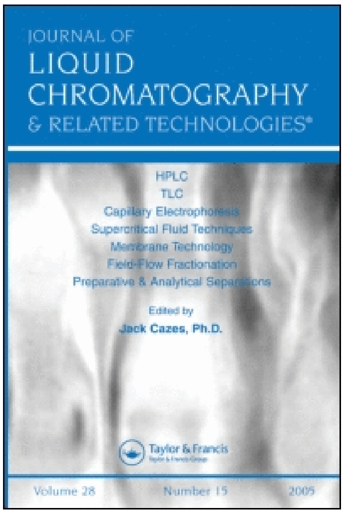

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SEPARATION OF LANTHANOIDS AND ACTINOIDS BY CENTRIFUGAL PARTITION CHROMATOGRAPHY

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ABSTRACT

The separation of actinoids such as Am from lighter lanthanoids has been investigated based on the liquid-liquid extraction principle. An extractant, 5, 8-diethyl-7-hydroxy-dodecan-6-one oxime (LIX 63), is suitable for separation of actinoids heavier than Am from lanthanoids lighter than Eu. On the basis of extraction behavior, multistage separation has been performed by centrifugal partition chromatography (CPC) provided with a series of micro cells. A kerosene solution of LIX 63 was retained in a column as a stationary phase without any solid support. The element substituted for heavier actinoids was chromatographically separated from lighter lanthanoids by CPC.

INTRODUCTION

The reprocessing of spent nuclear fuel has been performed by a purex process, in which U and Pu are recovered by solvent extraction with tributylphosphate (TBP). The high-level liquid waste (HLLW) condensed raffinate solutions contains transplutonium elements (TPEs) and fission products involving lanthanoids.

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The TPEs have very long half lives with α emitter, therefore it is preferred to separate TPEs from other fission products (FPs). Group separation of TPEs and lanthanoids mainly lighter than Eu is one of the most important subjects in nuclear reprocessing technology.[1,2] For the separation of these two groups of elements, solvent extraction process has been widely used, owing to differences in complex formation. Extractability of lanthanoids with acidic extractants usually increases with increasing atomic number.[3,4] For the separation of TPEs from lighter Ln, a distribution ratio (*D*) of Am is preferred to be higher than that of Eu. Recently, extraction selectivity for Am over lanthanoids has been found in some extraction systems involving soft donor ligands.[5,6,7]

Centrifugal partition chromatography (CPC) conveniently realizing multiple liquid-liquid extraction, affords great possibilities for chromatographic separation of chemically similar materials.[8,9] This liquid-liquid partition chromatography employing a stationary phase without any solid support is very attractive, because it offers flexibility for the selection of a stationary phase on the basis of liquid-liquid extraction behavior.[10] This will be advantageous for applications of large-scale chromatographic processes. Group separation of TPEs and lahthanoids has been performed by an alternative countercurrent chromatography having a coiled column,[11,12] and the separation of microamounts of TPEs from macroamounts of lanthanoids was accomplished by employing neutral bidentate organophosphorus extractants as a stationary phase.

This paper deals with the possibility of new chromatographic separation of lighter Ln and trivalent TPEs and attainment of high resolution over 1.0. The liquid-liquid extraction with 5, 8-diethyl-7-hydroxydodecan-6-one oxime (LIX 63) having relatively soft donor N was applied to multistage separation by means of CPC. Optimum conditions using an organic solution of LIX 63 as the stationary phase were investigated for the chromatographic separation of TPEs from lighter lanthanoids.

EXPERIMENTAL

Materials

An extractant, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPA) (PC-88A, Daihachi Chemical Ind. Co. Ltd.), was washed with sodium hydroxide solution to remove acidic impurities, and its concentration was determined by potentiometric titration with a standard solution of sodium hydroxide in an ethanol-water mixture. An extractant, 5,8-diethyl-7-hydroxydodecan-6-one oxime (LIX 63; Henkel), was diluted with kerosene (Wako Pure Chemical Ind.). Radioisotopes ^{152}Eu (Amersham) and ^{241}Am (Radio Chemical Centre) were also used for liquid-liquid extraction. Arsenazo III

(Dojindo Lab.) was employed as a post column reagent. 2-Morpholineoethanesulfonic acid (MES; Dojindo Lab.) was used as a pH buffer. The other chemicals used were of reagent grade.

Apparatus

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 and the stripped solution from the organic phase. A centrifugal partition chromatography (Sanki Engineering Ltd.) was used by arranging 6 cartridges (250W), where one cartridge was composed of 400 microcells and its volume was 20.8 cm^3. 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).

Procedure

A kerosene solution containing 0.2 M (= mol dm^{-3}) LIX 63 was used as a stationary phase in a series of micro-cells. Under centrifugal force, an aqueous mobile phase was pumped into the stationary phase through a rotary seal joint at a flow rate of 3 cm^3 min^{-1}. The mobile phase was passed through the stationary phase in the column rotating at 800 rpm at 60°C. After equilibration between two phases, a sample solution containing 10^{-3} M of each lanthanoid was injected through a sample loop (1 cm^3). The eluted stream was monitored by measuring the absorbance at 650 nm of lanthanoid complexes with Arsenazo III (0.014 % w/v) introduced at a flow rate of 0.5 cm^3 min^{-1}.

RESULTS AND DISCUSSION

Extraction by EHPA

Extraction equilibrium of Eu and Am was examined in order to apply liquid-liquid extraction to the mutual separation of lanthanoid and actinoid by CPC. Distribution ratios of Eu and Am were obtained by measuring the gamma radiation of ^{152}Eu and ^{241}Am. At a definite concentration of EHPA, plots of log *D* against pH gave straight lines with slopes of 2.9 for Eu and 2.6 for Am and both of R^2 coefficients were over 0.99. Overall extraction equilibrium can be expressed by:

Table 1

Distribution Separation Factor Between Am and Eu

Reagents	α_D
LIX 51	0.54
LIX 54	0.36
BPHA	0.46
VA10	0.76
LIX 63	2.86

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

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

where M denotes Eu or Am and $(HA)_2$, the dimmer of EHPA, and K_{ex} is the extraction constant. The distribution ratio of Eu was larger than that of Am, however this is undesirable for preferential extractants of actinoids. Distribution separation factors ($\alpha_D = D_{Am}/D_{Eu}$) between Am and Eu obtained by various extractants were shown in Table 1. The distribution ratio of Am was larger than that of Eu only with LIX 63.

Extraction by LIX 63

At a definite concentration of 0.2 M LIX 63 in kerosene, plots of log *D* against pH gave straight lines with slopes of 2.2 for Eu and 2.1 for Am and both of R^2 coefficients were over 0.99. These slopes, being smaller than 3, imply that some species such as ML^{2+} or ML_2^+ exist in the aqueous phase. The distribution ratio of Am with LIX 63 was higher than that of Eu as expected; LIX 63 with a relatively soft donor atom N has a strong affinity for Am compared with the case for Eu.

Effect of Metal Concentration

In order to obtain optimum conditions for separation, variation in distribution ratio was investigated in a concentration region from 10^{-4} to 10^{-8} M Eu. Here, the exact control of pH value is rather difficult, and the *D* values at a definite pH were estimated by interpolation from the observed *D* values obtained in the vicinity. A plot of log *D* at equilibrium pH 5.0 against log [Eu] gave a straight line with a slope of -0.2. Distribution ratio slightly decreased with increasing Eu concentration. The concentration of free reagent remains almost unaltered irrespective of the formation of metal complex, because of the presence of a large excess reagent. Any precipitation and adsorption of metal species on the vessel were not observed and there was no loss in γ-activities of Eu. Hydrolysis of metal ions would be negligible in the aqueous phase around pH 5.[13] The reason for the slight decrease in distribution ratio remains obscure.

The distribution ratio of Am in the presence of Nd, which is the major component of lanthanoids in HLLW, decreased with increasing concentration of Nd. A plot of log *D* against log [Nd] at equilibrium pH 5.0 was found to be close to a straight line with slope of -0.2, implying that the distribution ratio of Eu and Am decreased in a similar manner.

Surrogate for Am

Experimental works using Am are usually restricted, because special care is required for handling of long lived α-emitters. A suitable lanthanoid element is allowed to substitute for Am. Distribution ratios of lanthanoids with acidic extractants ordinarily increase with increasing atomic number. A prospective lanthanoid having the distribution ratio close to that of Am is expected to be a lanthanoid heavier than Eu. Liquid-liquid extraction was examined between the organic phase containing 0.2 M LIX 63 in kerosene and the aqueous phase containing 10^{-5} M of each lanthanoid mixture. The plots of log *D* vs pH gave straight lines; their slopes, R^2 coefficients and log *D* values at pH 5.0 are listed in Table 2. The distribution ratio of heavy lanthanoids increased with increasing atomic number, and the extractability was in the order, Yb < Am < Lu. If Eu and Yb can be separated, the separation of Am from Eu will be possible. Hence, Yb was employed as a surrogate for Am.

Application to CPC System

In chromatography the retention volume (V_R) is related to the distribution ratio of the desired component between the stationary and mobile phases:

$$V_R = V_M + D\,V_S \tag{3}$$

where V_S and V_M are the volumes of the stationary and mobile phases, respectively. The *D* value will be optimized by varying pH and/or the extractant concentration.

Table 2

Extraction Parameters of Lanthanoids and Am

Element	**log D at pH 5.0**	**Slope**	**R^2**
Eu	-0.869	1.83	>0.99
Gd	-0.809	1.81	>0.99
Tb	-0.477	1.82	0.98
Dy	-0.392	1.90	>0.99
Ho	-0.335	1.99	>0.99
Er	-0.327	1.91	>0.99
Tm	-0.211	2.01	>0.99
Yb	-0.053	1.84	>0.99
Lu	0.201	1.83	>0.99
Am	0.128	2.07	>0.99

The CPC system including detector was preliminarily tested for the elution behavior of Eu. A sample solution (1 cm^3) containing lanthanoids was injected into the front of the column of 6 cartridges holding 0.2 M LIX 63 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.

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

$$N = 16\left(\frac{V_R}{W}\right)^2 \tag{4}$$

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

$$\alpha_C = \frac{V_{R,2} - V_0}{V_{R,1} - V_0} \tag{5}$$

where V_0 is the elution volume for an unretained component. The degree of separation of two adjacent bands is defined as resolution (R_S):

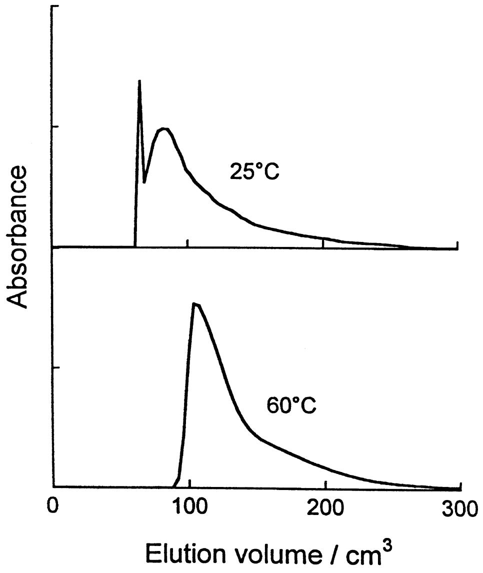

Figure 1. Effect of temperature on the chromatogram of 10^{-3} M Eu. Stationary phase: 0.2 M LIX 63 in kerosene/(250W×6); mobile phase: 0.1 M $NaNO_3$, 0.05 M MES; 900 rpm. pH 5.8.

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

Effect of Temperature on Chromatogram

The chromatographic separation by CPC was enhanced at higher temperatures.[14] The chromatographic elution was examined using CPC column containing 0.2 M LIX 63 in kerosene as a stationary phase. The elution peak of Eu was obtained by passing the mobile phase composed of 0.1 M $NaNO_3$ and 0.05 M MES through the column. Chromatograms of Eu in 25°C and 60°C are shown in Figure 1.

The elution profile obtained at 25°C was split into two peaks, while that at 60°C gave a single peak due to the relatively fast rate of reaction. Further, since the distribution ratio of Eu increased with increasing temperature, Eu was strongly retained in the stationary phase.

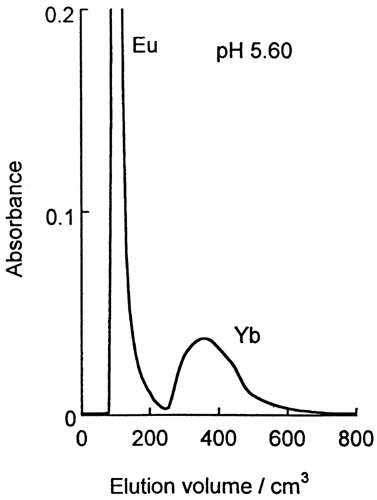

Figure 2. Chromatographic separation of Eu and Yb (surrogate for Am). Stationary phase: 0.2 M LIX 63 in kerosene/(250W×6); mobile phase: 0.1 M $NaNO_3$, 0.05 M MES. Sample: 10^{-3} M Eu, Yb 1cm^3; 900 rpm. pH 5.6.

Table 3

Effect of Temperature on Chromatographic Separation

Temperature °C	V_r cm^3	α_c	W cm^3	N	R_s
25	Eu 132	5.3	78	46	0.88
	Yb 348		414	11	
60	Eu 102	14	45	82	1.67
	Yb 360		264	30	

Chromatogram for Binary Mixture

The elution behavior of Eu and Yb was tested by means of CPC holding 0.2 M LIX 63 in kerosene as the stationary phase in order to select suitable conditions for adequate separation. Figure 2 shows typical chromatogram obtained by passing the mobile phase of pH 5.60 for the binary mixture of Eu

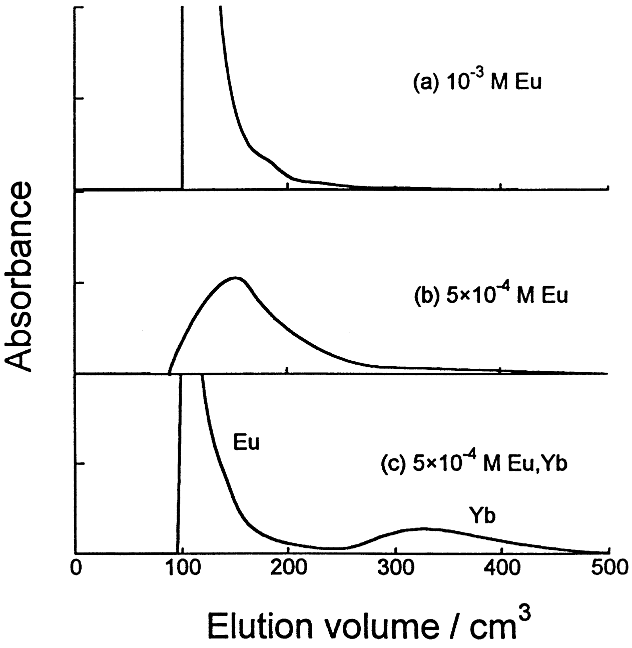

Figure 3. Effect of metal concentration on the CPC. Stationary phase: 0.2 M LIX 63 in kerosene/(250W×6); mobile phase: 0.1 M $NaNO_3$, 0.05 M MES; 900 rpm.

and Yb at 60°C. Each lanthanoid gave the individual peaks; Eu was less strongly retained. The separation parameters evaluated from the chromatograms are listed in Table 3. Under these experimental conditions at 60°C Yb was well separated from Eu.

Effect of Metal Concentration on CPC Chromatogram

As mentioned above, the distribution ratio decreased with increasing metal concentration in liquid-liquid extraction. The metal concentration of mobile phase partially varies in the CPC column, and then it affects the peak profile and separation. Figure 3 shows CPC chromatograms of Eu of different concentrations. In the case of 10^{-3} M Eu, Eu was slightly retained on the stationary phase because its distribution ratio decreased at high metal concentration (Figure 3 (a)). At lower Eu concentration of 5×10^{-4} M, Eu was eluted as a typical single peak (Figure 3 (b)).

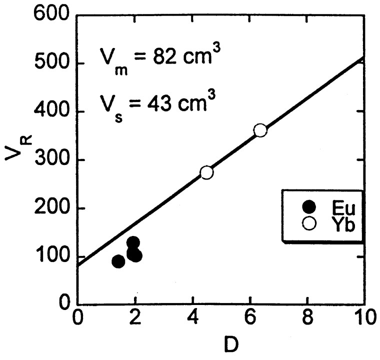

Figure 4. Correlation between V_R and D. Stationary phase: 0.2 M LIX 63 in kerosene/(250W×6); mobile phase: 0.1 M $NaNO_3$, 0.05 M MES. Sample: 10^{-3} M Eu, Yb 1cm^3; 900 rpm.

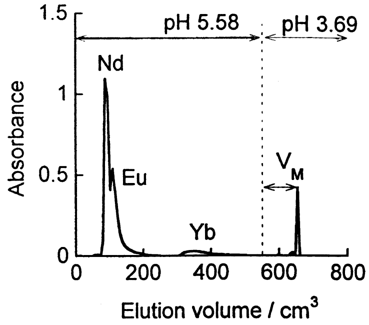

Figure 5. Chromatographic separation of Nd, Eu and Yb (surrogate for Am). Stationary phase: 0.2 M LIX 63 in kerosene/(250W×6); mobile phase: 0.1 M $NaNO_3$, 0.05 M MES. Sample: 10^{-3} M Eu, Yb 1cm^3; 900 rpm.

A chromatogram for the mixture of Eu and Yb of each 5×10^{-4} M is shown in Figure 3 (c). The peak of Eu shifts left compared with the case of (b), indicating a peak profile similar to the case of (a). The elution chromatogram for Eu was influenced by high concentration of metals as well as liquid-liquid extraction.

Table 4

Separation Parameters for CPC Chromatogram

Element	V_R cm^3	α_c	W cm^3	N	R_S
Nd	90		22	256	
		3.1			0.55
Eu	110		51	75	
		8.9			2.6
Yb	348		132	11	

Relation Between V_R and D

The elution volume in CPC can be related to the equilibrium distribution ratio of a desired species between the stationary and mobile phase as expressed by Eq. (3). Figure 4 illustrates the plots of V_R values obtained under different conditions of the mobile phase against the distribution ratios determined by liquid-liquid extraction at comparable conditions. The solid line was estimated by Eq. (3). The V_R value for Eu is smaller than the estimated value, while that for Yb agreed with the calculated one. The reduced V_R value for Eu owing to high concentration of metals rather improved the separation of Eu and Yb.

Separation of Ternary Mixture

The total amounts of lighter lanthanoids are much larger than those of TPEs in HLLW. Here, lighter lanthanoids were represented by Nd of the major component of HLLW, and then the elution behavior of Nd, Eu, and Yb was tested by using the mobile phase buffered with MES. As Figure 5 shows, the peak of Nd and Eu overlapped each other, while Yb was completely separated from Nd and Eu. For the separation of lighter lanthanoids and TPEs, insufficient separation of Nd and Eu was not major problem. The separation parameters evaluated from the chromatograms are listed in Table 4.

The residue in column cartridges was eluted by the mobile phase of lower pH. The eluted fraction was found to contain only Yb without Nd and Eu by ICP-AES analysis. The peak height of Yb was much lower than that of Eu, because a part of Yb was retained in micro cells, however, this portion was easily eluted by an acidic solution.

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