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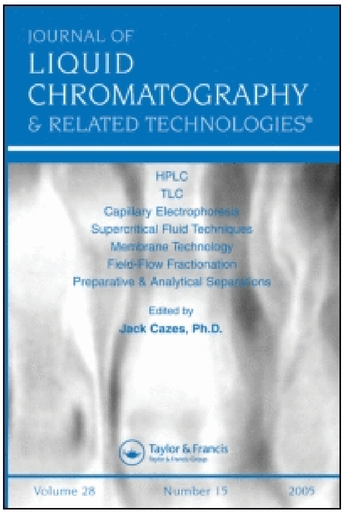

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HIGH-SPEED COUNTERCURRENT CHROMATOGRAPHIC PURIFICATION OF MIDDLE LANTHANOIDS

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ABSTRACT

Separation of selected lanthanoid elements was performed by high speed countercurrent chromatography (CCC) employing a support-free stationary phase of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA) in toluene. Middle lanthanoids (Sm, Eu, Gd, Tb, Dy) were chromatographically eluted in their increasing order of extractability by passing the aqueous mobile phase of pH buffers. The mixtures of lanthanoid elements of different concentrations were isolated into individual elements of high purity by one-step chromatographic operation.

INTRODUCTION

Lanthanoid elements are widely used as functional materials in various products owing to their specific physical and chemical properties.[1] In mineral resources, e.g., xenotime, the even atomic numbered lanthanoid

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elements are three to ten times as abundant as the odd numbered adjacent elements.[2] Middle lanthanoids contribute to advanced materials; e.g., samarium for magnets, europium for phosphors, gadolinium for nuclear controllers, and terbium and dysprosium for magneto-optical recording media.[1,2]

A major problem is the difficulty in the separation of trivalent lanthanoids from each other into their pure states. The development of separation procedures based on cation exchange resins resulted in isolation of lanthanoids of similar chemical properties.[3] The ion exchange method is a powerful separation technique, however, its application to the production of macro amounts of lanthanoids has been limited, because it requires a large amount of eluents containing complexing agents, and then the solubilities of reagents and their complexes are rather low.

Solvent extraction has been used for the separation of lanthanoids by most widely employing various kinds of acidic organophosphorus compounds owing to better selectivity in adjacent elements.[4-6] Further, these extractants have become of interest in an application to column components of high-speed countercurrent chromatography (CCC).[7-11] Lanthanoid elements have been separated into individual elements through a coiled column containing an acidic organophsphorus extractant as a stationary phase without any solid matrix. Moreover, CCC is convenient for preparative purification of chemical materials, by selecting an appropriate two-phase solvent system based on the liquid-liquid partition behavior.[12-17] A large capacity liquid stationary phase will be advantageous for the separation of metals of high concentrations.

In the preceding study, small amounts of lanthanoid elements were chromatographically removed from a large amount of yttrium yielding a highly purified product.[16]

The present study deals with the separation of middle lanthanoids consisting of high abundant samarium, gadolinium, and dysprosium together with low abundant erbium and terbium by CCC employing an acidic organophosphorus compound as a stationary phase.

EXPERIMENTAL

Reagents

2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA) was obtained from Daihachi Chemical Ind. Co., Ltd., and purified as described previously.[6] Arsenazo III (Dojindo Lab.) was used as a post-column complexing-reagent for the detection of lanthanoids.

CCC Apparatus

A prototype model of a high speed countercurrent chromatograph apparatus (HCC-1A; Shimadzu Corporation) is equipped with two holders (15 cm diameter) in symmetrical positions.[9] The multilayer coiled column was prepared by winding a 150 m PTFE tubing (i.d. 1.5 mm) in three layers of 300 helical turns total. The volume of the column was approximately 268 cm^3. The apparatus was placed in an air-thermostat box kept at 35°C.

Liquid-Liquid Extraction

Equal volumes of a toluene solution of $(EHPA)_2$ and an aqueous solution containing lanthanoid elements were shaken for 2 h to attain equilibrium at 35°C. The aqueous pH values were controlled with buffer solutions of 0.1 M (= mol dm^{-3}) $(H,Na)CH_2ClCOO$, $(H,Na)CHCl_2COO$ and $(H,Na)CCl_3COO$. After phase separation, the metal concentrations in the aqueous phase were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The concentrations of metals in the organic phase were determined in a similar manner after stripping the metal species into 2 M nitric acid.

Stationary Phase

The tubing coils were first filled with a toluene solution of $(EHPA)_2$ as a stationary phase, and the column was equilibrated with the aqueous mobile phase under revolution. A speed of revolution of 800 rpm and a flow rate of 5 cm^3 min^{-1} for the mobile phase were adopted, and then the stationary phase occupied about a half column volume, i.e., 130 ~134 cm^3.[9]

Chromatographic Procedures

The pH values of the mobile phase were controlled with buffer solutions mentioned above, and a sample solution (10^{-3} M HNO_3, 1 cm^3) was injected through a sample port. Lanthanoids eluted were detected at 650 nm by adding 0.014% (w/v) Arsenazo III in 50% (v/v) ethanol to the effluent as previously described.[6]

In the separation of lanthanoids of high concentrations, the effluent was fractionated in order to check the extent of purification. Metal ions in each fraction (100 cm^3) were concentrated by solvent extraction with 0.02 M $(EHPA)_2$ in toluene at pH 3.2 ~ 3.9, stripped with 1 M HNO_3, evaporated to dryness and dissolved in 0.1 M HNO_3 (10 cm^3), and then their concentrations were determined by ICP-AES.[16,17]

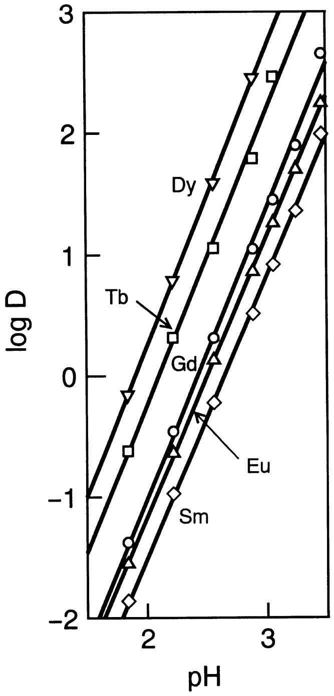

Figure 1. Distribution ratios of lanthanoid elements with 0.02 M $(EHPA)_2$ in toluene as a function of pH. 2 x 10^{-5} M each element; 0.1 M $(H,Na)CH_2ClCOO$.

RESULTS AND DISCUSSION

Liquid-Liquid Distribution of Lanthanoid Elements

The solvent extraction of chemically similar lanthanoids was preliminarily investigated by employing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA) to choose optimal chemical conditions for the stationary and mobile phases. Figure 1 shows the distribution ratio D (= $[M]_{org}/[M]_{aq}$) of selected lanthanoid elements between the organic and aqueous phases at 35°C as a function of pH of the aqueous phase. Plots of log D against pH were found to be straight lines with slopes around 2.9. Extraction equilibrium of lanthanoid ion (M^{3+}) with EHPA (HA) is expressed by

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

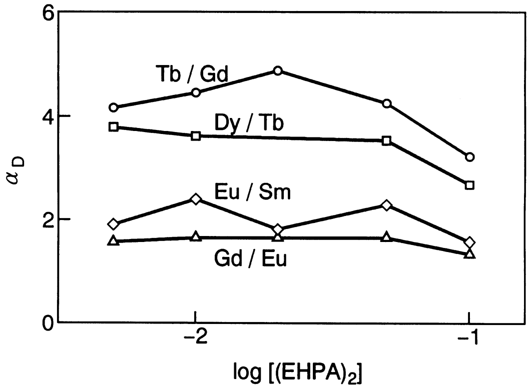

Figure 2. Extraction separation factors as a function of extractant concentration. 2 x 10^{-5}M each element.

The extractability of lanthanoid with EHPA was found to increase with increasing atomic number. The difference in extractability between two lanthanoids is expressed by means of the separation factor α_D (= D_{M2} / D_{M1}; D_{M2} > D_{M1}). Figure 2 shows the effect of (EHPA)$_2$ concentration on the α_D value. The separation factors for each pair have no significant variation in a wide concentration region of (EHPA)$_2$. From the α_D values, separations of europium from gadolinium and of samarium from europium seem to be rather difficult compared with that for others.

Chromatographic Separation with (EHPA) Stationary Phase

The chromatographic retention of a solute can be expected from the liquid-liquid extraction data. The retention volume (V_R) of a desired element is related to the volumes of the mobile and stationary phases (V_m and V_s, respectively) and the distribution ratio,

$$V_R = V_m + D V_s \tag{2}$$

The chromatographic behavior of lanthanoid elements was investigated through a coiled column containing 0.02 M (EHPA)$_2$ in toluene as the stationary phase. Figure 3 presents an example of CCC chromatogram for the sample solution (1 cm^3) containing equimolar (5 x 10^{-4} M) of each lanthanoid. The selected lanthanoids, samarium, europium, and gadolinium were chromatographically eluted in the sequence in their extractability by passing a mobile phase of pH 2.71, and terbium and dysprosium were subsequently eluted with a mobile phase of lower pH 2.12.

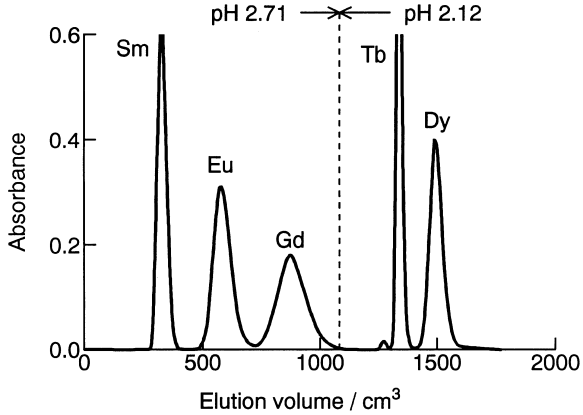

Figure 3. Chromatographic separation of lanthanoid elements through the stationary phase of 0.02 M $(EHPA)_2$ in toluene. Sample: 5 x 10^{-4} M each element; mobile phase: 0.1 M $(H,Na)CH_2ClCOO$ (pH 2.71), 0.1 M $(H,Na)CHCl_2COO$ (pH 2.12).

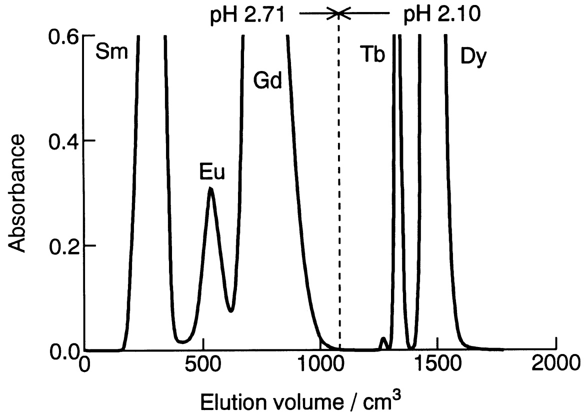

Figure 4. Chromatographic separation of lanthanoid elements of different concentrations through the stationary phase of 0.02 M $(EHPA)_2$ in toluene. Sample: 5.5 x 10^{-3} M Sm, Gd, Dy and 5 x 10^{-4} M Eu, Tb; mobile phase: 0.1 M $(H,Na)CH_2ClCOO$ (pH 2.71), 0.1 M $(H,Na)CHCl_2COO$ (pH 2.10).

Each element was mutually separated, yielding sufficient resolution $R_S > 1$; the adjacent pair Eu/Sm and Gd/Eu having rather low α_D values were also well separated as $\alpha_C = 2.45$ and $R_S = 2.33$ for Eu/Sm, and $\alpha_C = 1.69$ and $R_S = 1.54$ for Gd/Eu.

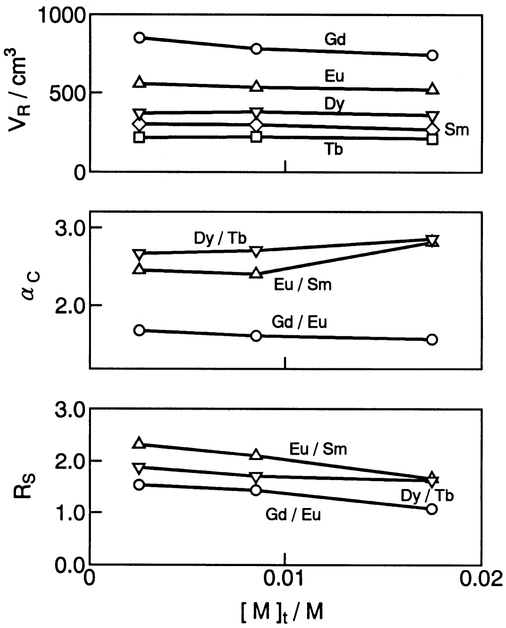

Figure 5. Effect of total concentration of lanthanoid elements on chromatographic parameters. Experimental conditions are the same as those in Figure 4.

Separation of Lanthanoids of Different Concentrations

Separation of a mixture composed of even atomic numbers (Sm, Gd, and Dy) of high contents (5.5 x 10^{-3} M) and odd atomic numbers (Eu and Tb) of low contents (5 x 10^{-4} M) was performed. Figure 4 shows the typical chromatogram obtained through the stationary phase of 0.02 M $(EHPA)_2$. Although the peaks were broadened for metals of high contents, the peaks corresponding to high and low contents were separated into individual elements.

The retention volume (V_R), chromatographic separation factor (α_C) of adjacent peaks and their resolution (R_S) evaluated for the sample solution containing a mixture of lanthanoid elements of different concentrations are illustrated as a function of initial total concentration ($[M]_t$) of lanthanoids in Figure 5. The V_R values for each pair were almost unchanged in their concentration regions studied. Variations in the α_C values were found to be small, while slight increases in α_C were observed for Dy/Tb and Eu/Sm at high lanthanoid concentration.

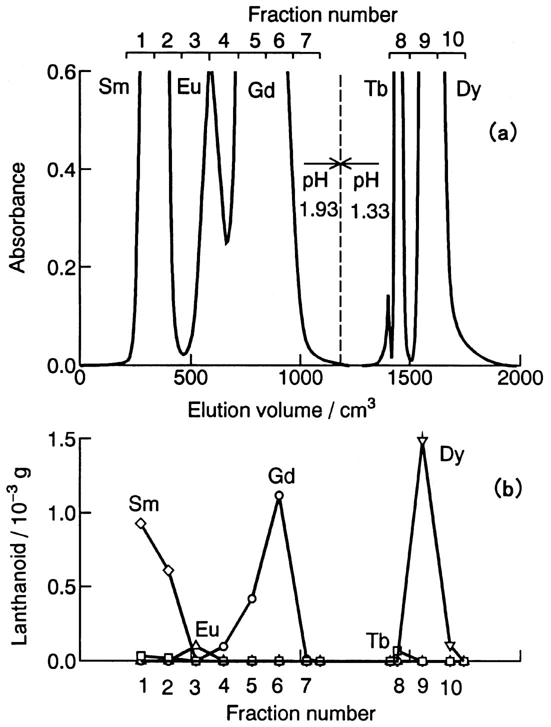

Figure 6. Chromatographic separation of lanthanoid elements of different concentrations through the stationary phase of 0.1 M $(EHPA)_2$ in toluene. Sample: 10^{-2} M Sm, Gd, Dy and 10^{-3} M Eu, Tb; mobile phase: 0.1 M $(H,Na)CHCl_2COO$ (pH 1.93), 0.1 M $(H,Na)CCl_3COO$ (pH 1.33); (a) chromatogram, (b) lanthanoid contents in eluent fraction (100 cm^3) determined by ICP-AES.

Resolution of adjacent peaks was reduced to a small degree with increases in lanthanoid concentrations, however, the R_S values were found to be larger than 1, indicating reasonably good separation. Thus middle lanthanoid elements were effectively separated from others, even in the case of large differences in their concentrations. These results are similar to the case of those recently obtained for the purification of yttrium by CCC.[16, 17]

Separation of Lanthanoids with High (EHPA) Concentration Stationary Phase

The stationary phase containing $(EHPA)_2$ of a higher concentration will be available for high loading of lanthanoids. The subsequent study was performed for the purification of a mixture containing Sm, Gd, Dy of high concentration

(10^{-2} M each) and Eu, Tb of low concentration (10^{-3} M each) through the high capacity stationary phase consisting of 0.1 M $(EHPA)_2$. As the chromatograms in Figure 6 (a) shows, samarium, europium, and gadolinium were well separated from each other with the buffer of pH 1.93, and then terbium and dysprosium were eluted with the buffer of pH 1.33. Mutual separation of lanthanoids was achieved with adequate resolution, i.e., R_s = 1.46 for Eu/Sm, 0.99 for Gd/Eu, and 1.47 for Dy/Tb; even though the chromatographic peaks of the metals of even atomic numbers were considerably broadened.

Fractionation of Lanthanoid Elements

The degree of separation of each component was further confirmed by fractionating the effluent. The metal components determined by ICP-AES in each fraction of 100 cm^3 are presented in Figure 6 (b). The contents of lanthanoids in each fraction corresponded to the chromatogram, and then individual lanthanoids were isolated in limited fractions. Samarium was predominant in the fractions No 1 (96.5 mol% with respect to lanthanoids) and No. 2 (96.4 mol%); Gd in No. 5 (99.7 mol%) and No. 6 (99.8 mol%); Dy in No. 9 (100 mol%) and No. 10 (100 mol%). Lanthanoids of low contents were confirmed to be also isolated from others; Eu in the fraction No. 3 with the adequate purity of 96.8 mol% and Tb in No. 8 with the purity of 98.6 mol%. The separation of small and large amounts of lanthanoids was thus achieved, yielding high purity of individual lanthanoids.

CONCLUSIONS

The CCC technique employing the stationary phase of $(EHPA)_2$ having excellent separation properties afforded a convenient method for separation of lanthanoid elements. The stationary phase of high capacity contributed to isolation and purification of lanthanoids of different contents. The mixture of middle lanthanoids was separated from each other into individual elements of high purity.

ACKNOWLEDGMENT

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