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Separation of scandium, yttrium and lanthanum in high-performance centrifugal partition chromatography with *S*-octyl phenyloxy acetic acid

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Abstract

Separation of scandium(III), yttrium(III) and lanthanum(III) was performed by high-performance centrifugal partition chromatography (HPCPC) employing the stationary phase of *S*-octyl phenyloxy acetic acid (CA-12). The liquid–liquid extraction behavior of CA-12 for Sc(III), Y(III) and La(III), the acidity of aqueous phase, and the operation conditions of HPCPC were examined. The retention volume (V_R) increased with the order of Y(III), La(III) and Sc(III) accompanied with the elution of the mobile phase in different pH, which is lowered from 4.6 to 2.1.

Keywords: Separation; Scandium(III); Yttrium(III) and Lanthanum (III); High-performance centrifugal chromatography; *S*-octyl phenyloxy acetic acid (CA-12)

1. Introduction

Yttrium occurs in natural sources along with lanthanoid elements. The separation and purification of Y often requires multi-stage processes due to chemical similarities. Liquid–liquid extraction has provided effective separation methods for rare earth elements. Industrial separation of Y has been performed by means of series of mixer–settlers employing various types of extractants [1]; however, it has required a large number of stages and long separation times for complete isolation of high-purity elements.

High-performance centrifugal partition chromatography (HPCPC) has been developed as an analytical and separation method for chemically similar materials [2]. In this chromatographic technique, both mobile and stationary phases are liquid without any solid support, and an organic solution containing an extractant can be employed as a stationary phase. The volume ratio of stationary to mobile phase is definitely much higher, which leads to higher capacities and better resolution with no need of a high number of theoretical plates. Any two-phase solvent mixture may be used as the mobile and stationary phases at any pH, to perform normal, reverse phase and chiral chromatographic separation on the basis of liquid–liquid extraction behavior, which allows one to modify the selectivity of a system in order to get a pure compound. The polarities of both phases can be smoothly modified also in HPCPC. Separation accomplished with laboratory HPCPC can be directly scaled up to the production scale HPCPC.

In recent years, the mutual separation of trivalent rare earth elements was successfully performed with CPC employing stationary phases containing acidic organophosphorous extractants [3,4]. *S*-octyl phenyloxy acetic acid (CA-12) is a new kind of carboxylic acid extractant with a higher extraction capability, acidity and separation coefficient for rare earth elements, good chemical stability and it is easy to remove industrially. CA-12 has been studied to separate rare earth elements in liquid–liquid solvent extraction [5], but it is difficult to separate yttrium from lanthanide elements unless one uses multiple liquid–liquid extractions, a process which is very inconvenient. In this paper the mutual separation of scandium(III), yttrium(III) and lanthanum(III) was

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performed in the two-phase system of a hexane solution of CA-12 and an aqueous chloroacetate buffer.

2. Experimental

2.1. Materials

An extractant, CA-12 (Tianjin Beichen Xiandai Chemical), was washed with 2% sodium carbonate, 2 M hydrochloric acid and distilled water to remove the impurities. Standard solutions of 1 mg/mL of Sc^{3+}, Y^{3+}, La^{3+} in hydrochloric acid were evaporated and the residue was dissolved in deionized water. The aqueous chloroacetate buffer was composed of 0.1 M chloroacetic acid and sodium hydroxide. The amount of sodium hydroxide was controlled by the pH value of the aqueous. Arsenazo III was used as a post-column reagent.

2.2. Apparatus

Chromatographic separation was performed by means of HPCPC (Model LLB-M, Sanki Engineering, total volume 230 mL, 2136 microcells). A mobile phase was sent into the HPCPC by a pump (Model 204 Dual Pump, Ever Seiko). The detection system consisted of a detector (Model LINEAR 200 UV–VIS, Eppendorf), a post-column reactor (a Eppendorf CH-30 column heater, a A-30-S pump made in Eldex Laboratories) and a CHROM KING workstation.

2.3. HPCPC process

The heptane solution of 0.03 M CA-12 was held in microcells of HPCPC-cartridges as the stationary phase. The aqueous solution containing 0.1 M chloroacetic acid–sodium hydroxide was chosen for the mobile phase. The mobile phase was equilibrated with the corresponding organic phase before use. This mobile phase was pumped into the stationary phase through a rotary seal joint at a flow rate of 2.0–10 mL/min. Under the rotation of HPCPC-rotor at 200 rpm, the mobile phase flowed through the column as small droplets, replacing a part of the stationary phase in the microcells. At a constant volume ratio of two phases, the sample solution containing 0.001 M of each rare earth ion was charged into the column through a sample loop. The rare earth elements eluted from the column were continuously determined by measuring the absorbance of their complexes with arsenazo III at 650 nm.

3. Results and discussion

3.1. The parameters of HPCPC

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

$$V_R = V_M + DV_S, \tag{1}$$

where V_S and V_M are the volumes of the stationary and mobile phase, respectively. The D can be optimized by changing pH of the mobile phase and/or the extractant's concentration.

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

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

The degree of separation of two adjacent bands is defined as resolution (R_S):

$$R_S = 2\frac{V_{R,2} - V_{R,1}}{W_1 + W_2}. \tag{3}$$

3.2. Extraction by CA-12

Mutual separation of rare earth elements is based on the difference in the distribution ratios between the stationary and mobile phases. Extraction equilibrium of Sc, Y and La with CA-12 in heptane was examined on HPCPC in order to optimize separation conditions. Distribution ratios of Sc, Y and La were obtained by measuring the absorbance of rare earth ion-arsenazo III complexes at 650 nm in the post-column deriving system. Fig. 1 represents the distribution ratio (D) of Sc, Y and La as a function of pH. For a given concentration of CA-12, $\log D$ against pH gave straight lines with slopes of 2.20 for Sc, 1.92 for Y, 1.89 for La and all of R^2 coefficients were over 0.99. The slopes were

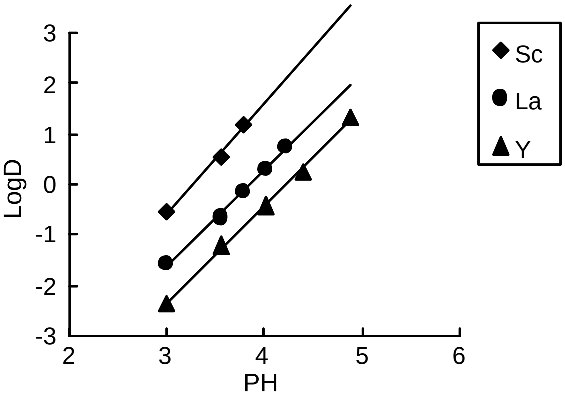

Fig. 1. Extraction of rare earth elements with 0.03 M CA-12 in heptane, 0.1 M chloroacetate buffer aqueous.

near to 2 and not equal to the charge of rare earth elements. It was because that the rare earth ions had hydrolyzed on these pH conditions. So the extraction equilibrium for the rare earth ions into the heptane solution of CA-12 can be expressed by [5–7]

$$M^{3+}_{\mathrm{aq}} + 2(\mathrm{HA})_{2,\mathrm{org}} + \mathrm{OH}^{-} = \mathrm{MOH(HA_2)}_{2,\mathrm{org}} + 2\mathrm{H}^{+}, \qquad (4)$$

where M denotes the rare earth element and $(\mathrm{HA})_2$, the dimer of CA-12, since the carboxylic acid extractants are commonly present as dimeric species in nonpolar diluents. From Fig. 1, the $\mathrm{pH}_{1/2}$ can be calculated when $\log D$ equals zero, for Sc 3.27, for Y 4.22 and for La 3.81. The factor of separation β for Sc with Y is 707.95 and for Y with La is 16.99, calculated according to the formulae $\log\beta \approx 3\ \Delta\mathrm{pH}_{1/2}$. The values of separation factor β were so big that the mutual separation of Sc, Y and La were very easy on HPCPC.

3.3. Relation between VR and D

The elution volume in HPCPC can be related to the equilibrium distribution ratio of a desired species between the stationary and mobile phases as expressed by Eq. (1). The plots of the V_R value against the D value determined by liquid–liquid extraction are shown in Fig. 2. The solid line and points indicate the calculated value from Eq. (1) by employing the experimental values of $50\,\mathrm{cm}^3$ for V_S and $175\,\mathrm{cm}^3$ for V_M. The retention volumes for Y, La and Sc were in proportion to their distribution ratios. Thus, the position of the eluted peak can be predicted from the D value provided the values of V_M and V_S.

3.4. Effect of the flow rate of mobile phase on HPCPC

According to the theory of liquid dynamics and the special structure of HPCPC system, the separation efficiency is controlled by the flow rate of the mobile phase mainly. Fig. 3 shows that the extraction rate% comes down while the flow rate of the mobile phase goes up for a given pH. It means that the amount of rare earth elements in the stationary phase becomes lower at a higher flow rate of the mobile phase. On the other hand, High flow rate of the mobile phase controlled in HPCPC can reduce the total runtime. So it was not the slower the better. In this paper 1.0 mL/min is appropriate.

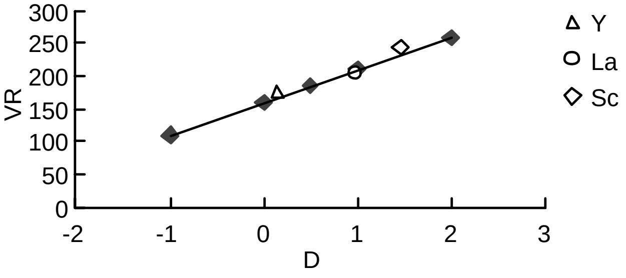

Fig. 2. Relation between retention volume and distribution ratio.

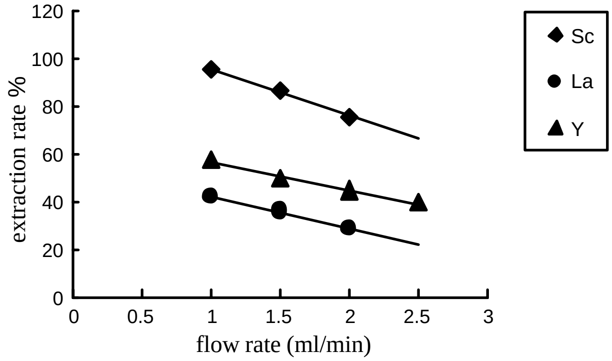

Fig. 3. Effect of flow rate of mobile phase in HPCPC on extraction rate of rare earth elements.

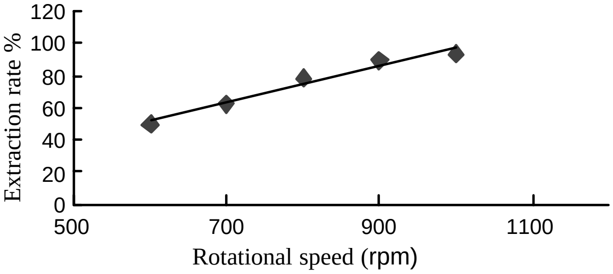

Fig. 4. Effect of rotational speed of HPCPC on extraction rate of Y 0.03 M CA-12, pH = 4.22, flow rate1.0 mL/min, 0.015 M Y.

3.5. Effect of the rotational speed of HPCPC system

The rotational speed of HPCPC system is another important factor to affect the separation efficiency. The chance of meeting and being extracted by the stationary phase was increased on the high rotational speed of HPCPC system for rare earth ions. Fig. 4 shows that the extraction rate% of Y is in direct ratio with the rotational speed of HPCPC. It is distinct that the rare earth elements would be reserved in the stationary phase mainly if the HPCPC system were kept on high rotational speed. But it was difficult to elute them from the column at the same time, also the pressure of the system would increase. So the condition of separating Sc, Y and La in this paper was selected at 900 rpm.

3.6. Separation of Sc, Y and La by HPCPC

A chromatogram for the mixture of Sc, Y and La of each $1 \times 10^{-3}\,\mathrm{mol/L}$ is shown in Fig. 5. Peaks of Sc, Y and La were completely separated from each other under the condition as below: the flow rate of mobile phase—1.0 mL/min, The rotational speed of HPCPC

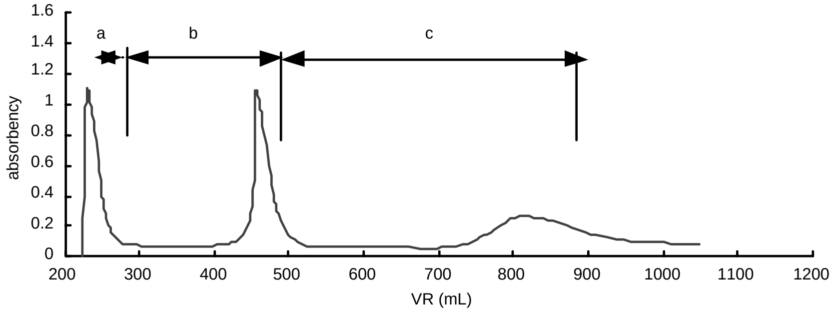

Fig. 5. Chromatogram of Sc, Y, La by HPCPC with CA-12 (a) pH 4.6, Y; (b) pH 4.1, La; (c) pH 2.1, Sc.

system—900 rpm, The flow rate of the arsenazo III in the post-column system—1.0 mL/min, 0.2 mL sample.

The retention volume (V_R) increased with the order of Y(III), La(III) and Sc(III) accompanied with the elution of mobile phase, whose pH is turned from 4.5 to 2.1.

4. Conclusion

The separation of scandium, yttrium and lanthanum was performed by high performance centrifugal partition chromatography employing the stationary phase of a heptane solution of CA-12 and the mobile phase of an aqueous chloroacetate buffer. The extractability of CA-12 for Sc, Y and La was different in the mobile phase with different pH. This is the foundation of separation The flow rate of the mobile phase and the rotational speed of the system were determined to be two important effects on the separation. The mutual separation of Sc, Y and La was carried out through a simple step on HPCPC.

Acknowledgments

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