

Forced-Flow Chromatography of Rare Earths Using Sensitive Spectrophotometry

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The sensitive spectrophotometric method for the rare earth elements with xylenol orange in the presence of cetylpyridinium bromide was applied to the continuous detection system of liquid chromatography. Fourteen rare earth elements were completely separated within 130 min by cation-exchange chromatography using 2-hydroxy-*iso*-butyric acid. The eluted ions were determined with absorption maxima of their complexes at around 610 nm. A linear relationship between the peak height and the amounts of rare earth elements was also obtained over the range 0.04 to 0.5 μg .

KEY WORDS: Forced-flow chromatography/ Rare earths/ Xylenol orange/ Spectrophotometric detector/

INTRODUCTION

Cation exchange chromatography is the most useful method for rare earth separation. Recently, the rapid separations of the rare earths by forced-flow chromatography have been reported by Campbell,¹⁾ Story and Fritz,²⁾ Takata and Arikawa,³⁾ and Yamabe.⁴⁾ Nevertheless, much attention has not been paid to the detection system for trace amounts of rare earth elements.

Xylenol orange reacts with rare earth ions in the presence of cetylpyridinium bromide to form the blue chelates with the high molar absorption coefficient ($\epsilon \approx 10^5$).⁵⁾ As the rare earth chelates have the absorption maxima at around 610 nm, it is necessary for the photometric determination of rare earths to separate them from each other. However, such non-selective but sensitive spectrophotometry appears to be a favourable choice for coupling to a chromatographic column.

Previously, authors obtained the rapid separation and sensitive quantitation of alkaline earth ions by using sodium chloride as an eluent and by on-stream addition of a color-forming reagent, *o*-cresol phthalein complexone.⁶⁾

This paper describes the forced-flow chromatography of rare earths, in which they are detected photometrically after addition of a sensitive color-forming reagent.

EXPERIMENTAL

Apparatus and Reagents

The apparatus used is shown diagrammatically in Fig. 1. A Yanagimoto liquid

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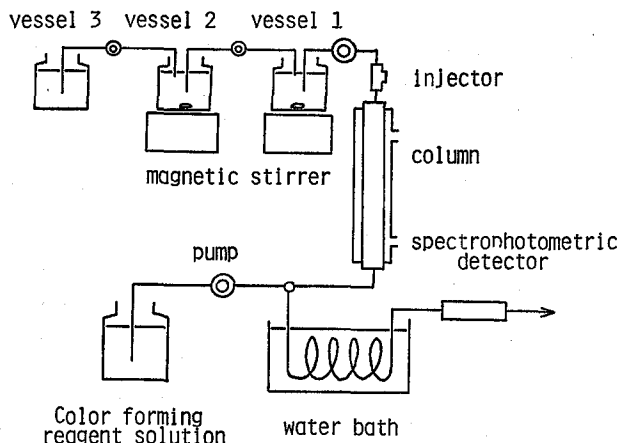


Fig. 1. Schematic diagram of liquid chromatograph.

chromatograph Model L-1031 was employed. The glass column (3 mm in i.d. 300 mm in length) which was packed with a strongly acidic cation-exchanger, Hitachi Custom Ion-Exchange Resin 2611, was kept at 60°C with a water jacket. The detector consisted of a spectrophotometer, Hitachi Parkin Elmer 139 equipped with a 8 μ l micro-flow cell (supplied by Kyowa Seimitsu Co., Ltd.) having a path length of 10 mm. The pH gradient elution was performed by the means shown in Fig. 1. The pH of eluent in vessel 1 increased gradually by sending successively the higher pH eluents in vessels 2 and 3 into vessel 1 with stirring. All stock rare earth solutions were prepared by dissolving the 99.9% or 99.99% pure oxides (Shinetsu Chem. Ind. Co., Ltd.) in hydrochloric acid; standard solutions were prepared by suitable dilution. 2-Hydroxy-*iso*-butyric acid solution was prepared by dissolving the acid form (Tokyo Kasei Co., Ltd.) in water, and insoluble impurities were filtered out. As the eluent were used 0.4 M 2-hydroxy-*iso*-butyric acid and 0.1 M sodium chloride solutions at pH 2.9–5.0. A color forming reagent, xylenol orange (XO), which was purchased from the Dojindo Co., Ltd., Research Laboratories, was used without further purification. Cetylpyridinium bromide (CPE) was obtained from Wako Pure Chemical Ind. Ltd., and the reagent was purified by recrystallizing from methanol. As the solution for the in-stream colorimetric analysis was used 20% methanol-water solution containing 5.0×10^{-5} M XO, 2.0×10^{-3} M CPB, and 1.0 M ammonia-ammonium chloride buffer (pH 9.8). Methanol was added because of protecting the precipitation.

Procedure

The gradient elution was carried out as described above. The flow rate of eluent was 0.3 ml/min and that of color forming solution was 0.27 ml/min. Metal samples (1–10 μ l) were injected into the column with a micro-syringe through a septum injector. The mixed solution of eluent and color forming reagent was flowed into the detection cell after passing through the tube in the thermostatic bath. The absorbance of colored complexes was measured at 610 nm.

RESULTS AND DISCUSSION

A gradient elution decreases the time required for the separation of rare earths with keeping good resolution. Therefore, a pH gradient elution was adopted in this work. Equal volume (10 ml) of the eluent at pH 2.9, 3.0 and 5.0 was placed in vessels 1, 2, and 3, respectively. The eluent was sent by mini pumps from vessels 2 and 3 into vessel 1 at the rate 0.3 ml/min, which was the same as that of the column eluent. Figure 2 shows a gradient curve gained in this case. A typical separation chromatogram based on this gradient was shown in Fig. 3. Fourteen rare earth elements containing $0.214 \mu\text{g}$ each were completely separated within 130 min. The resolutions obtained between the neighboring elements were 1.3 or above.

A mixing tube was used for advancing color development between the metal ions and the colorimetric reagent. The tube (1 mm in i.d. $\times$ 100 cm in length) was warmed in thermostated water bath, and eighty minutes was spent until the sample solution reached to the flow cell after mixing. The change of peak area with temperature of water bath was shown in Fig. 4, in which, as a typical example, Lu, Tb, and Nd were illustrated. The peak areas of Nd and Tb increased as the temperature was raised. However, the peak area of each rare earth element had constant values over 50°C . The peak areas of Nd and La decreased with the decrease of the tube length, while the longer or the wider bore of the tube gave the poorer resolution. The most appropriate length and inner diameter of the tube was 100 cm and 1 mm, respectively.

Figure 5 shows the relationship between the peak height and the amounts of metals. On any rare earth elements from 0.04 to $0.3 \mu\text{g}$, linear curves were obtained. A linear relationship between the peak area and the amounts of elements is also obtained over the range 0.04 to $0.5 \mu\text{g}$.

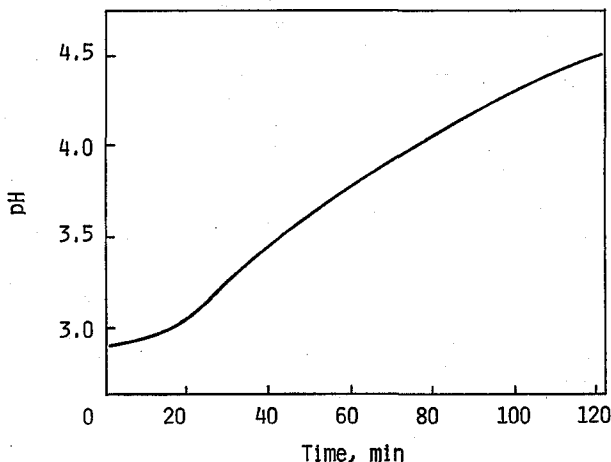


Fig. 2. pH gradient of eluent.

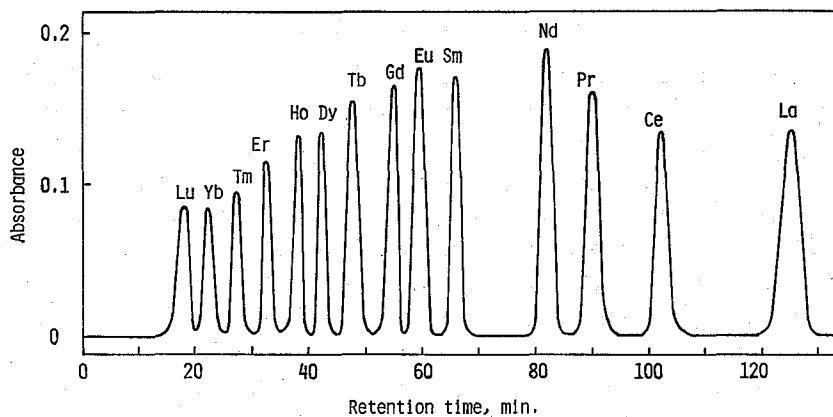


Fig. 3. Separation of rare earths.

Resin: Hitachi Custom Ion Exchange Resin 2611,
 Column: 3 mm i.d. $\times$ 30 cm, 60°C,
 Eluent: 0.4 M α -HIBA, 0.1 M NaCl, pH 2.9–3.0–5.0,
 Color forming reagent solution: 5×10^{-5} M XO, 0.2×10^{-3} M CPB, 1 M $\text{NH}_3\text{--NH}_4\text{Cl}$ (pH 9.8),
 20% methanol,
 Flow rate: 0.3 ml/min (eluent), 0.27 ml/min (color forming reagent solution),
 Metal: 0.214 μg ,
 Mixing tube: 1 mm i.d. $\times$ 100 cm, 60°C,
 λ : 610 nm

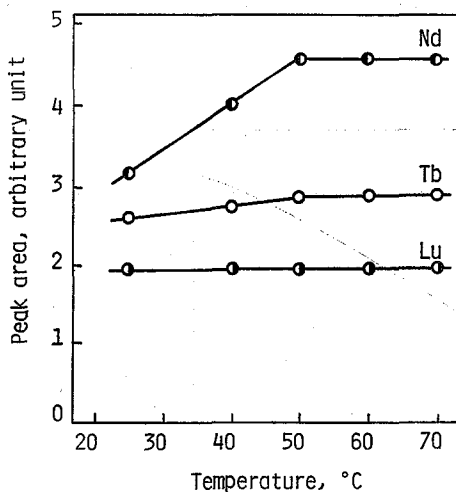


Fig. 4. Effect of temperature of mixing tube on peak area.

Tube: 1 mm i.d. $\times$ 100 cm

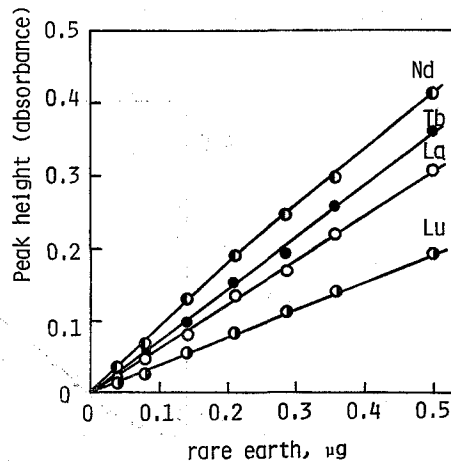


Fig. 5. Calibration curves.

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