Enrichment separation of rare earth elements by high-speed countercurrent chromatography in a multilayer coiled column

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Abstract

Mutual separation of rare earth elements has been investigated by high-speed countercurrent chromatography equipped with a multilayer coiled column. Rare earth elements were first enriched into the stationary phase comprised of the toluene solution of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester from a large volume of aqueous solution, and then chromatographically eluted by the mobile phase with stepwise pH gradient. Enrichment separation of a series of rare earth elements including yttrium was accomplished with sufficient resolution.   © 1997 Elsevier Science B.V.

Keywords: Multilayer coiled column; Rare earth elements; Yttrium

1. Introduction

Liquid–liquid partition chromatography having a support-free stationary phase offers a promising method for preparative separation of chemically similar materials. In particular, centrifugal partition chromatography (CPC) employing a series of microcells and countercurrent chromatography (CCC) employing a multilayer coiled column have been widely used for separation and purification of organic substances such as natural products [1–4]. These multistage procedures are attractive also for separation of inorganic substances, because the stationary and mobile phases can be flexibly selected on the basis of liquid–liquid extraction behavior of metal species. A great deal of accumulative data on various solvent extraction systems would be available for optimization of chromatographic procedures. The CPC method has been introduced to the mutual separation of lanthanoid elements and precious metals [5–7]; however, the resolution of some elements

such as europium–gadolinium was found to be rather low [5,6]. The CCC method has been applied to the separation of inorganic materials such as lanthanoids, fission products and heavy metals by employing extracting reagents as the stationary-phase components [8–10].

Multistage processes are required for the mutual separation of lanthanoids having similar ionic properties in aqueous solutions. In ion-exchange column chromatography, appropriate complexing agents such as α-hydroxyisobutyric acid were added in the mobile phase in order to enhance the selectivity of separation [11]. On the other hand, certain extracting-reagents such as acidic organophosphorus compounds have high selectivity for adjacent lanthanoid elements, and have been widely used for solvent extraction separation of a series of lanthanoids [5,12,13]. These extractants are available for stationary-phase components in the CCC coiled column, and this enables the mutual separation of resemble lanthanoids without further addition of complexing agents. The separation of lanthanoids was accomplished by using the stationary phase of

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di(2-ethylhexyl)phosphoric acid [8]. Lanthanoids and chemically similar yttrium are usually grouped as rare earth elements, and the separation of yttrium from others was also accomplished through a CCC stationary phase comprised of organophosphonic acid ester [14].

The CCC column can also offer preconcentration of trace elements from a large volume of aqueous samples [9]. Enrichment and subsequent separation through a single CCC column are favorable, because this eliminates an extra enrichment step, contamination and loss of desired materials. In previous papers, the selective enrichment from a large volume of aqueous solution and subsequent chromatographic separation have been demonstrated by means of a single CCC column for heavy rare earth elements including yttrium [15,16].

This paper describes enrichment of a series of rare earth elements and their mutual separation through the multilayer coiled column filled with a toluene solution of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester.

2. Experimental

2.1. Reagents

2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA; PC-88A, Daihachi Chemical Ind. Co. Ltd.) was employed as an extracting reagent and an stationary-phase component in a CCC column. Arsenazo III (Dojindo Lab.) was used as a post-column reagent.

2.2. CCC apparatus

A prototype high-speed countercurrent chromatograph (HCC-1A; Shimadzu Corporation) was symmetrically provided with two multilayer coils [14]. The coiled column consisted of PTFE tubing with a 1.5-mm inner diameter and ca. 150 m length, and had the total capacity of approximately 268 cm^3. This apparatus was placed in an air-thermostat box kept at 35°C.

2.3. Liquid–liquid extraction

A toluene solution of 0.02 M (M=mol dm^{-3}) (EHPA)$_2$ and an equal volume of the aqueous solution containing 2×10^{-5} M each rare earth element were mechanically shaken for 2 h at 35°C. The pH of aqueous phase was controlled with a buffer solution of 0.01 M (H,Na)HCOO, 0.1 M (H,Na)CH$_2$ClCOO or 0.1 M (H,Na)CHCl$_2$COO. After phase separation, the metal concentration in the aqueous phase was determined by inductively coupled plasma atomic emission spectrometry.

2.4. CCC procedure

The tubing column was filled with 0.02 M (EHPA)$_2$ in toluene. A revolution rate of 800 rpm and a flow-rate of 5 cm^3 min^{-1} were adopted to retain an appropriate volume (about 130 cm^3) of the stationary phase in the tubing column. A sample solution was directly injected into the coiled column through a inlet path for the mobile phase without equilibration between the stationary and mobile phases [15,16], and then the aqueous mobile phase was pumped into the column. Metal ions eluted with the mobile phase were detected by measuring the absorbance of colored complexes at 650 nm by a post-column reaction with 0.014% (w/v) Arsenazo III in 50% (v/v) ethanol [5]. The mobile-phase volume (V_M) in the CCC column was obtained from the elution volume for La as an unretained compound by using a mobile phase with low pH, and that of stationary phase (V_S) was evaluated by subtracting V_M from the total column volume. These values were confirmed to be fair agreement with the volumes of column contents expelled by introduction of nitrogen gas after CCC experiments.

3. Results and discussion

3.1. Liquid–liquid extraction

The distribution ratio (D) of each rare earth element in liquid–liquid extraction with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA) was investigated under appropriate conditions related to chromatographic procedures at 35°C. The plots of
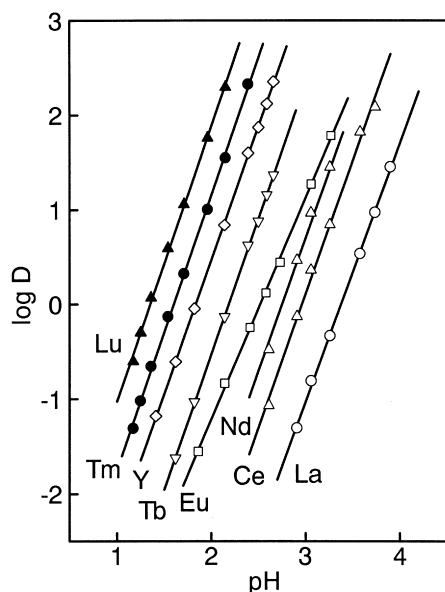
Fig. 1. Liquid–liquid extraction of rare earth elements with 0.02 M (EHPA)$_2$ in toluene at 35°C. Aqueous phase: 0.01 M (H,Na)HCOO for La, Ce and Nd; 0.1 M (H,Na)CH$_2$ClCOO for Eu; 0.1 M (H,Na)CHCl$_2$COO for Tb, Y, Tm and Lu.

log D against pH gave a series of straight lines with slopes close to 3, as illustrated in Fig. 1 for typical rare earth elements. The extractability of lanthanoid elements at a definite pH increased with increasing atomic number, and yttrium was situated between holmium and erbium. The extraction of trivalent rare earth ions (M^{3+}) with EHPA (HA) can be expressed by

$$M_{aq}^{3+} + 3(HA)_{2,org} \rightleftarrows M(HA_2)_{3,org} + 3H_{aq}^+ \qquad (1)$$

The separation factors, α_D ($= D_{M2}/D_{M1}$, $D_{M2} > D_{M1}$), evaluated from individual D values are summarized in Table 1. The α_D values of 1.66 for Gd/Eu, 1.45 for Er/Y and 1.74 for Lu/Yb are found to be rather small indicating particular difficulty in their mutual separation. With the aid of extraction characteristics of metal ions, chromatographic conditions of the stationary and mobile phases in CCC can be estimated for effective separation of a series of rare earth elements.

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

Table 1
Distribution separation factors and chromatographic parameters

Rare earth	α_D	α_c	N	R_s
0.01 M (H,Na)HCOO, pH 2.99				
La			676	
	14.1	12.4		3.80
Ce			322	
	1.86	2.21		2.19
Pr			241	
	2.09	1.68		1.56
Nd			218	
0.1 M (H,Na)CH$_2$ClCOO, pH 2.68				
Sm			260	
	2.51	2.54		2.00
Eu			202	
	1.66	1.66		1.25
Gd			163	
0.1 M (H,Na)CHCl$_2$COO, pH 2.07				
Tb			282	
	2.80	2.35		1.37
Dy			185	
	1.94	2.01		1.40
Ho			160	
	1.79	1.77		1.25
Y			123	
	1.45	1.30		0.58
Er			106	
0.1 M (H,Na)CHCl$_2$COO, pH 1.54				
Tm			181	
	3.06	3.92		1.56
Yb			77	
	1.74	1.96		1.02
Lu			74	

Stationary phase: 0.02 M (EHPA)$_2$ in toluene, 35°C.

$$V_R = V_M + DV_S \qquad (2)$$

The retention volume can be controlled by varying the pH value of the mobile phase, by variation in the distribution ratio, and it can be expected that the lanthanoid elements will be eluted in the increasing order of atomic number.

3.2. Enrichment separation of light rare earth elements

Rare earth elements of low concentration were effectively enriched and separated even from a large volume of aqueous solution [15,16]. Preliminary experiments on enrichment in the CCC coiled column were performed, by keeping the quantity of metals constant. The peak areas of resulting chro-

matograms obtained after enrichment from a solution (1000 cm^3) containing 10^{-6} M Ho and Er were fond to be approximately equal to those obtained without enrichment for a solution (1 cm^3) of 10^{-3} M of each metal ion. This implies that the rare earth elements in the dilute solution can be almost quantitatively collected in the CCC column. In the preceding study, lanthanoid elements of different concentrations were separated from each other with good resolution in a wide concentration region [15].

In a series of rare earth elements, the light elements have been known to be readily separated from each other compared with heavy ones [5,8]; the optimum conditions were confirmed for mutual separation of light rare earth elements.

The chromatographic separation of light rare earth ions was tested through a coiled column containing 0.02 M (EHPA)$_2$ in toluene as the stationary phase. Fig. 2 presents an example of a CCC chromatogram obtained by the injection of a sample solution (1000 cm^3) containing 5×10^{-7} M of each rare earth. A
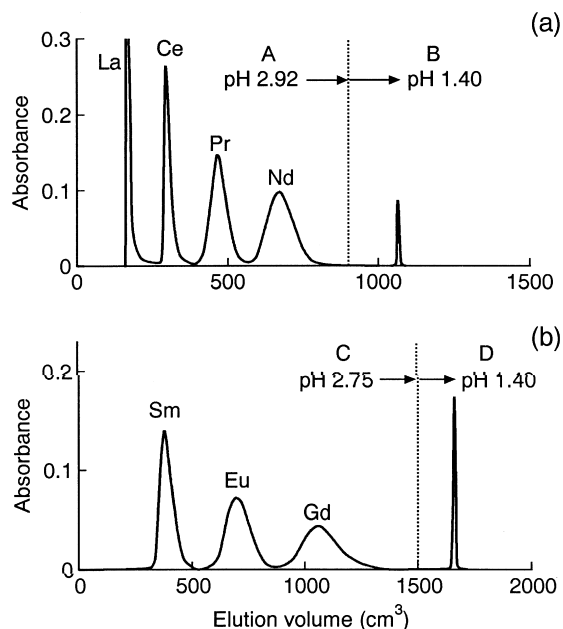
high pH value of the sample solution was adopted for the complete concentration into the stationary phase, based on the liquid–liquid extraction data. Lanthanum, Ce, Pr and Nd were separated by isocratic elution with a mobile phase of pH 2.92, yielding an excellent resolution (Fig. 2a). After the elution of these rare earth elements, the acid concentration in the mobile phase was increased, and then an errant elution peak was observed; this is attributable to the elution of residual rare earth elements with high acidity.

The rare earth elements, Sm, Eu and Gd, enriched into the stationary phase from 1000-cm^3 sample solution were chromatographed with a mobile phase of pH 2.75 (Fig. 2b). The resulting peaks were sufficiently separated from each other; however, a coeluted peak was also observed, when the acidity of the mobile phase was raised to pH 1.40.

The mixture of these light rare earth elements, as a sample solution, was injected for concentration and separated by stepwise elution. As Fig. 3 shows, the lighter rare earth elements, La, Ce, Pr and Nd, were eluted by a mobile phase of pH 2.92; then, by changing the pH of the mobile phase to a lower value, Sm, Eu and Gd were eluted. These light rare earth elements were mutually separated with excellent peak resolutions ($R_s > 1.4$). A small peak in front of the Sm peak appears to correspond to the coelution of strongly retained rare earth elements, which were not completely eluted at pH 2.92, and forced out together when the pH of the mobile phase
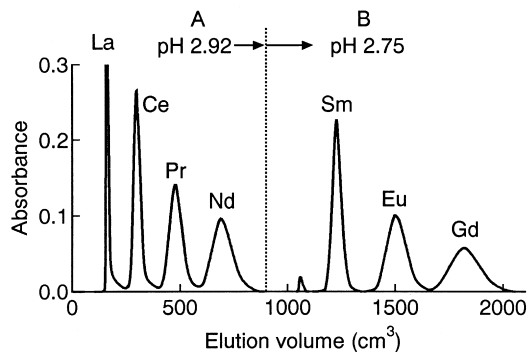

Fig. 2. Chromatographic separation of light rare earth elements. Sample: 5×10^{-7} M of each rare earth element, 1000 cm^3; 10^{-3} M (H,Na)CH$_3$COO; (a) pH 5.18; (b) pH 4.75. Stationary phase: 0.02 M (EHPA)$_2$ in toluene. Mobile phase: (A) 0.01 M (H,Na)HCOO; (B) 0.1 M (H,Na)CHCl$_2$COO; (C) 0.1 M (H,Na)CH$_2$ClCOO; (D) 0.1 M (H,Na)CHCl$_2$COO.

Fig. 3. Chromatographic separation of light rare earth elements by stepwise elution. Sample: 5×10^{-7} M of each rare earth element, 1000 cm^3; 10^{-3} M (H,Na)CH$_3$COO, pH 5.15. Stationary phase: 0.02 M (EHPA)$_2$ in toluene. Mobile phase: (A) 0.01 M (H,Na)HCOO; (B) 0.1 M (H,Na)CH$_2$ClCOO.
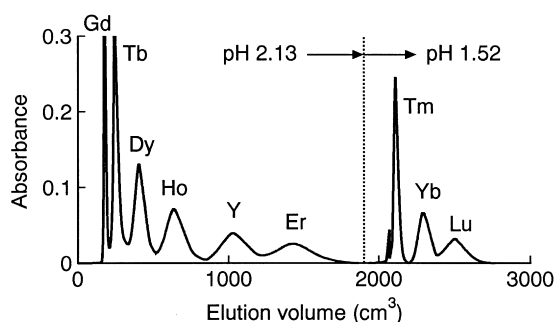
Fig. 4. Chromatographic separation of heavy rare earth elements including yttrium. Sample: 5×10^{-7} M of each rare earth element, 1000 cm^3; 10^{-3} M (H,Na)CH$_3$COO, pH 5.14. Stationary phase: 0.02 M (EHPA)$_2$ in toluene. Mobile phase: 0.1 M (H,Na)CHCl$_2$COO.

decreased to 2.75. This small peak was completely separated from individual rare earth peaks.

3.3. Enrichment separation of heavy rare earth elements

The heavy rare earth elements including yttrium were enriched from sample solution (1000 cm^3) of pH 5.14 containing 5×10^{-7} M of each metal ion, and their elution behavior was examined by a stepwise change of acid concentration in the mobile phase. As Fig. 4 shows, these rare earth elements were chromatographically eluted by the mobile phase of pH 2.13 for Gd, Tb, Dy, Ho, Y and Er, and pH

1.52 for Tm, Yb and Lu. Yttrium and the most similar elements, Ho and Er, were eluted as separated peaks with a little tailing. The separation of individual rare earth elements was thus accomplished with sufficient resolution.

3.4. Enrichment separation of a series of rare earth elements

The enrichment and subsequent separation have been confirmed to have been accomplished for both heavy and light rare earth groups in the above experiments. These findings will be extended to sequential separation of all rare earth elements, including yttrium.

Enrichment separation of all rare earth elements was performed by the injection of 1000 cm^3 of 5×10^{-7} M of each metal. The elements enriched were eluted by stepwise gradient of the mobile phase, and the resulting chromatogram is given in Fig. 5. On the basis of the chromatographic behavior of the individual elements, the pH values of the mobile phase were adjusted to four steps, i.e., pH 2.99 for La to Nd, 2.68 for Sm to Gd, 2.07 for Tb to Er and 1.54 for Tm to Lu. Lanthanoids were successively eluted according to increasing atomic number, and yttrium was eluted between holmium and erbium owing to its extractability. All of the rare earth elements, except for Pm of no natural abundance, were reasonably separated.
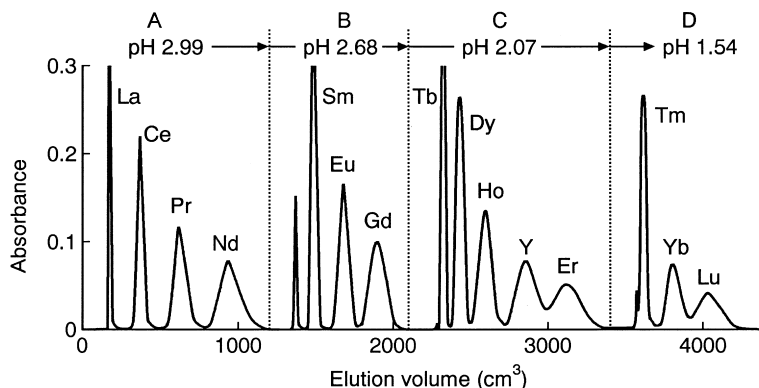

Fig. 5. Chromatographic separation of a series of rare earth elements including yttrium. Sample: 5×10^{-7} M of each rare earth; 1000 cm^3, 10^{-3} M (H,Na)CH$_3$COO, pH 5.16. Stationary phase: 0.02 M (EHPA)$_2$ in toluene. Mobile phase: (A) 0.01 M (H,Na)HCOO; (B) 0.1 M (H,Na)CH$_2$ClCOO; (C) 0.1 M (H,Na)CHCl$_2$COO; (D) 0.1 M (H,Na)CHCl$_2$COO.

3.5. Chromatographic parameters

The chromatographic parameters evaluated from individual peaks are listed in Table 1. The V_R values used for the calculation of chromatographic parameters were evaluated as the elution volumes after changing the lower pH of the mobile phase.

The chromatographic separation factor (α_C) varied in a similar manner to the distribution separation factor (α_D). The retention volumes of individual rare earth elements evaluated from the chromatogram for each stepwise elution are plotted in Fig. 6 against the D values in liquid–liquid extraction at desired pH. The V_R value varied almost linearly with the D value; the solid line was calculated from Eq. (2) by employing the experimental values of $V_M = 139$ cm^3 and $V_S = 128$ cm^3. Though some scatter is observed, the experimental points are close to the calculated line, indicating that the V_R value can be predicted from the distribution ratio.

The number of plates (N) was not so high owing to rather broad elution peaks, and decreased from the first peak to the last peak in the same group of given mobile phase. This substantially influences the separation of resulted chromatogram peaks.

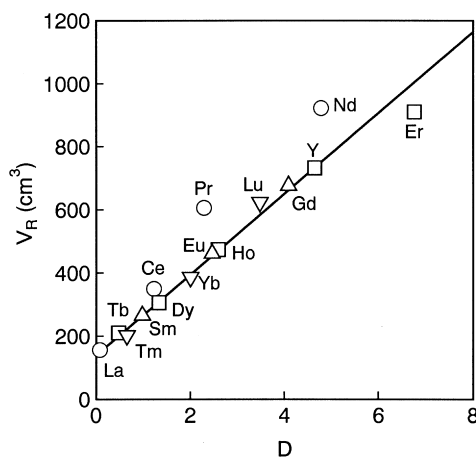Sufficient peak resolution ($R_s > 1$) was accomplished except for the Y–Er pair with lowest separation factor. Resolutions for light rare earths seem to be larger than for heavy rare earths with comparable values of separation factors. This is attributable to the lower N value for the heavy rare earth elements.

4. Conclusions

This study demonstrates that CCC is a promising technique for extracting low concentration of rare earth elements from aqueous samples and the proposed approach results in a high efficiency of enrichment and separation. A series of rare earth elements including yttrium was effectively enriched into the organic stationary phase, and excellent separation was accomplished by the stepwise gradient of acidity of the mobile phase.

Acknowledgements

Fig. 6. Correlation between V_R and D for rare earth elements. ○, 0.01 M (H,Na)HCOO, pH 2.99 for La, Ce, Pr, Nd; △. 0.1 M (H,Na)CH$_2$ClCOO, pH 2.68 for Sm, Eu, Gd; □, 0.1 M (H,Na)CHCl$_2$COO, pH 2.07 for Tb, Dy, Ho, Y, Er; ▽, 0.1 M (H,Na)CHCl$_2$COO, pH 1.54 for Tm, Yb, Lu.

References

[1] A.P. Foucault (Ed.), Centrifugal Partition Chromatography, Marcel Dekker, New York, 1995.

[2] N.B. Mandava, Y. Ito (Eds.), Countercurrent Chromatography, Theory and Practice, Marcel Dekker, New York, 1988.

[3] Y. Ito, W.D. Conway (Eds.), High-Speed Countercurrent Chromatography, Wiley, New York, 1966.

[4] A. Marston, K. Hostettmann, J. Chromatogr. A 658 (1994) 314.

[5] K. Akiba, S. Sawai, S. Nakamura, W. Murayama, J. Liq. Chromatogr. 11 (1988) 2517.

[6] T. Araki, T. Okazawa, Y. Kubo, H. Ando, H. Asai, J. Liq. Chromatogr. 11 (1988) 267.

[7] Y. Surakitbanharn, S. Muralidharan, H. Freiser, Solvent Extract. Ion Exchange 9 (1991) 45.

[8] E. Kitazume, M. Bhatnagar, Y. Ito, J. Chromatogr. 538 (1991) 133.

[9] Yu.A. Zolotov, B. Ya Spivakov, T.A. Maryutina, V.L. Bashlov, I.V. Pavlenko, Fresenius Z. Anal. Chem. 335 (1989) 314.

[10] E. Kitazume, N. Sato, Y. Saito, Y. Ito, Anal. Chem. 65 (1993) 2225.

[11] A.W. Al-Shawi, R. Dahl, J. Chromatogr. A 671 (1994) 173.

[12] F. Peppard, G.W. Mason, J.L. Maier, W.J. Driscoll, J. Inorg. Nucl. Chem. 4 (1957) 334.

[13] B. Pierce, P.F. Peck, Analyst 88 (1963) 217.

[14] K. Akiba, H. Hashimoto, S. Nakamura, Y. Saito, J. Liq. Chromatogr. 18 (1995) 1273.

[15] K. Akiba, H. Hashimoto, S. Nakamura, Y. Saito, J. Liq. Chromatogr., in press.

[16] S. Nakamura, H. Hashimoto, K. Akiba, Y. Saito, Anal. Sci., in press.