Mutual Separation of Lanthanoid Elements by Centrifugal Partition Chromatography

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MUTUAL SEPARATION OF LANTHANOID ELEMENTS BY CENTRIFUGAL PARTITION CHROMATOGRAPHY

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ABSTRACT

Multistage separation based on liquid-liquid extraction has been investigated by means of centrifugal partition chromatography (CPC). A kerosene solution of 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPA) was employed as a stationary phase without any solid support. Metal ions eluted by the aqueous mobile phase were detected by the post-column reaction with Arsenazo III. The retention volumes are approximately linear with the distribution ratios of metals. The mutual separation of adjacent lanthanoids was accomplished by CPC.

INTRODUCTION

Considerable interest has been focused on the liquid-liquid extraction of rare earth elements, and some regularities in

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extraction equilibria have been presented for a variety of extraction systems (1-7). However, potential works directly concerned with separation of lanthanoid elements have been restricted to a few cases (8,9), since this group of metal ions is particularly difficult to separate due to similarities in the charge of +3 and the ionic radius. Multistage processes are required for quantitative separation of this series of ions; such well known processes as batteries of mixer-settlers or counter current extraction have partial resolution between adjacent lanthanoids and require long separation times.

Centrifugal partition chromatography (CPC) developed by Murayama and coworkers would afford great possibilities for chromatographic separation of chemically-similar materials (10). This new liquid-liquid partition chromatography employing a stationary phase without any solid support is very attractive, because it offers flexibility for selection of a stationary phase on the basis of data on liquid-liquid extraction (11). This will be advantageous for large-scale applications of chromatographic processes.

In an industrial-scale separation of rare earth elements, di(2-ethylhexyl) phosphoric acid (DEHPA) has been most commonly used as an extractant in acidic media, due to its high extractability and high separation factors between these elements. An acidic extractant, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPA) has recently accessible for the extraction of rare metals including lanthanoids (12). Its low extractability compared with DEHPA is rather preferable to strip lanthanoid elements with dilute acid solutions.

The present paper deals with the possibility of new chromatographic separation of lanthanoid elements. The liquid-liquid extraction process was applied to multistage separation by means of CPC provided with an organic solution of EHPA as the stationary phase. Optimum conditions for chromatographic procedures were ascertained and mutual separations of adjacent lanthanoid elements were accomplished.

EXPERIMENTAL

Materials

An extractant, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPA) (PC-88A, Daihachi Chemical Ind. Co. Ltd.), was washed with a sodium hydroxide solution to remove acid impurities, and then its concentration was determined by potentiometric titration with a standard solution of sodium hydroxide in an ethanol-water mixture. Arsenazo III (Dojindo Lab.) was used as a post column reagent. Radioisotopes ^{152,4}Eu (Radiochemical Centre, England) was also used for liquid-liquid extraction. The other chemicals used were of reagent grade.

Apparatus

A centrifugal partition chromatograph (Sanki Engineering Ltd.) was used by arranging 6 or 12 cartridges (30E), where one cartridge was composed of 54 microcells (10). For continuous analysis of elution stream, the detection system consisted of a post column-reactor (Model ICA-3041; Toa Electronics Ltd.), a photometric detector with a flow cell (Model ICA-3020; Toa Electronics Ltd.) and a pen recorder. Flow lines from CPC to the detector were connected with Teflon tubing (1 mm inner diameter). In liquid-liquid extraction, the concentrations of mixed lanthanoids were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (SPS 1200A, Seiko Instruments & Electrics Ltd.) for the aqueous phase or the stripped solution from the organic phase.

Procedure

A kerosene solution containing 0.02 M (M = mol dm^{-3}) (EHPA)$_2$ was hold as the stationary phase in the cartridge-column. Under centrifugal force, the aqueous mobile phase was pumped into the stationary phase through a rotary seal joint at a flow rate of 3 cm^3 min^{-1}. Small drops of the mobile phase were passed through the stationary phase in the column rotating at 800 rpm at 55°C

unless otherwise noted in the text. After equilibration between two phases, the sample solution containing 10^{-3} M of each lanthanoid was injected through a sample loop (1 cm^3). Metal ions were eluted with the mobile phase buffered at desired pH with 0.1 M $(H,Na)Cl_2CHCOO$. The eluted stream was monitored by measuring the absorbance of lanthanoid complexes at 650 nm based on the post-column reaction with Arsenazo III (0.014% w/v) at a flow rate of 0.5 cm^3 min^{-1} (13).

RESULTS AND DISCUSSION

Extraction Equilibrium of Lanthanoids

Equilibrium of lanthanoid extraction was examined in order to apply liquid–liquid extraction to the mutual separation of lanthanoids by CPC. Distribution ratios of a series of lanthanoids of interest, La, Pr, Nd, Sm, Eu, Gd, Tb and Dy, were obtained by determining the concentration of lanthanoids in the aqueous solution by ICP-AES. The aqueous phase initially contained the mixture of these lanthanoid ions of 50 ppm for Pr, 20 ppm for Nd, and 10 ppm for others. Plots of log D vs. pH gave a series of parallel lines with slopes of close to 3, as shown in Fig. 1, and the slopes of the plots of log D vs. log $[(EHPA)_2]$ were found to be 2.8. Overall extraction equilibrium can be expressed by,

$$M^{3+}{}_{aq} + 3(HA)_{2,org} \rightleftharpoons M(HA_2)_{3,org} + 3H^+{}_{aq} \qquad (1)$$
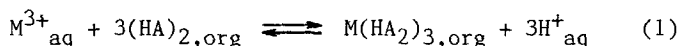
$$K_{ex} = \frac{[M(HA_2)_3]_{org}\,[H^+]^3{}_{aq}}{[M^{3+}]_{aq}\,[(HA)_2]^3{}_{org}} \qquad (2)$$

where M denotes the lanthanoid and $(HA)_2$, the dimer of EHPA, and K_{ex} is the extraction constant.

Application to CPC System

In chromatography the retention volume (V_R) is related to the distribution ratio (D) of the desired component between the stationary and mobile phases:
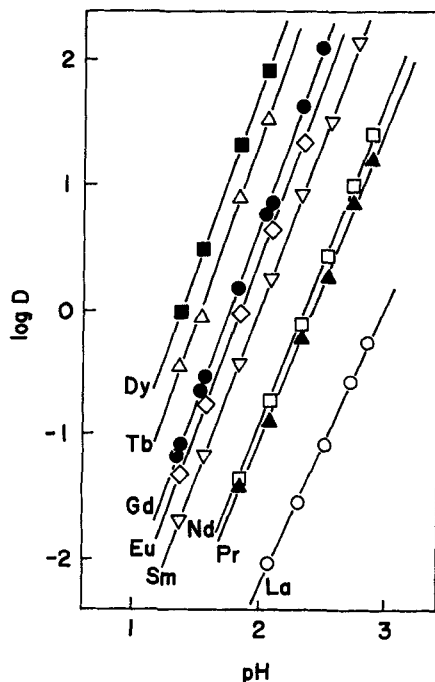
FIGURE 1. Distribution ratios of lanthanoids as a function of pH.
0.02 M (EHPA)$_2$ in kerosene, 0.1 M (H,Na)Cl$_2$CHCOO, 25°C.

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

where V_s and V_m are the volumes of the stationary and mobile
phases, respectively. When these fundamental values for indi-
vidual lanthanoids are known, it is possible to predict proper
conditions for desired separation; values of D will be optimized
by varying pH and/or the extractant concentration.

All the CPC system including detector was preliminarily
tested for the elution behavior of Eu. An europium solution of 1
cm^3 was injected into the front of the column of 6 cartridges
holding 0.02 M (EHPA)$_2$ in kerosene. Arsenazo III was continuously
added to the end of elution stream. It was confirmed that the
post column reaction causes no noticeable extra broadening of

elution bands. From chromatograms obtained at different pH, the V_R values for Eu were found to be approximately proportional to the distribution ratios, as given by Eq.(3).

The theoretical plate number (N) is related to the retention volume and the bandwidth (W):

$$N = 16 \; (\; V_R \; / \; W \;)^2 \tag{4}$$

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

$$\alpha_c = \frac{V_{R,2} - V_o}{V_{R,1} - V_o} \tag{5}$$

where V_o is the elution volume for an unretained component. The degree of separation of two adjacent bands is defined as resolution (R_s):

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

Chromatogram for Binary Mixture

Based on the extraction data given in Fig. 1, the elution behavior of Sm and Gd was tested by means of CPC holding EHPA in kerosene as the stationary phase in order to select suitable conditions for adequate separation. Figure 2 shows a representative chromatogram having individual peaks; the first peak for Sm was followed by the broad peak for Gd, however, they exhibited pronounced tailing and substantial overlap each other. This band spreading may be due to slow equilibration of liquid–liquid extraction including complex formation.

Water-Miscible Organic Solvent as Mobile Phase

The elution behavior of Sm and Gd was examined whether these bands can be resolved better or not by the addition of ethanol (EtOH) in the aqueous mobile phase.. As Fig. 3 shows, it is noticeable that 10 and 20% v/v EtOH additives appreciably improve the resolution of these two bands.
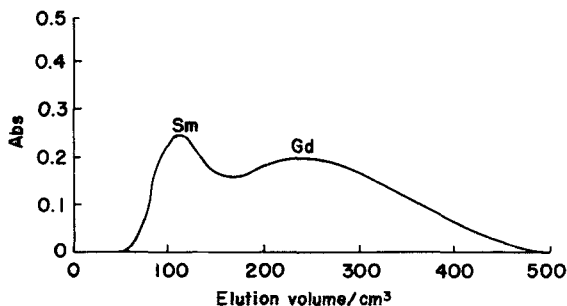
FIGURE 2. Elution curve of the binary mixture of Sm and Gd.
CPC: 6 cartridges, 900 rpm, 25°C;   stationary phase: 0.02 M
$(EHPA)_2$ in kerosene;   mobile phase: 0.1 M $(H,Na)Cl_2CHCOO$ in water,
pH 1.90;   sample: 5×10^{-4} M Sm and 1.5×10^{-3} M Gd, 1 cm^3.
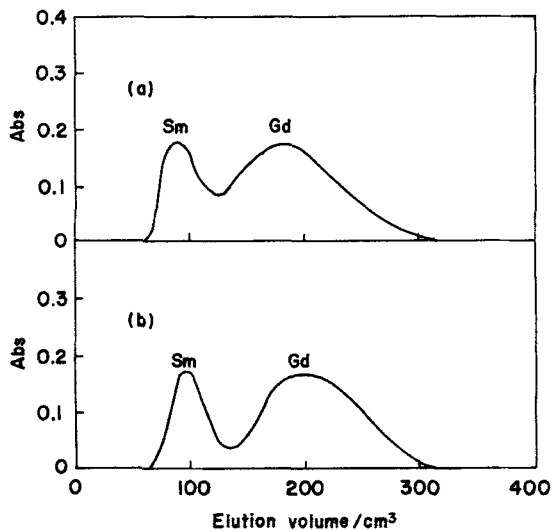

FIGURE 3. Effect of ethanol in the mobile phase on the separation
of Sm and Gd by CPC.   EtOH: (a) 10% v/v, (b) 20% v/v.
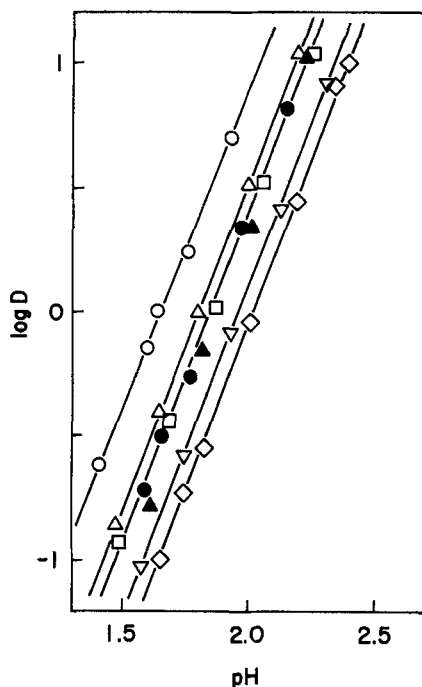Experimental conditions are same as those in FIG. 2.

FIGURE 4. Effect of water–miscible organic solvents on the distribution ratio of [152,4]Eu. 0.02 M (EHPA)$_2$ in kerosene, 0.1 M (H,Na)Cl$_2$CHCOO in 20% v/v miscible organic solvent–water. (O) AN, (Δ) MeOH, (●) EG, (□) EtOH, (∇) DMSO, (◇) DMF, (▲) water alone.

Further, several organic solvents miscible with water were tested as components of the mobile phase to accelerate extraction and to increase the theoretical plate number. Figure 4 illustrates the distribution ratios of Eu between the organic phase and the aqueous phase containing 20% v/v miscible organic solvents. Plots of log D vs. pH, which is an apparent value indicated by pH meter in these mixed solvent systems, gave straight lines with slopes of 2.6 – 2.9, indicating the analogous extraction behavior as expressed by Eq.(1). They decreased in the following order: acetonitrile (AN) > methanol (MeOH) > EtOH ≃ ethylene glycol (EG) ≃ water > dimethyl sulfoxide (DMSO) > N,N–dimethylformamide (DMF).

TABLE 1
Effect of 20% v/v Miscible Organic Solvents-Water in the
Mobile Phase on the Separation of Sm and Gd by CPC

Solvents	Peak shapes	N_{Sm}	N_{Gd}	α_c	R_s
Acetonitrile	No peak	—	—	—	—
Methanol	Tailing	29.0	17.5	3.0	0.83
Ethylene glycol	Symmetry	31.2	23.6	3.8	1.15
Ethanol	Symmetry	31.7	21.7	2.9	0.95
Dimethyl sulfoxide	Symmetry	28.1	23.3	3.6	1.14
N,N-Dimethyl-formamide	Asymmetry	19.5	11.9	3.4	0.75
Water alone	Asymmetry	27.1	15.5	2.9	0.82

Six cartridges, 0.02 M (EHPA)$_2$, 900 rpm, 55°C.

Experimental results are summarized in Table 1 for the separation of Sm and Gd by CPC with 6 cartridges using mixtures of 20% v/v organic solvents-water. The AN-water mixture was not applicable to the mobile phase because of its nondistinct peaks. The mixtures with DMF and MeOH yielded asymmetric peaks which have sharp fronts and extended tails; these mobile phases yielded rather low resolution due to relatively low N values. Symmetrical chromatographic peaks were obtained by the use of mixtures with EG, EtOH and DMSO; the N values for individual peaks and the separation factors (α_c) appreciably increased compared to those for water alone. In subsequent experiments, the mixture of 20% v/v EG-water was employed as the mobile phase.

While little is known about the kinetics of separation processes in CPC, the influence of miscible organic additives may be

related to a number of factors; 1) a lowering of surface tension
causes a decrease in drop sizes, 2) an increase in distribution of
EHPA into the aqueous phase accelerates of the rate determining
step such as the formation of the first complex $M(HA_2)^{2+}$, 3) a
decrease in water activity reduces the extent of hydration of
metal ion. These associated factors are considered to enhance the
extraction rate and to improve band resolution.

Effect of Temperature

The effect of temperature on the chromatographic separation
of a pair of adjacent elements Sm and Eu was examined using the
mixed mobile phase of 20% EG-water. Figure 5 shows variations of
separation parameters with a rise in temperature from 25 to 55°C.
The retention volumes of Sm and Eu increased with temperature and
the V_R values at 55°C were about 1.7 times those at 25°C for both
of Sm and Eu. This finding indicates that the rise of temperature
enhances the distribution ratio between the stationary and mobile
phases inside the microcells. Similar progressive increases in V_R
for Sm and Eu gave a small effect on the separation factor which
decreased only slightly with rising temperature. On the other
hand, the N values of each element considerably increased with
temperature, and resolution for two adjacent elements therefore
increased almost linealy with rising temperature mainly depending
on the increased N, as is evident in Fig. 5.

Effect of Rotational Speed

Figure 6 shows the effect of the speed of rotation on reso-
lution obtained by varying a rotational speed from 400 to 1000
rpm. The N values for Sm and Gd increased linearly with the
rotational speed, and thereby the R_s value varied almost in pro-
portion to the N values. As the dropsize of the mobile phase
decreases with increasing gravity resulting from rotation, the
rate of extraction is enhanced. Thus, a high speed of rotation
will be preferable for better resolution, as long as the pressure
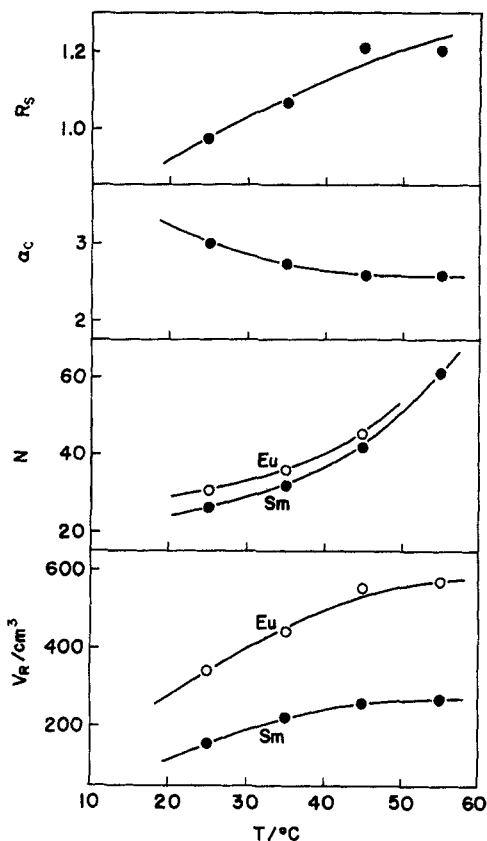does not exceed a limited value of 60 kg/cm^2 of this system.

FIGURE 5. Effect of temperature on the separation of Sm and Eu by
CPC. CPC: 6 cartridges, 800 rpm; stationary phase: 0.02 M
$(EHPA)_2$; mobile phase: 0.1 M $(H,Na)Cl_2CHCOO$ in 20% v/v EG-water,
pH 2.04; sample: 10^{-3} M lanthanoids, 1 cm^3.

Mutual Separation of Lanthanoids by CPC

The distribution ratios of a series of lanthanoid elements
were determined between the kerosene solution of EHPA and the
mixture of 20% EG-water initially containing each lanthanoid ion.
Plots of log D vs. pH gave a family of parallel lines with slopes
of close 3. This extraction behavior is substantially the same as
that from water alone, as expressed by Eq.(1). Table 2 lists the
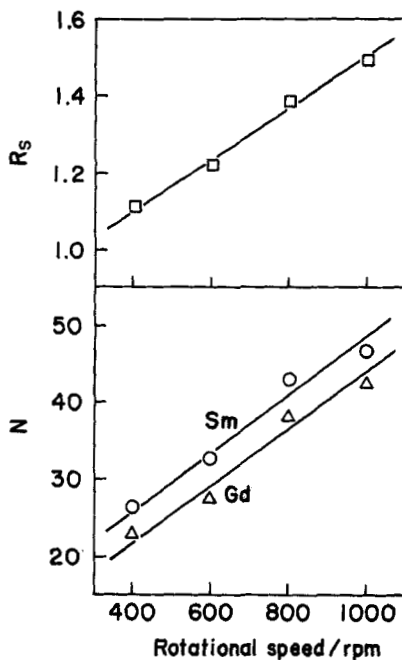values of pH at D=1 by the given concentration of EHPA and the

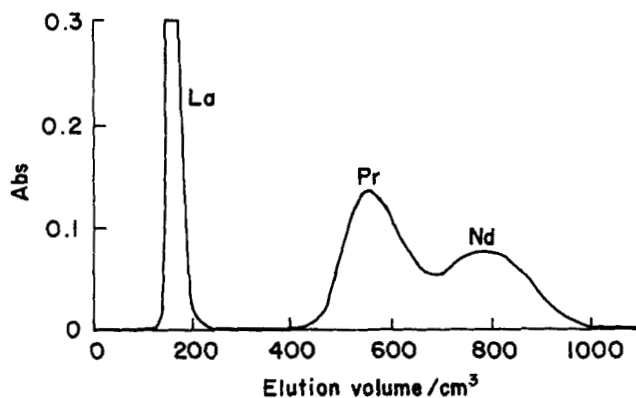FIGURE 6. Effect of rotational speed on the separation of Sm and Gd by CPC.   pH 1.88, 25°C.

FIGURE 7. Separation of the ternary mixture of La, Pr and Nd by CPC. CPC: 12 cartridges, 800 rpm, 55°C; stationary phase: 0.02 M (EHPA)$_2$; mobile phase: 0.1 M (H,Na)Cl$_2$CHCOO in 20% v/v EG–water, pH 2.50; sample: 10^{-3} M lanthanoids, 1 cm^3.

TABLE 2
Liquid–Liquid Extraction of Lanthanoids by EHPA–Kerosene
from 20% v/v Ethylene Glycol–Water at 25°C

Lanthanoids	pH(D=1)	log K_{ex}	α_D
0.02 M (EHPA)$_2$			
La	2.94	-3.74	
			31.6
Pr	2.45	-2.24	
			1.66
Nd	2.37	-2.02	
			13.5
Sm	2.00	-0.89	
			3.16
Eu	1.83	-0.39	
			1.78
Gd	1.75	-0.14	
			5.75
Tb	1.49	0.62	
			3.09
Dy	1.33	1.11	
0.005 M (EHPA)$_2$			
Dy	1.93	1.11	
			2.24
Ho	1.81	1.46	
			2.45
Er	1.68	1.85	
			3.09
Tm	1.52	2.34	
			3.39
Yb	1.34	2.87	
			1.82
Lu	1.26	3.13	

extraction constant evaluated from the distribution data; the K_{ex} value increases in the order of increasing atomic number. The separation factor (α_D) in liquid–liquid extraction is given by the ratio of D values for components 1 and 2:

$$\alpha_D = \frac{D_2}{D_1} = \frac{K_{ex,2}}{K_{ex,1}} \tag{7}$$

The α_D values for lanthanoid pairs are also listed in Table 2. No significant variation in separation factor occurred along with the addition of 20% EG. The α_D values were found to be high for La–

Pr, Nd-Sm and Gd-Tb pairs, while those for adjacent elements Pr-Nd, Eu-Gd, Dy-Ho and Yb-Lu were rather low. This discontinuity in α_D values is attributed to the "tetrad effect" in the series of lanthanoid ions (14,15).

Chromatographic separations of a mixture of light lanthanoids were carried out by CPC at 55°C. For the mutual separation of lanthanoids with low α_D, we employed 12 cartridges containing the stationary phase of about 160 cm^3 and the mobile phase of about 50 cm^3. Figure 7 shows a typical chromatogram obtained at pH 2.50 for the ternary mixture of La, Pr and Nd. Each lanthanoid gave the individual peaks; lighter lanthanoids were less strongly retained and were preferentially eluted with a mild acid solution. Under these experimental conditions, La was slightly retained on the stationary phase due to its low distribution ratio and first eluted with the mobile phase buffered at pH 2.50. Praseodymium was completely separated from La as expected from the large α_D (=31.6) value, while the peaks of Pr and Nd with low α_D (=1.66) were incompletely resolved. The separation parameters evaluated from the chromatograms are listed in Table 3. Though the separation of Nd and Sm is not yet tried, quantitative separation between them will be accomplished from its high separation factor of α_D (=13.5).

It is important to control 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 8 represents the elution curve for the separation of the mixture of Sm, Eu and Gd. The pH of the mobile phase was adjusted to 1.91 to control the D value in the optimum range for the Eu-Gd pair of low α_D value. Satisfactory separation having $R_s \geq 1$ was accomplished between Sm and Eu, but the separation of Eu and Gd was still incomplete.

Figure 9 illustrates the resulting chromatogram for the mixture of Gd-Tb-Dy eluted with the mobile phase of pH 1.48. Each
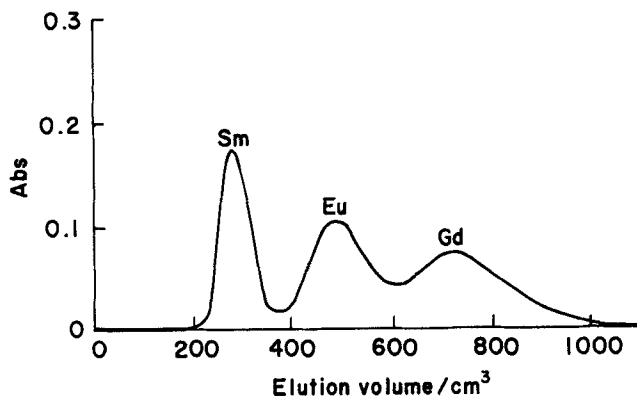
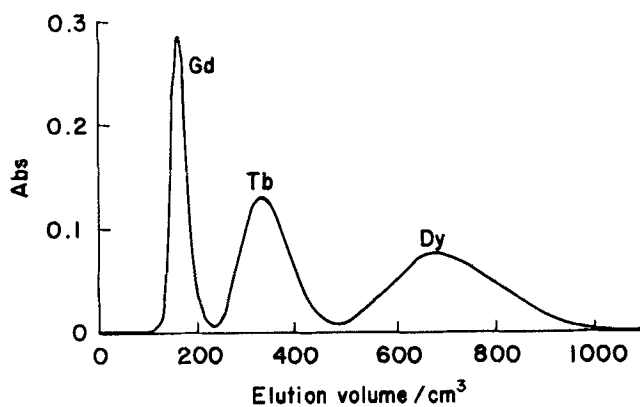FIGURE 8. Separation of Sm, Eu and Gd by CPC.   pH 1.91.

FIGURE 9. Separation of Gd, Tb and Dy by CPC.   pH 1.48.

TABLE 3

Separation Parameters for CPC Chromatogram

Lanthanoids	N	α_c	R_s
La	169.0		
		9.86	2.70
Pr	85.8		
		1.51	0.77
Nd	86.2		
Sm	91.8		
		2.23	1.14
Eu	64.0		
		1.64	0.72
Gd	49.4		
Gd	108.2		
		4.71	1.33
Tb	51.4		
		2.70	1.17
Dy	41.6		
Ho	67.6		
		2.19	0.68
Er	27.0		
		2.99	0.93
Tm	19.5		
Tm	40.7		
		3.00	—
Yb	—		
		—	—
Lu	—		

These values ware evaluated from the chromatograms in Fig. 7–11.

pair was quantitatively separated as expected based on its rela-
tively large separation factor, i.e. α_D=5.75 for Gd–Tb and 3.09
for Tb–Dy. Thus, most of the pairs of lanthanoids having high α_D
(>2) were resolved with fairly good resolution $R_s \geq 1$ as is
evident in Table 3. However the pairs of low α_D (<2) such as Pr–
Nd and Eu–Gd were partially resolved with low R_s less than 1. In
these cases, the chromatographic separation factor α_c values were
close to the α_D values, therefore separation processes in CPC
seems to essentially correspond to those in liquid-liquid extrac-

tion provided that the distribution ratios for each element were close to optimum. Resolution was nevertheless markedly low owing to band broadening; the values of N were around one-tenth compared with the number (650) of microcells of twelve cartridges.

Heavy Lanthanoids

Heavy lanthanoid elements such as Tm and Lu are more strongly retained and it is sometimes difficult to elute metal ions from the stationary phase even by the mobile phase of relatively low pH. The stationary phase was replaced by the lower concentration (5×10^{-3} M) of EHPA for optimum operation. Figure 10 represents the resulting chromatogram for a Ho-Er-Tm mixture. Even the pairs with relatively high α_D values were incompletely separated, and these bands were rather broadened and their N values were too small to separate quantitatively. Figure 11 shows the elution behavior of the heaviest ternary mixture of Tm, Yb and Lu. The resulting bands were considerably broadened and only partially resolved; this is probably due to a decrease in extraction rate with an increase in the atomic number of the lanthanoids (16). More detailed investigation is necessary to enhance the extraction rate and to choice appropriate conditions for mutual separation of these heavy lanthanoids.

Relation between V_R and D

The retention volume in CPC can be related to the equilibrium distribution ratio of a desired species between the stationary and mobile phases as expressed by Eq.(3). Figure 12 illustrates the plots of V_R values obtained under different conditions of the mobile phase at 55°C against the distribution ratios determined by liquid-liquid extraction at 25°C. The closed circles correspond to the peaks of bands in Figs. 7 - 11. The V_R values were roughly linear with D values, however, they were significantly larger compared to the solid line predicted from Eq.(3) employing $V_m = 50$ and $V_s = 160$ cm^3. The V_R values at 55°C were found to be about 1.7 times those at 25°C as illustrated in Fig. 5 for Sm and Eu,
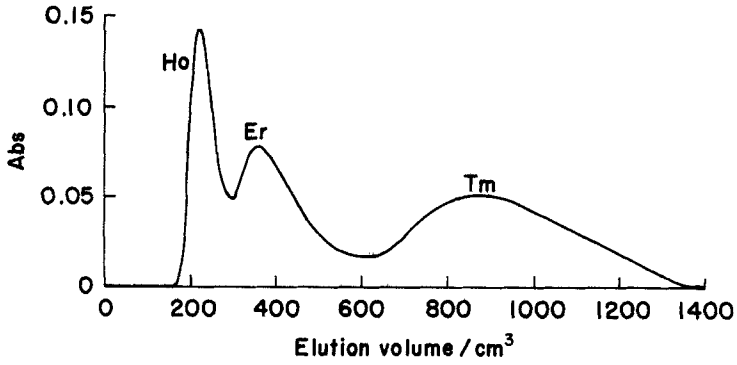
FIGURE 10. Separation of Ho, Er and Tm by CPC. 5×10^{-3} M (EHPA)$_2$, pH 1.69.
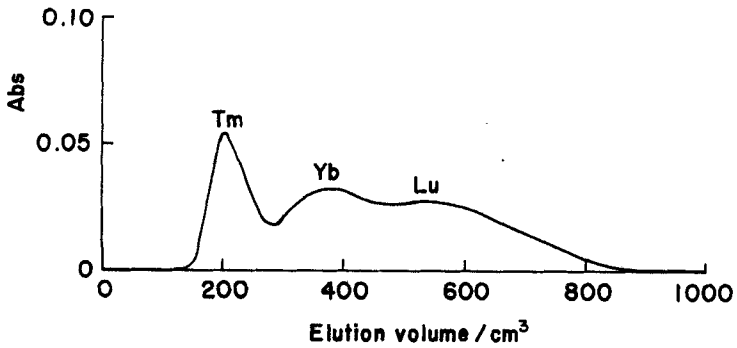

FIGURE 11. Separation of Tm, Yb and Lu by CPC. 5×10^{-3} M (EHPA)$_2$, pH 1.35.
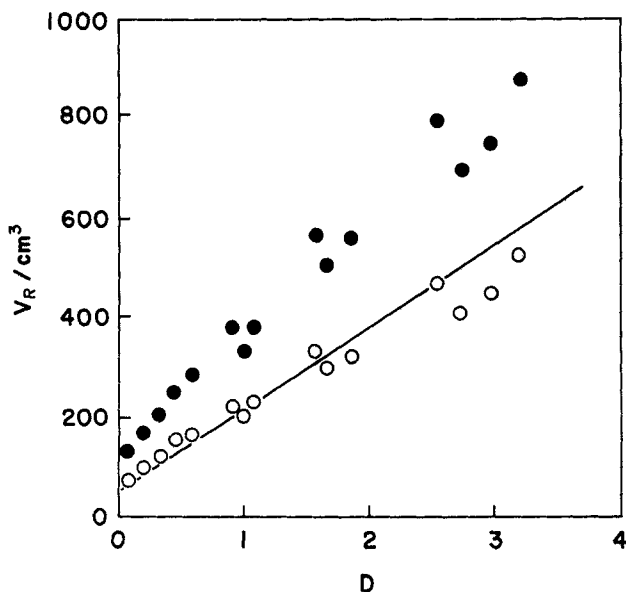
FIGURE 12. Correlation between the retention volume and the distribution ratio. CPC: 12 cartridges, 800 rpm. D values were obtained at 25°C; (●) V_R obtained at 55°C; (○) V_R corrected at 25°C. The solid line was predicted from Eq.(3).

and hence it can be expected that the V_R values at 25°C are about 0.6 times those at 55°C by assuming the same temperature effect for each lanthanoid element. The estimated V_R values at 25°C were given by the open circle in Fig. 12. While some scatters were observed, most of values were close to the solid line, indicating that the distribution ratio is a useful guide for the prediction of the retention volume.

ACKNOWLEDGMENT

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