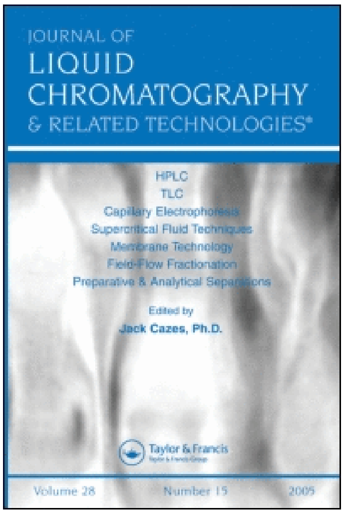

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SEPARATION OF LANTHANIDES BY HIGH-SPEED COUNTERCURRENT CHROMATOGRAPHY WITH ORGANOPHOSPHATE ESTER

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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 separation 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 the trivalent lanthanides La, Ce, Pr and Nd was performed with 0.15M P_{507}(2-ethylhexyl-2-ethylhexyl hydrogen phosphate) chloroform : hydrochloric acid, pH=2.93, (1:1, V/V) solvent system. The resolution of adjacent bands was enhanced with increasing rotational speed, and was reduced with increasing flow rate of the mobile phase. This enhancement resulted from an increasing number of theoretical plates. Mutual separation of adjacent lanthanides was accomplished with adequate resolution.

INTRODUCTION

Countercurrent chromatography (CCC) is an efficient technique of partition chromatography that totally eliminates the use of solid supports. Since 1971, Ito and his coworkers have developed a series of flow-through coil planet centrifuge schemes for performing CCC.[1,2] High-speed countercurrent chromatography (HSCCC) has been developed by Ito and his coworkers, based on the discovery of a unique hydrodynamic phenomenon in a rotating coil. It is characterized 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 centrifuges have been constructed for performing high-speed countercurrent chromatography.[3]

In the 1970's, R. Kroebel and A.Meyer[4] put forth the separation of lanthanides with partition chromatography. Holzapfel et al.[5] separated lanthanides with layer chromatography, silica-gel plate with P_{507} as the stationary phase. E. Kitazome et al.[6] successfully separated lanthanides with HSCCC in 1979.

The present paper describes the separation of a mixture trivalent lanthanides, La, Ce, Pr and Nd by high-speed countercurrent chromatography with a two phase solvent system containing 0.15M P_{507} chloroform: hydrochloric acid, pH=2.93, (1 :1 V/V).

EXPERIMENTAL

Apparatus

The apparatus was designed by our laboratory and fabricated by Zhejiang University Instrument Factory. The details of this apparatus have been described in References 7 and 8. The apparatus employed was a high-speed planet centrifuge with a 192 mm revolutional radius and 1.6 mm diameter multilayer coiled column whose rotational radius is 100 mm. The holder revolves around the central axis of the centrifuge and simultaneously rotates 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, 1.6 mm I.D. and 70 m long (Shanghai Industrial Products, P. R. China) by being wound tightly onto the coil spool 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.

Reagents

Chloroform and hydrochloric acid were analytical reagent grade, water was distilled.

P_{507} 2-ethylhexyl-2-ethylhexyl hydrogen phosphate, $(2\text{-}C_2H_5C_6H_{12}O)(2\text{-}C_2H_5\ C_6H_{12})PO(OH)]$, whose purity was greater than 93%, was purchased from Shanghai Organic Institute, P. R. China. P_{507} was washed with a sodium hydroxide solution for several times to remove acidic impurities and was then diluted with chloroform.

Preparation of Two-Phase Solvent System and Sample Solution

Experiments were performed with the two-phase system 0.15M P_{507} chloroform:hydrochloric acid, pH=2.93, (1:1, V/V). The two-phase solvent system was prepared by thoroughly equilibrating the solvent mixture in a separatory funnel at 35°C.

The solutions, each containing one of lanthanides were prepared by heating lanthanide oxides and hydrochloride (1:1,V/V), and evacuated by heating to remove water, then cooled to room temperature; the solutions were diluted to 0.1 mol/L.

The lanthanide oxides were purchased from Shanghai Chemical Co. with the purity of 99.99%.

The sample of lanthanide contained $LaCl_3$, $CeCl_3$, $PrCl_3$ and $NdCl_3$; the concentration of each lanthanide ion was adjusted to 1.0×10^{-3} mol/L with the upper phase of the two-phase solvent system.

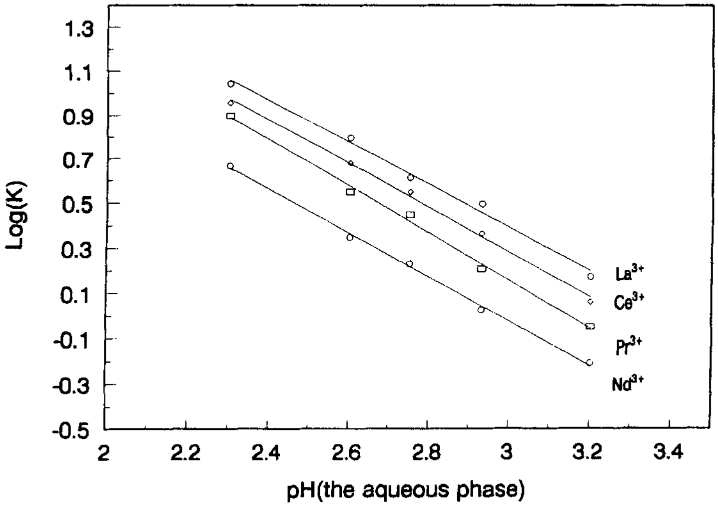

Figure 1. The relationship between the logarithm of the partition coefficients of lanthanides and pH of the upper aqueous phase of the two-phase solvent system. Organic phase was 0.15M P_{507} in chloroform and the aqueous phase was hydrochloric acid.

Measurement of Partition Coefficients

To measure partition coefficients, 1 mL of the lanthanide solutions, respectively, were added to 15 mL of the two-phase solvent system, and the mixture was shaken for 2 min, then kept in a thermostat at 35°C for 15 min.

After separation, 5 mL of each layer was taken. The lower layer was extracted with 5 mL 4N HCl, the aqueous phase was taken, whose pH was adjusted to 3.0 with NaOH, added to 4 mL HCl-NaAc, pH=2.93, and 0.25 mL coloring agent, azoarsine, and then diluted to 25 ml with water. The upper layer was neutralized, added to 4 mL HCl-NaAc and 0.25 mL coloring agent, azoarsine, and then diluted to 25 mL.

The absorbance was determined with a UV monitor (Mode 752 spectrophotometer, Shanghai Analytic Instrument, P. R. China) at 650 nm. The partition coefficient of each lanthanide was calculated from the following equation:

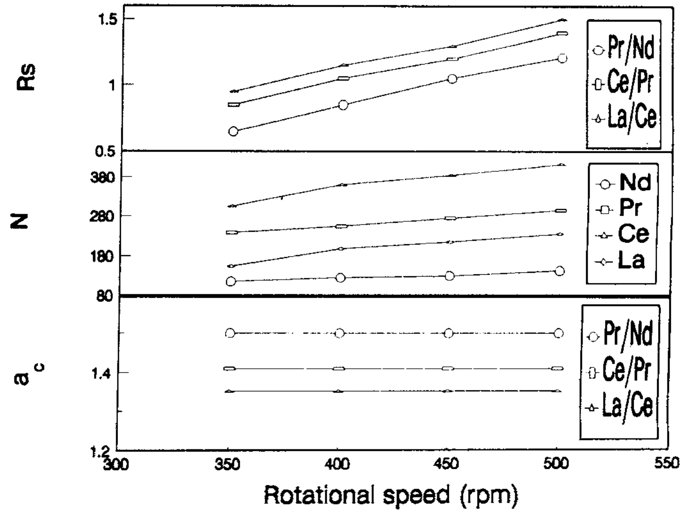

Figure 2. The effects of rotational speed on resolution, efficiency (theoretical plates) and separation factor.

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

where K is the partition coefficient, C_U and C_L are the concentration of each lanthanide in upper layer and lower layer, 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 Figure 1.

Separation Procedure

The sample separations were performed in the following manner. First, the entire column was completely filled with the upper, aqueous stationary phase. the samples were followed by sample injection through the sample port, respectively. Then the column was rotated at the speed of 350-500 rpm while the lower, non-aqueous mobile phase was pumped into the column at a flow rate of 0.5 ~ 5.0 mL/min in a head-to-tail elution mode. The effluent from the outlet of the column was fractionated with a fraction collector (Ultrorac, LKB) for 5 minutes.

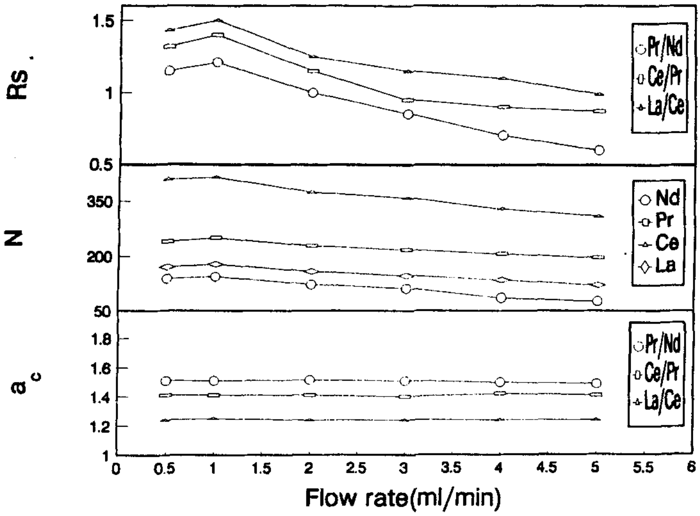

Figure 3. The effects of flow rate of the mobile phase on resolution, efficiency (theoretical plates) and separation factor.

Each fraction (5 mL) was extracted with 5 mL 4N HCl, then the pH was adjusted to 3.0 with NaOH. 2 mL of HCl/NaAc, pH=2.93, and 0.1 mL coloring agent, azoarsine, were added and the mixture 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 x-ray fluorescence.

DISCUSSION

Liquid-Liquid Extraction

Liquid-liquid extraction of lanthanides was investigated to choose the suitable solvent system of 0.1 5M P_{507} chloroform:hydrochloric acid, pH=2.93, (1:1, V/V) and suitable conditions of the stationary and mobile phases. From Figure 1, it is obvious that the relationship between the logarithm of the partition coefficient of lanthanide and pH of the aqueous phase is linear, with slope close to 1.

It was speculated, from Figure 1, that the order of constants, K, with respect to lanthanide was $K_{La}>K_{Ce}>K_{Pr}>K_{Nd}$ and the partition coefficients of lanthanides decreased directly with the pH of the aqueous phase of the solvent system. So, the solvent system of 0.15M P_{507} chloroform:hydrochloric acid, pH=2.93, (1:1, V/V) was suitable for separating the mixture of trivalent lanthanides, La, Ce, Pr, and Nd.

Formulae Applied to CCC Data

Fundamental retention parameters of CCC were obtained from the experimental chromatogram. The number of theoretical plates, N, is related to the V_R and its bandwidth, W:

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

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

$$\alpha_C = \frac{V_{R2} - V_0}{V_{R1} - V_0} \qquad (3)$$

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

$$R_S = \frac{2(V_{R2} - V_{R1})}{W_1 + W_2} \qquad (4)$$

Effect of the Rotational Speed

The effects of the centrifugal field were examined at different rotational speeds from 350 ~ 500 rpm, as illustrated in Figure 2. The value of N was observed to increase directly with rotational speed.

The number of microdroplets of the mobile phase probably increased at higher rotational speed, and this would accelerate the rate of distribution. The separation can be improved with an increase in the rotational speed and the length of column, as long as the pressure remains within a limited range of values.

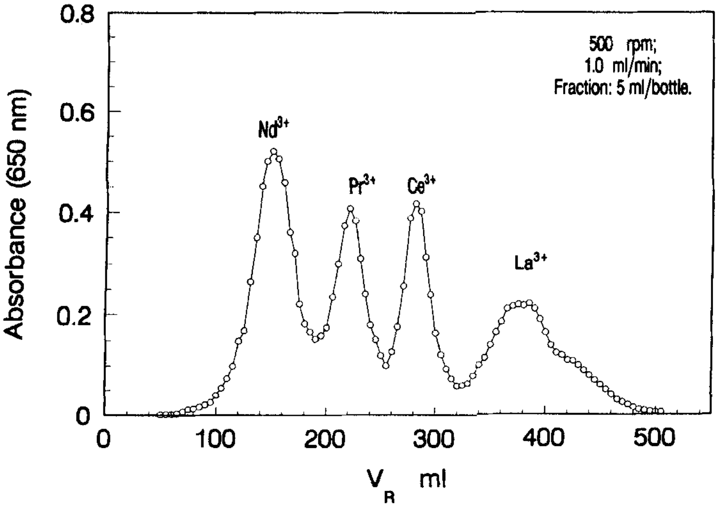

Figure 4. Chromatogram obtained with a long column on the gear side holder. Separation of lanthanides on 0.15M P_{507} $CHCl_3$ / pH=2.93 Hcl (1:1, V/V). Stationary phase: aqueous phase.

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 to 5.0 mL/min. Experimental results are summarized in Figure 3. Both R_s and N showed the best efficiency of peak separation at a flow rate of 1.0 mL/min, whereas the α_C value remained nearly constant. The bandwidth was considerably 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 equilibrium between the stationary and mobile phases, because these equilibria involve slow reactions such as complex formation of lanthanide during extraction.

Mutual Separation of Nd, Pr, Ce and La

The mutual separation of Nd, Pr, Ce and La by HSCCC was attempted under optimum conditions, at a flow rate of 1mL/min and a rotational speed of 500 rpm. Figure 4 shows the typical chromatogram for 3 mL of the mixture of 1.0 x 10^{-3}M Nd, Pr, Ce and La. The separating efficiencies of lanthanides by HSCCC were similar to that observed by extraction chromatography and thin-layer chromatography.

REFERENCES

1. Y. Ito, R. L. Bowman, Anal. Chem., **43(13)**, 69A (1971).

2. Y. Ito, R. L. Bowman, J. Chromatogr., **136**, 187 (1971).

3. Y Ito, H. Oka, Y. Weilee, J. Chromatogr., **498**, 169 (1990).

4. R. Kroebel, A. Meyer, D.T. 2162951 (1971).

5. H. Holzapfel, et al., J. Chromatogr., **24**, 153 (1966).

6. E. Kitazome, Y. Ito, S. Ficca, **Separation of Rare-Earth Element Compounds with HSCCC**, C. A., 21224, 1979, NTIS order No. Pat-Appl-6-485 317.

7. Z. M. Ma, Ph.D. thesis, Zhejiang University, Zhejiang, P. R. China (1995).

8. Z. M. Ma, "Design and Test of the Apparatus of Countercurrent Chromatography," Acta Instrument & Meter (China), in press, 1996.

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