Short communication

Separation of samarium, gadolinium, terbium, gysprosium, erbium and ytterbium by high-speed countercurrent chromatography with organophosphate ester

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Abstract

High-speed countercurrent chromatography is a recently developed separation method that has been remarkably improved in both separating efficiency and separating time. In this paper, this advanced countercurrent chromatographic method was applied to the separation of lanthanides. In combination with the measurement of the partition coefficient of lanthanides, a suitable solvent system was chosen. The separation of a mixture containing trivalent lanthanides (Sm, Gd, Tb, Dy, Er and Yb) was performed with a two-phase solvent system consisting of 0.15 M di(2-ethylhexyl)phosphate in chloroform (lower phase) and hydrochloric acid (upper phase). As the rotational speed increased, the resolution of adjacent bands was enhanced. While the resolution first increased with increasing the flow-rate of the mobile phase, it reached a maximum at a flow-rate of 1 ml min^{-1} and then decreased with increasing the flow-rate of the mobile phase. This enhancement resulted from an increasing number of theoretical plates. Mutual separation of adjacent lanthanides was accomplished with sufficient resolution.

Keywords: Lanthanides; Di(2-ethylhexyl)phosphate; Samarium; Gadolinium; Terbium; Gysprosium; Erbium; Ytterbium

1. Introduction

Countercurrent chromatography (CCC) is an efficient technique of partition chromatography that totally eliminates the use of solid supports. Since 1971, Ito et al. have developed flow-through coil planet centrifuge schemes for performing CCC [1,2]. High-speed countercurrent chromatography (HSCCC) has been developed by Ito and his co-workers, based on the discovery of a unique hydrodynamic phenomenon in a rotating coil. It is char-

acterized by high partition efficiency and large retention capacity of the stationary phase at high flow-rate of the mobile phase. Several types of coil planet centrifuge have been constructed for performing high-speed countercurrent chromatography [3].

In the 1970s, Kroebel and Meyer [4] advanced the separation of lanthanide by partition chromatography. Holzapfel et al. [5] separated lanthanide by thin-layer chromatography on a silica-gel plate impregnated with di(2-ethylhexyl)phosphate (P_{507}). Kitazome et al. [6] successfully separated lanthanides with HSCCC in 1979.

The present paper describes the separation of a

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mixture of trivalent lanthanides Sm, Gd, Tb, Dy, Er and Yb by high-speed countercurrent chromatography with a two-phase solvent system containing 0.15 M P_{507} in chloroform (lower phase) and hydrochloric acid (upper phase).

2. Experiment

2.1. Apparatus

The apparatus was designed by our laboratory and fabricated by Zhejiang University instrument factory. The details of this apparatus have been described [7]. The apparatus employed was an improved high-speed planet centrifuge with a holder coupled to the central axis with a gear, and another holder coupled to the central axis with a pulley. The two holders are termed as gear side holder and pulley side holder, respectively. The revolutional radius is 192 mm. A PTFE tube of 1.6 mm diameter were coiled in a multilayer form on the holders with a rotational radius of 100 mm. The holder revolved around the central axis of the centrifuge and simultaneously rotated about its own axis at the same angular velocity. This particular type of planetary motion permitted the flow tubes to rotate around the central axis of the centrifuge without twisting, thus facilitating continuous elution of the mobile phase through the rotating column. The revolutional speed of the centrifuge was continuously adjustable up to 1000 rpm with a speed control unit.

The multilayer coiled column was prepared from a single piece of PTFE tubing, 70 m×1.6 mm I.D. (Shanghai Industrial Products, China) wound tightly onto the coil holder. The total capacity of the column was approximately 150 ml. To curb dislocation of the column from the holder, each layer of the coil was taped to the flanges with a piece of fiber-glass reinforced adhesive tape applied across the coil. The same tape was also used to wrap the entire column. Each terminal of the column was directly connected to a flow tube of 0.85 mm I.D. which was inserted and then fused with heat from a heat gun.

2.2. Reagents

Chloroform and hydrochloric acid were analytical

grade reagents, water was distilled. P_{507}, whose purity was greater than 93%, was purchased from Shanghai Organic Institute, China. P_{507} was washed several times with a sodium hydroxide solution to remove acidic impurities and then diluted with chloroform.

2.3. Preparation of two-phase solvent system and sample solution

The organic phase was 0.15 M P_{507} in chloroform, the aqueous phase was HCl (pH 1.41). Equal volumes of the two phases were mixed and prepared by thoroughly equilibrating in a separatory funnel at 35°C.

The solutions containing one of the lanthanides were prepared by heating lanthanide oxides and hydrochloride (1:1, v/v) and evaporated by heating to remove water, then cooled to room temperature, the solutions were diluted to 0.1 mol l^{-1}. The lanthanide oxides were purchased from Shanghai Chemical with a purity of 99.99%.

The sample of lanthanide contained $SmCl_3$, $GdCl_3$, $TbCl_3$, $DyCl_3$, $ErCl_3$ and $YbCl_3$. The concentration of each lanthanide ion was adjusted to 1.0×10^{-3} mol l^{-1} with the upper phase of solvent system.

2.4. Measurement of partition coefficients

To measure partition coefficient, the lanthanide solutions (1 ml) were added to 15 ml of the two-phase solvent system, and the mixture was shaken for 2 min, then kept in thermostat at 35°C for 15 min. After separation, 5 ml of each layer was taken. The lower layer was extracted with 5 ml 4 M HCl, the aqueous phase was taken, its pH was adjusted to 3.0 with NaOH, 4 ml HCl–NaAc (pH 1.41) and 0.25 ml coloring agent azoarsine were added, and then it was made up to 25 ml with water. The upper layer was neutralized, 4 ml HCl–NaAc and 0.25 ml coloring agent azoarsine were added, and then it was diluted to 25 ml. The absorbance was determined with a UV monitor (Mode 752 spectrophotometer, Shanghai Analytic Instrument, China) at 650 nm. The partition coefficient of each lanthanide was calculated from the following equation:

$$K = \frac{C_U}{C_L} \qquad (1)$$

where K is the partition coefficient, C_U, C_L are the concentrations of each lanthanide in the upper and lower layers, respectively. The relationship between the logarithm of the partition coefficient of each lanthanide and pH of the upper aqueous phase of solvent system is shown in Fig. 1.

2.5. Separation procedure

The sample separations were performed in the following manner. First, the entire column was completely filled with the upper aqueous stationary phase and the sample was then injected through the sample port. Then the column was rotated at a speed of 300–500 rpm while the lower non-aqueous mobile phase was pumped into the column at a flow-rate of 0.5–5.0 ml min^{-1} in a head-to-tail elution mode. The effluent from the outlet of the column was fraction-
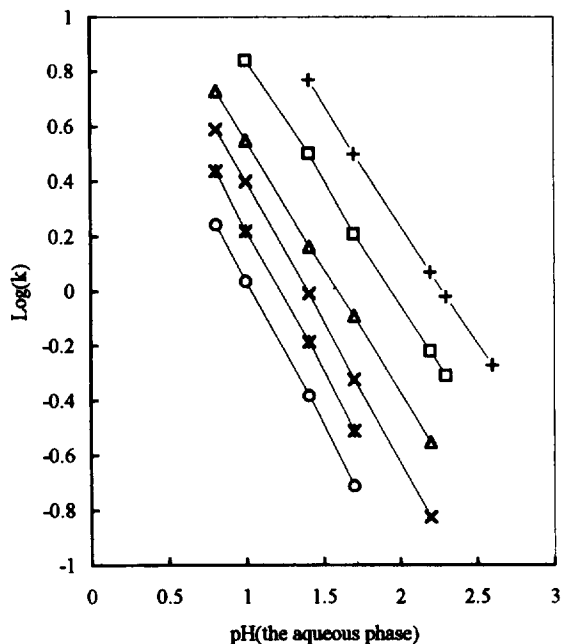

Fig. 1. The relationship between the logarithm of the partition coefficients of lanthanide and the pH of the upper aqueous phase of solvent system. (Organic phase: 0.15 M P$_{507}$ in chloroform; aqueous phase: HCl) – □ – Sm, – △ – Tb, – × – Dy, – ○ – Yb, – * –, Er – + – Gd.

ated with a fraction collector (Ultrorac, LKB) for 5 min. Each fraction (5 ml) was extracted with 5 ml 4 M HCl, then the pH was adjusted to 3.0 with NaOH, 2 ml HCl–NaAc (pH 1.41) and 0.1 ml coloring agent azoarsine were added, and it was diluted to 10 ml with water. The absorbance was determined at 650 nm. The analytical methods used to determine the lanthanide were spectrophotometry and fluorescent X-ray.

3. Results and discussion

3.1. Liquid–liquid extraction

Liquid–liquid extraction of lanthanide was investigated to choose a suitable solvent system and suitable conditions of the stationary and mobile phases. From Fig. 1, it is obvious that the partition coefficient decreased dramatically with increasing pH values, but the ratios of two adjacent lanthanides were almost constant. This means that the separation factors for the lanthanides are independent of the pH value. To obtain partition coefficients nearest to 1 for all six lanthanides, a pH value of 1.14 was chosen for the separation.

3.2. Effect of the rotational speed

The effects of centrifuge field were examined at different rotational speed from 300–500 rpm (Fig. 2a). The number of theoretical plates (N) increased 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 separation can be improved by increasing the rotational speed and the length of column, as long as the pressure remains within a limited value.

3.3. Effect of the flow-rate

Further improvement of separation was attempted by varying the flow-rate of the mobile phase in the region from 0.5–5.0 ml min^{-1}. Experimental results are summarized in Fig. 2b. Both the reduction and the number of theoretical plates were optimal at a flow-rate of 1 ml min^{-1}. The bandwidth was con-

(a) Resolution(Rs)

(b) Theoretical plate number
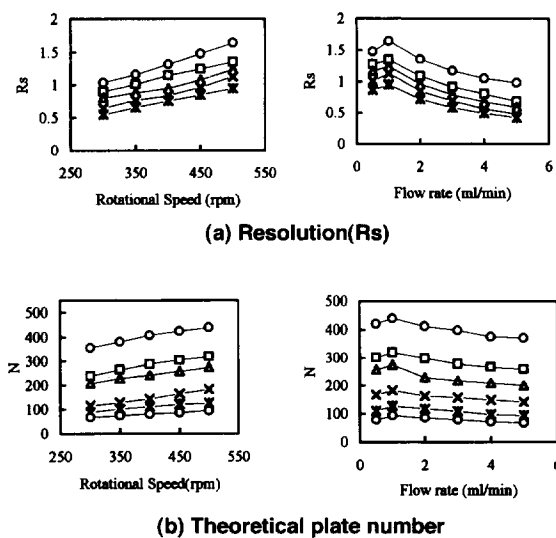
Fig. 2. The effects of the rotational speed and the flow-rate of the mobile phase on resolution (R_s) and theoretical plate number (N). (a) – □ – Tb/Dy, – △ – Dy/Er, – × – Sy/Gd, – ○ – Gd/Tb, – * – Er/Yb; (b) – □ – Er, – △ – Dy, – × – Tb, – ○ – Yb, – * – Sm.

siderably broadened at a high flow-rate and the value of N 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 lanthanide with extracting.

3.4. Mutual separation of Sm, Gd, Tb, Dy, Er and Yb

The mutual separation of Sm, Gd, Tb, Dy, Er and Yb by HSCCC was attempted under optimum conditions at a flow-rate of 1 ml min^{-1} and a rotational
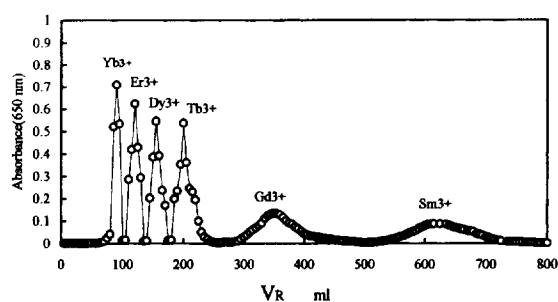

Fig. 3. Chromatogram obtained with a long column on the gear side holder for the separation of lanthanides. Mobile phase: 0.15 M P_{507} in CHCl$_3$; stationary phase: HCl (pH 1.41); rotational speed: 500 rpm; flow-rate: 1.0 ml min^{-1}; collected fraction: 5 ml/bottle.

speed of 500 rpm. Fig. 3 shows the typical chromatogram for 3 ml of the mixture of 1.0×10^{-3} M Sm, Gd, Tb, Dy, Er and Yb. The efficiency of HSCCC in separating lanthanides was similar to that of extraction chromatography and thin-layer chromatography.

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