ho and Er, together with Y are presented in Fig. 5. The separation factor between Dy and Y was relatively high as 3.0, and only a tailing of

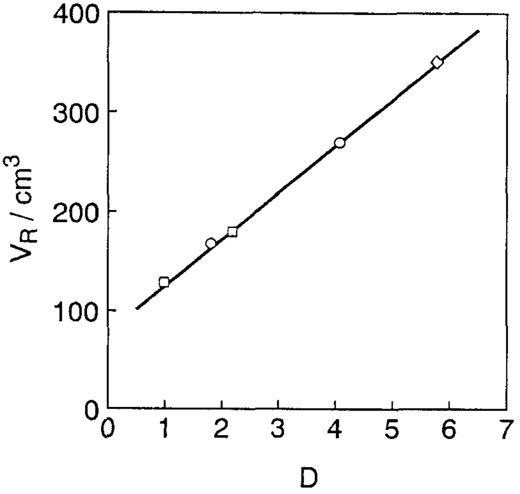

FIGURE 3 Relation between the retention volume and the distribution ratio in EHEHPA system at 25°C. (○) Y, (□) Ho, (◇) Er; the solid line indicates the calculated value from Eq.(5).

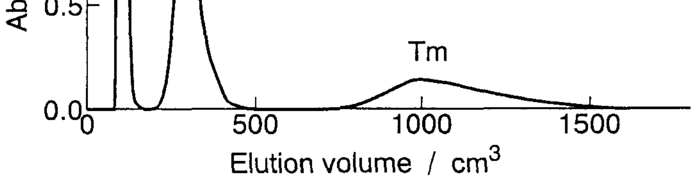

FIGURE 4 Separation of the ternary mixture of Y, Tb and Tm by CPC with EHEHPA; 40°C, pH 2.07; sample : 4 × 10^{-3} M Y, Tb and Tm, 1 cm^3.

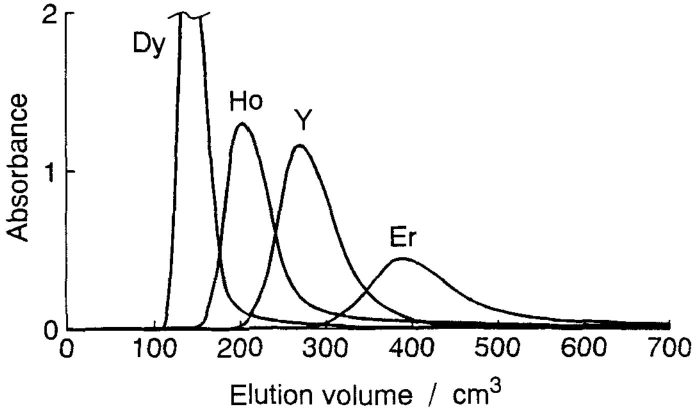

FIGURE 5 Chromatograms of Y, Dy, Ho and Er by CPC with EHEHPA. 40°C, pH 2.07; sample : 4 × 10^{-3} M each rare earth element, 1 cm^3.

the Dy peak reached the Y peak. Large parts of the chromatographic peaks of Ho and Er overlapped with that of Y, in which the separation factors were low such as 1.54 for Ho/Y and 1.62 for Y/Er, and the resolutions were still so low as 0.56 for Ho/Y and 0.72 for Y/Er. These findings suggest that the chromatographic separation of Y from Ho and Er is difficult by CPC with the EHEHPA stationary phase, and the Y fraction will accompany a little amount of Dy and considerable amounts of Ho and Er. Additional treatment is required for further purification of Y, that is, the removal of Dy, Ho and Er from the Y fraction.

Extraction with VA10

The extractability of lanthanoids by VA10 from 1 M (H,Na)NO_3 has been reported to increase with the atomic number and then Y is extracted very closely to middle lanthanoids rather than heavy lanthanoids (13). Therefore, the separation of Y from heavy lanthanoids may be performed by employing VA10 as the stationary phase.

The extraction of Y and related lanthanoids with VA10 in kerosene was examined. Figure 6 illustrates plots of the distribution ratios of Y and

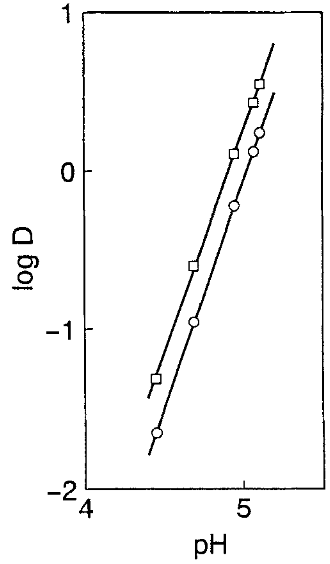

FIGURE 6 Extraction of Y and Ho with 0.25 M $(VA10)_2$ in kerosene. 0.1 M $NaNO_3$ and 0.01 M $(H, Na)CH_3COO$, 25°C, (○) Y, (□) Ho.

TABLE 2
Extraction Constants and Separation Factors between Lanthanoids and Y in VA10 System

M	25°C		40°C		55°C	
	log K_{ex}	$\alpha_D(M/Y)$	log K_{ex}	$\alpha_D(M/Y)$	log K_{ex}	$\alpha_D(M/Y)$
Y	-13.27	-	-12.47	-	-11.87	-
Gd	-13.12	1.4				
Tb	-12.94	2.1				
Dy	-12.88	2.5	-12.14	2.1	-11.55	2.1
Ho	-12.93	2.2	-12.16	2.0	-11.58	1.9
Er	-12.92	2.2	-12.12	2.2	-11.54	2.1

Organic phase : 0.25 M $(VA10)_2$ in kerosene.
Aqueous phase : 0.1 M $NaNO_3$, 0.01 M $(H,Na)CH_3COO$.

Ho from 0.1 M $NaNO_3$ solution against pH at 25°C. Yttrium was less extracted than Ho, in the reverse order by EHEHPA. The distribution ratios of Dy and Er were very close to that of Ho. These plots gave straight lines with slopes of about 3, and the extraction reaction also follows Eq. (4). (13,15)

The extraction constants and the separation factors between lanthanoids and Y are summarized in Table 2. The value of log K_{ex} increased with rising temperature in a similar extent for each element. The extraction constants of heavy lanthanoids were very close to each other, and the value for Y was smaller than those for heavy lanthanoids. The separation factor of Y was found to be relatively large above 2 for Tb, Dy, Ho and Er. The α_D values tend to decrease only slightly with rising temperature from 25°C to 55°C, but they are still close to 2 even at 55°C.

Chromatographic Behavior on CPC with VA10

On the basis of extraction behavior, the kerosene solution of 0.25 M $(VA10)_2$ was employed as the stationary phase and the mobile phase of 0.1 M $NaNO_3$ solution was adjusted to an appropriate pH with 0.01 M (H, $Na)CH_3COO$ for CPC separation of Y from heavy lanthanoids. Figure 7 illustrates the CPC chromatograms of a mixture of Y and Ho at different temperatures. Here, Ho was chosen as a typical accompanying heavy lanthanoid, because the separation factor for Ho/Y was the lowest among heavy lanthanoids. The pH of the mobile phase was adjusted to be lower at higher temperature, since the retention volume increased with the rise of temperature, due to the increase in the distribution ratios of rare earth elements.

Figure 8 shows the relationship between V_R and D evaluated from the liquid–liquid extraction for Y and Ho at different temperature. The V_R values increased linearly with increasing D values, indicating that the retention behavior of the metal ion corresponds to the distribution behavior. The V_R values were found to be a little larger than those calculated from Eq. (5) using experimental values of 65 cm^3 for V_m and 60 cm^3 for V_s. This deviation may be due to an increase in the distribution ratio, perhaps caused by a local rise in temperature in column cartridges near a heater.

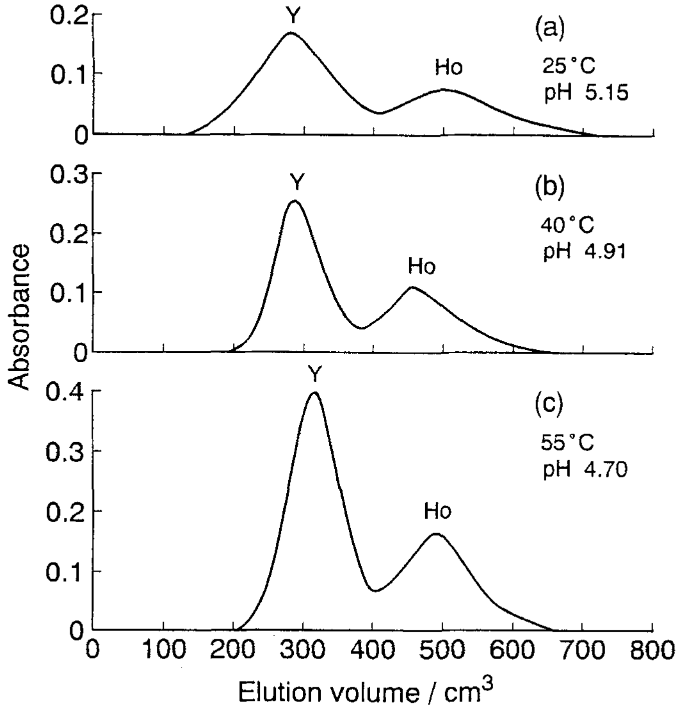

FIGURE 7 Chromatograms of the binary mixture of Y and Ho by CPC with VA10 at different temperature. CPC : 6 cartridges of 250W, 900 rpm; stationary phase : 0.25 M $(VA10)_2$ in kerosene; mobile phase : 0.1 M $NaNO_3$ and 0.01 M $(H, Na)CH_3COO$; sample : 1 × 10^{-3} M Y and Ho, 1 cm^3.

In Fig. 7, the values of N for both elements increased with rising temperature, while the separation factor slightly decreased. These opposite trends for separation efficiency were partially compensated, while the resolution for Y and Ho slightly increased, such as 0.89 at 25°C, 0.95 at 40°C and 1.0 at 55°C.

Figure 9 illustrates individual chromatographic peaks for Dy, Ho, Er and Y under the optimum conditions at 55°C. The retention volume for Ho was a little smaller than those for Dy and Er, as predicted from their extractabilities. The chromatogram of Y only slightly overlapped with those

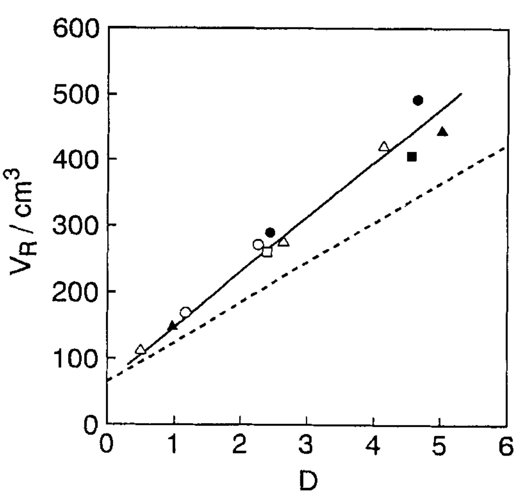

FIGURE 8 Relation between the retention volume and the distribution ratio in the VA10 system. open : Y, closed : Ho; (○,●) 25°C, (△,▲) 40°C, (□,■) 55°C; the broken line indicates the calculated value from Eq.(5).

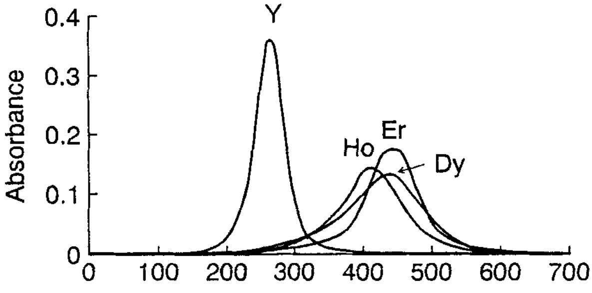

FIGURE 9 Chromatograms of Y, Dy, Ho and Er by CPC with VA10. 55°C, pH 4.70; sample : 1 × 10^{-3} M each rare earth element, 1 cm^3.

of lanthanoids, and good resolution between Y and each lanthanoid was accomplished as R_s = 1.1 (Ho/Y), 1.3 (Dy/Y) and 1.6 (Er/Y).

Separation of Y from Rare Earth Mixture

The separation and purification of Y from lanthanoid mixtures was performed through subsequent CPC separation steps with EHEHPA and VA10. A sample solution (1 cm^3) containing 4 x 10^{-3} M each of Y, Dy, Ho and Er was injected to the CPC system using the EHEHPA-toluene solution as the stationary phase, since other lanthanoids will be readily separated through the EHEHPA stationary phase. Figure 10 shows the chromatogram on CPC with 0.02 M $(EHEHPA)_2$-toluene. The chromatogram gave distinct peaks of Dy, Ho and Y, while the peak for Er was no longer distinguishable from the overlapped peak of Y. The effluent mobile phase was fractionated from around 230 cm^3 to 430 cm^3 corresponding to the Y elution.

The rare earth elements in the fractionated solution were concentrated by extraction into a 0.02 M $(EHEHPA)_2$-toluene solution at pH > 3, and then the extracted elements were stripped into 1 M HNO_3. The aqueous

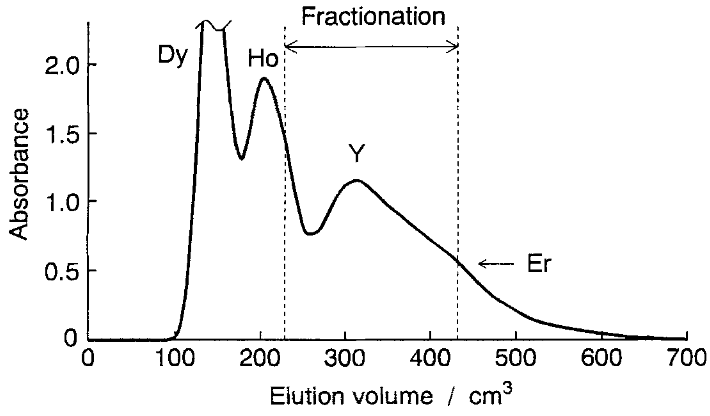

FIGURE 10 Fractionation of Y-rich effluent in the separation of the mixture of Y, Dy, Ho and Er by CPC with EHEHPA. 40°C, pH 2.07; *sample* : 4 x 10^{-3} M Y, Dy, Ho and Er, 1 cm^3.

solution was evaporated to dryness, and the residue was resolved into 8 cm^3 of water. In these procedures, the recovery of rare earths was confirmed to be quantitative.

Rare earth elements in the Y fraction through CPC with EHEHPA were further introduced into the VA10-CPC system. Figure 11 shows the chromatogram for 1 cm^3 of the solution on CPC with a 0.25 M $(VA10)_2$-kerosene solution at 55°C. Yttrium was eluted with a mobile phase of pH 4.70 yielding almost base-line separation from the accompanying lanthanoids. The Y fraction in the region of about 190 - 340 cm^3 was collected and analyzed by ICP-AES.

Isolation of Y from lanthanoid elements by subsequent CPC treatments is summarized in Table 3. In the CPC with EHEHPA, most of Dy was eliminated from the Y fraction, but considerable amounts of Ho and Er were remained in the Y fraction. By further separation through CPC with VA10, these residual lanthanoids were entirely removed to less than 0.003 against Y content.

In conclusion, the separation and isolation of Y from chemically similar lanthanoids was performed through two steps of CPC processes employing different kinds of stationary phases. Yttrium was fractionated

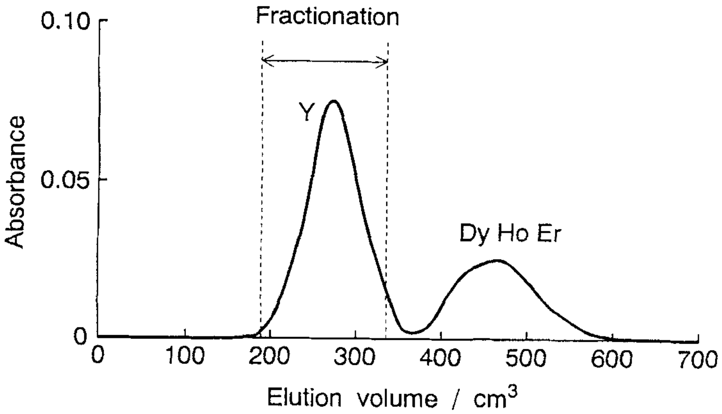

FIGURE 11 Separation of Y from Dy, Ho and Er by CPC with VA10. 55°C, pH 4.70.

TABLE 3
Separation of Y from Dy, Ho and Er by CPC

Element	EHEHPA		VA10	
	Yield	Relative content [M]/[Y]	Yield	Relative content [M]/[Y]
Y	0.89	-	0.91	-
Dy	0.0064	0.0071		0.0004
Ho	0.14	0.16		0.0019
Er	0.45	0.51		0.0026

accompanying only a few lanthanoids, Dy, Ho and Er, separated from other lanthanoid elements lighter than Dy and heavier than Er, by means of the EHEHPA stationary phase. The Y fraction was further purified by removing the accompanying lanthanoids through the stationary phase of VA10 having sufficient separation factor between Y and heavy lanthanoids.

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