SEPARATION OF THULIUM, YTTERBIUM AND LUTETIUM BY CENTRIFUGAL PARTITION CHROMATOGRAPHY WITH ORGANOPHOSPHINIC ACID

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Abstract - The elution behavior of trivalent heavy lanthanoids Tm, Yb and Lu was investigated by centrifugal partition chromatography (CPC) employing a kerosene solution of di(2,4,4-trimethylpentyl)phosphinic acid (DTMPPA) as a stationary phase. The retention volume (V_R) of lanthanoids varied linearly with the distribution ratio (D) as: $V_R = V_m + D V_s$. The resolution of adjacent bands was enhanced with increasing temperature, rotational speed and the number of cartridges, and was reduced with increasing flow rate of a mobile phase; this enhancement was resulted from increasing number of theoretical plates. Mutual separation of adjacent lanthanoids was accomplished with sufficient resolution.

Key words centrifugal partition chromatography, mutual separation of thulium, ytterbium and lutetium, di(2,4,4-trimethylpentyl)phosphinic acid.

Solvent extraction is a powerful separation method for lanthanoid elements; however, it requires a large number of stages for mutual separation of individual lanthanoids with a low separation factor.

A centrifugal partition chromatography (CPC) has become of interest in recent years as a multistage separation method for chemically-similar materials including rare metals[1-3]. In this apparatus, a liquid stationary phase can be held in microcells without any solid support and it is easy to select suitable stationary and mobile phases according to their requirements on the basis of the data on liquid-liquid extraction.

Some extraction systems of trivalent lanthanoids with acidic organophosphorous extractant have been modified to CPC[4,5]; however, they gave incomplete separation between heavy adjacent lanthanoids.

In this study, the elution behavior of Tm, Yb and Lu through CPC was examined in mild acidic conditions by employing di(2,4,4-trimethylpentyl)phosphinic acid (DTMPPA) having lower extractability compared with other acidic organophosphorous compounds. Important parameters for separation between adjacent bands were examined by varying conditions for CPC, and the mutual separation of heavy lanthanoids was accomplished.

EXPERIMENTAL

Liquid-liquid extraction DTMPPA (HA ; Cyanex 272) was washed with a sodium hydroxide solution for several times to remove acidic impurity and then diluted with kerosene. An aqueous phase was adjusted to an appropriate pH with 0.1 M ($M = \text{mol dm}^{-3}$) (H,Na)CHCl₂COO. The aqueous phase containing 5 ppm of each metal ion and an equal volume of the organic phase consisting of 0.02 M (HA)₂ were shaken for 1 h at 25-65°C. The concentrations of each element in both phases were measured by ICP-AES; the matrix composition of the aqueous phase was adjusted with (H,Na)NO₃ and the extracted metal in the organic phase was stripped with 1 M HNO₃.

CPC A CPC apparatus (Sanki Engineering Ltd.)[1] was operated by arranging ordinarily 6 cartridges (250W) in a rotor. One cartridge has 400 microcells and 20.8 cm³ of internal volume. A kerosene solution containing 0.02 M (HA)₂ was held as the stationary phase in microcells under a centrifugal field. An aqueous mobile phase buffered at an appropriate pH with 0.1 M (H,Na)CHCl₂COO was pumped into the stationary phase ordinarily at a flow rate of 3 cm³ min⁻¹ and passed through forming microdroplets. One cm³ of 10⁻³ M lanthanoid

solution was injected to the mobile phase through a sample loop. The eluted mobile phase was mixed with Arsenazo III, and then lanthanoid complexes were monitored by a spectrophotometer at 650 nm[5].

RESULTS AND DISCUSSION

Liquid-liquid extraction Liquid-liquid extraction of lanthanoids was investigated to choose suitable conditions of the stationary and mobile phases. As Fig. 1 shows, the extractability of lanthanoids increased in the order of the atomic number, and plots of log D (distribution ratio) vs. pH gave straight lines with slopes close to 3. The extraction equilibrium by DTPPPA is expressed by

The separation factors α_D (D_2/D_1) in distribution of lanthanoids are listed in Table 1. The value of α_D between Yb and Lu is relatively small. Figure 2 shows the effect of temperature on log D of heavy lanthanoids, Tm, Yb and Lu. The distribution ratio for each lanthanoid increased with temperature; however, the separation factor remained almost unaltered.

Application to CPC This extraction system was applied to mutual separation of Tm, Yb and Lu by CPC. The retention volume of a desired component varies linearly with distribution ratio as:

$$V_R = V_m + D V_s \quad (2)$$

where V_m and V_s denote the volumes of the stationary and mobile phases, respectively. Figure 3 shows a plot of V_R vs. D for Tm, Yb and Lu at different pH of the mobile phase. The dashed line was evaluated from Eq. (2) employing the experimental values of 80 cm³ for V_m and 45 cm³ for V_s . The plots of experimental values were roughly close to the evaluated line. Fundamental retention parameters of CPC were obtained from the experimental chromatogram. The number of theoretical plates (N) is related to the V_R and its bandwidth (W).

$$N = 16(V_R / W)^2 \quad (3)$$

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

$$\alpha_C = \frac{V_{R,2} - V_0}{V_{R,1} - V_0} \quad (4)$$

TABLE 1. Separation factor of lanthanoids(III)

M1-M2	α_D
La-Ce	11.0
Ce-Pr	1.82
Pr-Nd	1.41
Nd-Sm	6.31
Sm-Eu	1.95
Eu-Gd	1.32
Gd-Tb	3.63
Tb-Dy	2.57
Dy-Ho	1.55
Ho-Er	2.24
Er-Tm	3.02
Tm-Yb	2.82
Yb-Lu	1.58

Fig. 1 Extraction of lanthanoids(III).
Organic phase : 0.02 M $(HA)_2$ in kerosene.
Aqueous phase : 0.1 M $(H,Na)CHCl_2COO$.

Fig. 2 Effect of temperature on D.

where V_0 is the elution volume for an unretained component, which corresponds to the volume of mobile phase in cartridges. The resolution (R_s) is defined as the extent of separation of two adjacent bands.

$$R_s = \frac{2(V_{R,2} - V_{R,1})}{W_1 + W_2} \quad (5)$$

Resolution of each lanthanoid can be improved by increasing D ; however, this would result in a long retention time and dilution of eluted metals. The mobile phase was thus controlled at an appropriate pH where D for Tm was around 1 in subsequent experiments.

Effect of temperature Variations in individual retention parameters are illustrated in Fig. 4. These values were normalized under the conditions of a definite value of V_R for Tm, since the V_R value increased with temperature. The value of α_c was little affected by rising temperature. On the other hand, the value of N increased with a rise in temperature from 25 to 70°C. This can be attributed to high rate of distribution promoted with rise in temperature. This effect resulted in an enhancement of R_s values.

Effect of rotational speed Effects of centrifugal field were examined at different rotational speeds from 600 to 900 by employing 6 cartridges and from 800 to 1100 by employing 4 cartridges. The maximum speed and the number of cartridges are limited by a pressure limit of 60 kg cm⁻² of this apparatus. Effects of rotational speed on each parameter are illustrated in Fig. 5 for the case of 6 cartridges. The value of N increased linearly with rotational speed. The number of microdroplets of the mobile phase probably increased at high rotation, and this would accelerate the rate of distribution. The value of R_s for adjacent elements, Tm and Yb, exceeded 1 corresponding to a reasonably good separation. A similar behavior was observed also for employing 4 cartridges, although effects of rotational speed were rather mild in comparison with those for 6 cartridges. Separation can be improved with increases in the rotational speed and in the number of cartridges, as long as the pressure remains within a limited value.

Fig. 3 Correlation between V_R and D .
Solid line was evaluated from Eq.(2).
CPC : 250W x 6 cartridges, 70°C, 900 rpm.

Fig. 4 Effect of temperature.

Fig. 5 Effect of rotational speed in 6 cartridges.

Effect of flow rate Further improvement of separation was attempted by varying the flow rate of the mobile phase passing through the stationary phase in the region from 1 to 6 $\text{cm}^3 \text{min}^{-1}$. Experimental results are summarized in Fig. 6. The V_R value was almost unaltered at any flow rate and then the α_c value remained nearly constant, indicating normal retention conditions of both phases. On the other hand, the bandwidth was considerably broadened at a high flow rate and the value of N sharply decreased. A high flow rate of the mobile phase may be insufficient to attain distribution equilibria between the stationary and mobile phases, because these equilibria involve slow reactions such as complex formation of lanthanoid with extractant. Thus, the separation depends greatly on the N value, and relatively high R_s value above 2 was obtained at a low flow rate of around 1 $\text{cm}^3 \text{min}^{-1}$.

Mutual separation of Tm, Yb and Lu

The mutual separation of Tm, Yb and Lu by CPC was attempted under optimum conditions at a flow rate of 1 $\text{cm}^3 \text{min}^{-1}$. Figure 7 shows the typical chromatogram for 1 cm^3 of the ternary mixture of 10^{-3} M Tm, Yb and Lu. Each lanthanoid yielded individual peaks with sufficiently high N values, such as 150 for Tm, 160 for Yb and 170 for Lu. A quantitative separation of adjacent lanthanoids was thus achieved with sufficient resolution, 1.64 for Yb/Tm and 1.02 for Lu/Yb.

Fig. 6 Effect of flow rate.

Fig. 7 Separation of Tm, Yb and Lu by CPC.
CPC: 250W x 6 cartridges, 70°C, 900 rpm.
Stationary phase: 0.02 M $(\text{HA})_2$ in kerosene.
Aqueous phase: 0.1 M $(\text{H,Na})\text{CHCl}_2\text{COO}$,
pH 2.20, 1 $\text{cm}^3 \text{min}^{-1}$.

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