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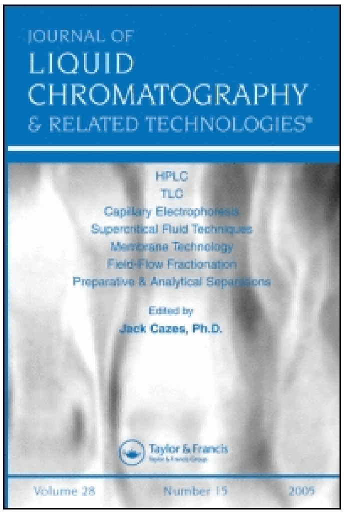

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Akiba, Kenichi , Hashimoto, Hiroyuki , Nakamura, Shigeto and Saito, Yoshihiro(1997) 'Enrichment and Separation of Holmium and Erbium by High-Speed Countercurrent Chromatography', Journal of Liquid Chromatography & Related Technologies, 20: 13, 1995 — 2007

To link to this Article: DOI: 10.1080/10826079708005559

URL: http://dx.doi.org/10.1080/10826079708005559

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J. LIQ. CHROM. & REL. TECHNOL., 20(13), 1995–2007 (1997)

ENRICHMENT AND SEPARATION OF HOLMIUM AND ERBIUM BY HIGH-SPEED COUNTERCURRENT CHROMATOGRAPHY

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ABSTRACT

Selective enrichment of rare earth elements and subsequent separation were performed by high-speed countercurrent chromatography (CCC) using a multilayer coiled column filled with a toluene solution of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester as a stationary phase. A large volume of aqueous solution containing adjacent rare earth elements, holmium and erbium, was passed through the column, and then the rare earth elements enriched in the stationary phase were chromatographically eluted by the mobile phase of an appropriate pH value.

Mutual separation with sufficient resolution was accomplished, and approximately linear relationship existed between the area of elution peak and the quantity of rare earth element injected.

INTRODUCTION

A high-speed countercurrent chromatography (CCC) using a multilayer tubing coil is a novel technique for the separation of chemically similar materials.[1-4] This chromatographic method is attractive because the stationary and mobile phases can be selected on the basis of liquid-liquid extraction behavior. The CCC method was applied to the separation of several organic materials in the beginning, and in recent years it has seen development in the application of separations of inorganic materials.[5-9]

Rare earth elements are chemically similar and this makes it difficult to separate one another. Mutual separation of rare earth elements has been accomplished through CCC by employing acidic organophosphorus compounds as stationary phase materials.[10-12] A CCC stationary phase consisting of an excellent extracting reagent, can afford good separation of rare earth elements, without the addition of any other chemicals such as complexing agents for enhancing metal separation.

For the determination of trace elements, a preconcentration step is required from a large amount of sample. The CCC column can also serve as a continuous extractor for selective preconcentration of trace elements in the column by the passing through of a large volume of sample solution.[5,7,9] The enrichment of materials of interest and their subsequent separation can be accomplished by means of a single CCC column.

This successive procedure through the CCC column is desirable, because it has no extra enrichment step and is free from problems such as, contamination and loss of desired materials sometimes attributed to support materials in the column.

The present study deals with enrichment and separation of small amounts of the adjacent rare earth pair, holmium and erbium, through the CCC column, containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA) in toluene as a stationary phase.

EXPERIMENTAL

Materials

The extractant, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA; PC-88A, Daihachi Chemical Ind. Co. Ltd.) was washed with a sodium hydroxide solution to remove acidic impurities and diluted with toluene.[13] Arsenazo III (Dojindo Lab.) was used as a post column reagent.

Apparatus

A prototype high-speed countercurrent chromatograph apparatus (HCC-1A; Shimadzu Corporation) holds two identical column holders. The column consists of three layers (about 300 helical turns) of polytetrafluoroethylene (PTFE) tubing with a 1.5 mm inner diameter and ca 150 m length, and a total capacity of coils is about 268 cm^3.[12] This apparatus was placed in an air-thermostated box kept at 35°C.

Procedure

The coiled column was first filled with a toluene solution containing 0.02 M $(EHPA)_2$ (M = mol dm^{-3}). An aqueous mobile phase was pre-equilibrated by contacting with toluene, and pumped "head to tail" into the column under operating conditions, i.e., a revolutional speed of 800 rpm, a flow rate of 5 cm^3 min^{-1} at 35°C. Two alternative methods of sample injection were employed as: a) Equilibrium injection - The column was fully equilibrated with the mobile phase before the sample injection; b) Nonequilibrium injection - A sample solution was directly injected into the column without equilibration of the two phases and then the aqueous mobile phase was passed through the column displacing a portion of organic stationary phase.

The sample solution, containing 10^{-7} to 10^{-3} M of holmium and erbium, was injected through a sample loop in the case of a small volume (1 cm^3) or through the feeder of the aqueous mobile phase in the case of a large volume, up to 2000 cm^3. The pH of sample solution was controlled with 10^{-2} M (H,Na)HCOO or 10^{-3} M $(H,Na)CH_3COO$.

Metal ions were eluted with the mobile phase of an appropriate pH buffered with 0.1 M $(H,Na)Cl_2CHCOO$. The eluted rare earth elements were monitored by spectrophotometric detection of the absorbance, at 650 nm of rare earth complexes, by a post-column reaction with 0.014%(w/v) Arsenazo III in 50%(v/v) ethanol.[13] The flow cell was periodically washed by flowing ethanol to obtain a stable base line.

After the desired rare earth elements were eluted, the apparatus was stopped, and by introducing a pressurized nitrogen gas into the column, the column contents were emptied into a graduated cylinder to measure the volume of the stationary phase retained in the tubing coil.

RESULTS AND DISCUSSION

Liquid-Liquid Extraction of Rare Earth Elements

Extraction equilibrium of rare earth elements (RE) with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA) has been studied previously.[12,13]

Overall extraction equilibrium with EHPA for the rare earth ions into the toluene solution of EHPA can be expressed by:

$$M^{3+}_{aq} + 3(HA)_{2,org} \Leftrightarrow M(HA_2)_{3,org} + 3H^+_{aq} \qquad (1)$$

$$K_{ex} = \frac{\left[M(HA_2)_3\right]_{org}\left[H^+\right]^3_{aq}}{\left[M^{3+}\right]_{aq}\left[(HA)_2\right]^3_{org}} \qquad (2)$$

where M denotes the rare earth element and $(HA)_2$, the dimer of EHPA.

The extraction constant (K_{ex}) and the separation factor (α_D), defined as the ratio of their K_{ex} values, were previously obtained in the toluene/ 0.1M(H,Na)Cl_2CHCOO system at 35°C; the log K_{ex} = -0.80 and -0.35 for holmium and erbium, respectively, and hence, their separation factor is 2.8.[12]

The extractability with EHPA in aromatic solvents such as toluene is lower than that in aliphatic solvents for rare earth elements.[14] For the chromatographic separation process, the low extractability in toluene is rather favorable, because a weakly acidic solution is available for a mobile phase.

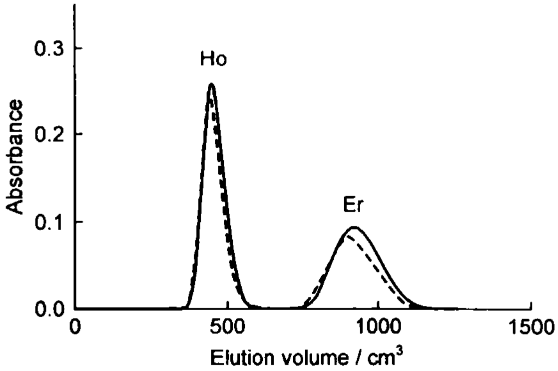

Figure 1. Comparison of equilibrium and nonequilibrium injections of the sample solution containing holmium and erbium. Revolutional speed: 800 rpm; flow rate: 5 cm^3 min^{-1}; 35°C. Stationary phase: 0.02 M $(EHPA)_2$ in toluene; mobile phase: 0.1 M $(H,Na)Cl_2CHCOO$, pH 2.05. Sample: 10^{-3} M RE, 1 cm^3; broken: equilibrium injection, solid: nonequilibrium injection.

Chromatographic Behavior by Equilibrium and Nonequilibrium Sample Injections

The retention volume (V_R) of a desired component is given by the mobile phase volume (V_m), the stationary phase volume (V_s) and the distribution ratio (D) as:

$$V_R = V_m + D\ V_s \qquad (3)$$

On the basis of the extraction data, chromatographic conditions of stationary and mobile phases were optimized for the separation of the adjacent elements.

In CCC separation, it is important to provide the stable retention of a suitable organic solution as the stationary phase in the coiled column. The volume of stationary phase retained in the column has been found to increase with increasing revolutional speed and with decreasing flow rate of mobile phase.[12] The revolution of 800 rpm and the flow rate of 5 cm^3 min^{-1} were adopted to retain an adequate volume of stationary phase.

Figure 1 illustrates typical chromatograms obtained for a mixture of holmium and erbium, by means of equilibrium and nonequilibrium injections of 1 cm^3 sample solution. The elution peaks after equilibrium injection are well separated, and almost the same elution peaks with good resolution are also obtained by nonequilibrium injection. Thus, these two sample injection methods before and after phase equilibration, gave no significant effect on chromatograms and yielded sufficient separation of individual peaks.

Extraction Enrichment of Rare Earth Elements in Column

The enrichment of rare earth elements from different volumes of sample solution was examined by keeping the total quantity of metal to be constant. A small volume of sample solution can be readily injected, usually, through a sample loop; however, a large volume of sample solution should be directly injected through a inlet path for the mobile phase. Figure 2 presents CCC chromatograms obtained by nonequilibrium injection of different volume solutions containing a constant amount (10^{-6} mol) of each of holmium and erbium at pH > 3. Rare earth elements of low concentration are sufficiently enriched and well separated.

In the nonequilibrium injection method, a large volume of aqueous sample solution passes through the column, simultaneously, displacing the part of organic solution and forming the suitable stationary phase. There is a considerable saving in time and in the volume of buffer solution over the equilibrium injection method. The stationary phase can be available for repeated runs in the equilibrium injection method, however the volume of the stationary phase was found to decrease about 1.5 % by one recycled use. In the present experiments, the V_s values before and after chromatographic operations or repeated runs were confirmed to remain within the region of 125 - 133 cm^3 through four repeated runs.

Figure 3 shows the effect of the volume of sample solution on the chromatographic parameters. The V_R values for erbium and holmium remain unaltered, irrespective of the sample volume, ranging from 1 to 2000 cm^3, and the almost constant value of the separation factor (α_c); a relatively high resolution (R_S) was obtained.

After the chromatographic operation, each elution fraction was collected in order to evaluate the recovery of metals. The rare earth elements fractionated were extracted into 0.02 M $(EHPA)_2$ in toluene, and then stripped and concentrated in the nitric acid solution. The recovery determined by ICP-AES was found to decrease slightly from almost quantitative at 1 cm^3 to around 85% at 2000 cm^3 of sample solution.

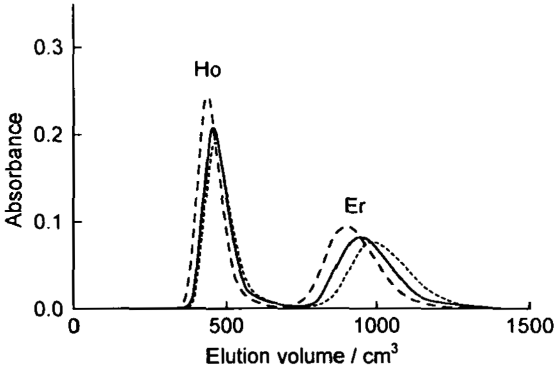

Figure 2. Chromatograms for a constant amount of holmium and erbium enriched from different volumes of sample solution. Mobile phase: pH 2.02-2.06. Nonequilibrium injection; broken: 5 x 10^{-6} M RE, 200 cm^3, pH 3.47; solid: 10^{-6} M RE, 1000 cm^3, pH 3.14; dotted: 5 x 10^{-7} M RE, 2000 cm^3, pH 3.46.

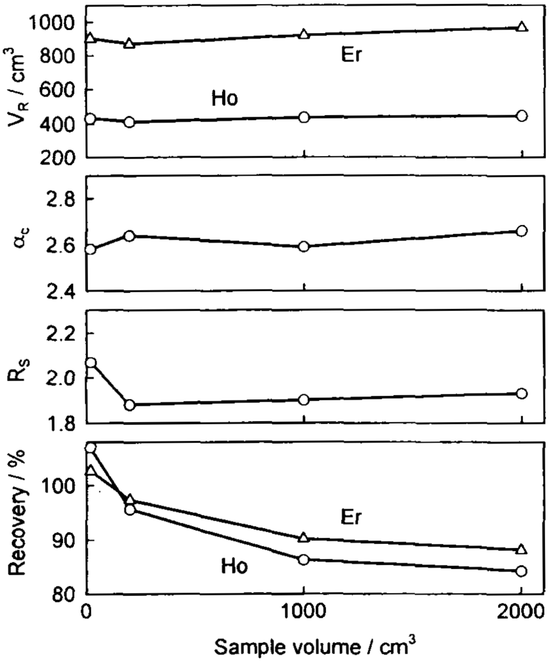

Figure 3. Effect of sample volume on the chromatographic parameters.

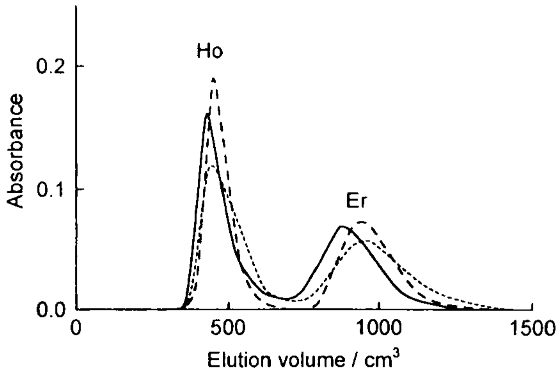

Figure 4. Chromatograms for different pH of sample solution. Mobile phase: pH 2.04-2.07. Sample: 10^{-6} M RE, 1000 cm^3; nonequilibrium injection; broken: pH 3.03, solid: pH 3.47, dotted: pH 4.63.

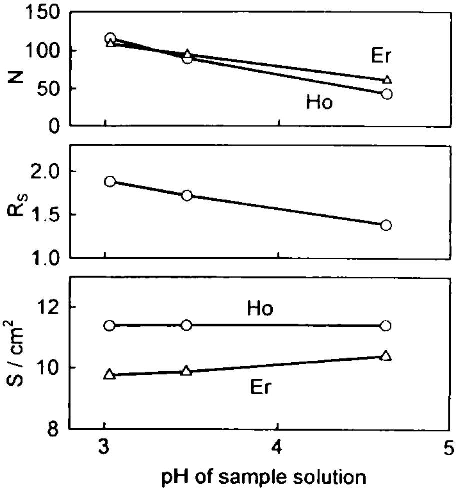

Figure 5. Effect of pH of sample solution on the chromatographic parameters.

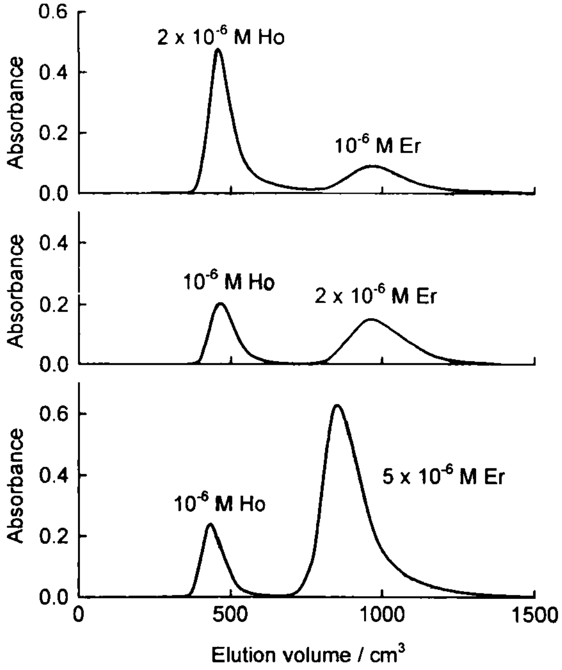

Figure 6. Chromatograms for different concentration ratios of holmium and erbium. Mobile phase: pH 2.05-2.06. Sample: pH 3.45, 1000 cm^3, nonequilibrium injection.

Effect of pH of Sample Solution

For the enrichment of rare earth elements in the column, the pH value is required to be high enough to extract these metals; that is, the distribution ratios of holmium and erbium, between the toluene solution of 0.02 M $(EHPA)_2$ and the sample solution, are expected to be larger than 100 at pH > 3. Chromatograms obtained after nonequilibrium injection of 1000 cm^3 solutions in the pH region from 3 to 4.6 are presented in Fig. 4. The elution peaks of holmium and erbium are considerably separated, but the peak profiles become slightly broader with an increase in pH values of sample solutions. The chromatographic parameters evaluated from individual elution peaks are illustrated in Fig. 5. The number of theoretical plate (N) increases in a lower pH region, and hence resolution is enhanced. When the sample solution of higher pH value is introduced into the column, EHPA in the "head" of the column may become slightly soluble in the mobile phase due to its acid dissociation. This slight decrease in EHPA concentration in the stationary phase appears to lead the broadening of the metal bands. In spite of deformed profiles of elution peaks, the peak area (S) for holmium and erbium remains almost unaltered independent of pH value of sample solution. This implies that quantitative analysis can be performed based on the peak area measurement. Higher pH value of sample solution is not always desirable, as long as the desired rare earth elements can be sufficiently collected.

Effect of Metal Concentration in Sample Solution

The enrichment of rare earth elements from a sample solution of 1000 cm^3 was carried out by varying the concentration of each element. As Fig. 6 shows, the elution peaks containing different quantity of rare earth elements are sufficiently separated from each other. Chromatographic parameters at different concentrations of erbium are presented in Fig. 7. The retention volume of erbium slightly decreases with increasing erbium concentration.

The concentration of free EHPA in the stationary phase would be depressed due to the reaction with higher concentration of erbium, and the reduced distribution ratio of erbium leads to a decrease in its V_R value and in the separation factor. The R_S value, however remains high, around 2.

The rare earth elements of different concentrations, ranging from 2×10^{-7} to 2×10^{-6} M each, were first enriched and then chromatographed with the mobile phase of pH 2.07. The resultant typical chromatograms are illustrated in Fig. 8. The individual peaks of holmium and erbium are well resolved, even in the case of low concentration of 2×10^{-7} M. Complete separation with the resolution, around 2, was accomplished in a wide concentration region.

Collection of rare earth elements from further dilute solution would be also possible by passing a large volume of sample solution into the column; however it takes a longer time, or resolution might be lowered with increasing flow rate owing to decreasing retention of the stationary phase.

The peak area obtained varying the concentration of holmium and erbium is plotted in Fig. 9. The peak area varies in proportion to the concentration of the desired elements. Even in the very low concentration region around 10^{-7} M level, the enrichment, separation and analysis of rare earth elements would become possible by successive procedure through CCC. The depicted chromatographic procedure implies not only a good resolution in the separation of rare earth elements, but also the applicability in their analysis.

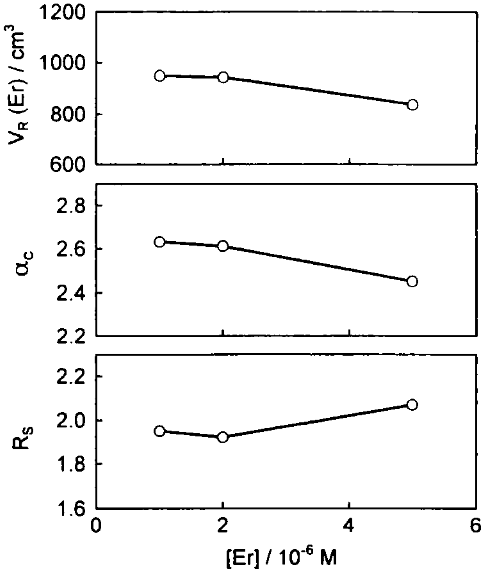

Figure 7. Effect of erbium concentration in the sample solution on the chromatographic parameters.

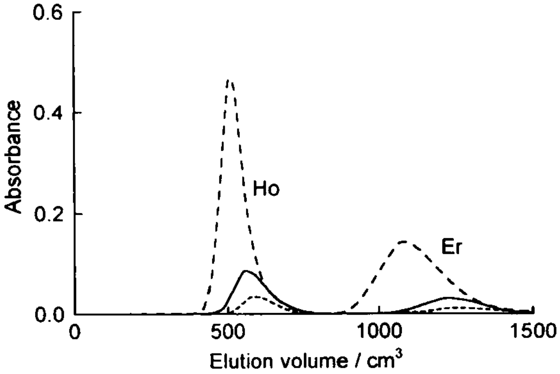

Figure 8. Chromatograms for different concentrations of holmium and erbium in the sample solution. Mobile phase: pH 2.07. Sample: 1000 cm^3, pH 3.43-3.44; equilibrium injection; broken: 2 x 10^{-6} M RE; solid: 5 x 10^{-7} M RE; dotted: 2 x 10^{-7} M RE.

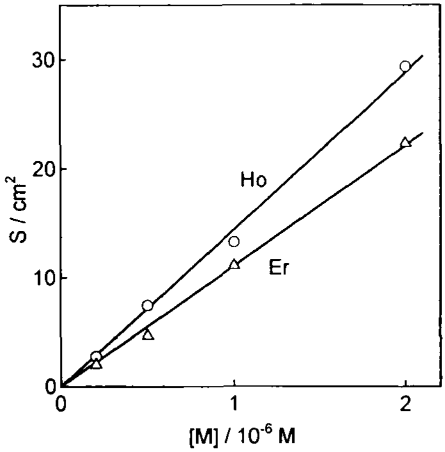

Figure 9. Effect of the metal concentration in the sample solution on peak areas of chromatograms.

CONCLUSION

The result of the present study with CCC are summarized as follows:

1. Similar chromatograms were observed through CCC by the alternative sample injections before and after equilibrium of the stationary and mobile phases.

2. Rare earth elements were efficiently enriched in the stationary phase from a large quantity of aqueous solution.

3. The rare earth elements enriched were separated from each other with sufficient resolution.

4. The area of the chromatographic peak varied in proportion to the quantity of desired metal injected.

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Received November 20, 1996
Accepted December 13, 1996
Manuscript 4331