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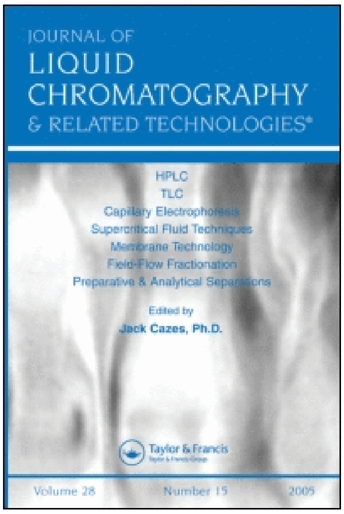

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Separating Behaviors of Heavier Rare Earth Metal Ions in Centrifugal Partition Chromatography with Di(2-Ethylhexyl) Phosphoric Acid

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To cite this Article Araki, Takeo , Asai, Hideaki , Ando, Hisanori , Tanaka, Nobuo , Kimata, Kazuhiro , Hosoya, Ken and Narita, Hiroshi(1990) 'Separating Behaviors of Heavier Rare Earth Metal Ions in Centrifugal Partition Chromatography with Di(2-Ethylhexyl) Phosphoric Acid', Journal of Liquid Chromatography & Related Technologies, 13: 18, 3673 — 3687

To link to this Article: DOI: 10.1080/01483919008049563

URL: http://dx.doi.org/10.1080/01483919008049563

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JOURNAL OF LIQUID CHROMATOGRAPHY, 13(18), 3673-3687 (1990)

SEPARATING BEHAVIORS OF HEAVIER RARE EARTH METAL IONS IN CENTRIFUGAL PARTITION CHROMATOGRAPHY WITH DI(2-ETHYLHEXYL) PHOSPHORIC ACID

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ABSTRACT

The separating behaviors of $SmCl_3$, $EuCl_3$, $GdCl_3$, $TbCl_3$, $DyCl_3$, $HoCl_3$, $ErCl_3$, $TmCl_3$, $YbCl_3$, and $LuCl_3$ in Centrifugal Partition Chromatography with the stationary phase containing a separator, Di(2-ethylhexyl)phosphoric acid (D2EHPA), are examined. The separation trends of these heavier rare earth metal ions were found to be almost as expected from the observations reported for the lighter rare earth metal ions. And the separator is also useful for mutual separation of these heavier rare earth metal ions.

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INTRODUCTION

The importance of Centrifugal Partition Chromatography (CPC) for separation of inorganic ions was shown in 1985.(1) As the extension, we reported(2,3) that CPC is useful also for the separation of lighter rare earth (RE) metal ions from $LaCl_3$ to $EuCl_3$, and the preliminary tests for separation of heavier RE ions by choosing $YbCl_3$ and $ErCl_3$.(2) When Di(2-ethylhexyl)phosphoric acid (D2EHPA) was used as separator in the stationary phase, the separation behaviors of these lighter RE ions were well correlated with the results of extraction experiments by using D2EHPA.

Namely, the key chemical equation both in CPC and extraction processes should be eq. 1 which was developed from the earlier extraction study:(4)

$$RE^{3+} + 3\,(HG)_2 \rightleftharpoons RE(HG_2)_3 + 3\,H^+ \qquad (1)$$

where HG denotes D2EHPA.

On the basis of that the chromatographic behaviors of selected heavier RE ions (Yb^{3+} and Er^{3+}) to be in a line of those for the lighter RE ions, we suggested the separation of heavier RE ions would be attained by suitably setting the experimental conditions such as increased polarity in the stationary solvent.(3) In fact, CPC separation of heavier RE ions was attained with the related separator of 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (EHPA or PC-88A)(5) by assuming that the equilibrium in CPC was eq. 2.

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

where HA denotes EHPA.

This paper refers to the studies on CPC behaviors of heavier RE ions of Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+},

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Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+} with the D2EHPA separator, and CPC separation of this series of ions was attained in a line of expectation.

EXPERIMENTAL

Materials: Following rare earth metal ions were obtained from commercial suppliers and used without further purification: $SmCl_3 \cdot 6H_2O$ (Nacalai tesque, 99.9 %), $EuCl_3 \cdot 6H_2O$ (Nacalai tesque, 99%), $GdCl_3 \cdot 6H_2O$ (Nacalai tesque, 99.9 %), $TbCl_3 \cdot 6H_2O$ (Nacalai tesque, 99.9 %), $DyCl_3 \cdot 6H_2O$ (Wako, >97%), $HoCl_3 \cdot 6H_2O$ (Wako, 99.9%), $ErCl_3 \cdot 6H_2O$ (Wako, >97%), $YbCl_3 \cdot 6H_2O$ (Wako, 99.9%). Two kinds of $RECl_3 \cdot 6H_2O$ (RE: Tm and Lu) were prepared from high purity oxides (Tm_2O_3 and Lu_2O_3, >99.99%, respectively; gifted from Professor H. Hashitani, Shimane University) by treating with aq. HCl solutions at elevated temperature according to general methods for rare earth elements. The purity of the chlorides were checked by absorption spectra. Ethyleneglycol (Wako, extra pure grade) was used. Other reagents and solvents were the same as used in the preceding papers.(2,3)

Apparatus: Centrifugal Partition Chromatography was performed with Sanki's apparatus as described in the preceding paper.(3) A Shimadzu double beam spectrophotometer Model UV-180 and a Hitachi-Horiba pH meter Model F-7 II were used for determination of rare earth concentrations in the eluted fractions.

Chromatographic Procedures and Conditions: General chromatographic procedures have been already reported. (2,3) The experimental conditions used in this work are as follows: Number of cartridges: 3 (Model 240W, total microcells of 400 x 3 = 1200); elution mode: ascending; mobile phase: 0.02-0.14 N aq. HCl solution with the flow

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rate of 1.10 mL·min^{-1}; stationary phase: $CHCl_3$ solution containing 0.1 M D2EHPA; rotation: 700 rev; temperature: 25 and 45 °C; sample: 8 mM aq. $RECl_3$ solution (0.54 mL) for RE = Sm, Eu(0.02 N HCl), Gd(0.02 N), Tb(0.04 N), Er (0.1 N), Tm, Yb, and Lu(0.10-0.14 N); 4 mM aq. $RECl_3$ solution (0.54 mL) for RE = Eu(0.03 N), Gd(0.03, 0.04 N), Tb(0.03 N), Dy, Ho, and Er(0.06, 0.08 N); Dead volume: 21 mL(25°C) and 20 mL(45 °C). Detection: the batch type analysis of RE ions in the eluted fractions (every 5 min's interval) was used as described in the preceding papers.(2,3) A fraction was diluted (2.5 times), and the analytical sample (pH 6.0) contains xylenol orange (1.12×10^{-4} M) and hexamine buffer (0.64 M). The RE concentrations were determined spectroscopically with the 580 nm band intensities precalibrated. This band was more sensitive for analysis of low-concentration samples than the 420 nm band used previously.

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RESULTS AND DISCUSSION

The previous observation suggests that stability of the RE salt formed with D2EHPA in the CPC stationary phase is increased with increase in the atomic number of the RE ion. In fact, it was effective to increase the polarity of the stationary solvent from toluene to chloroform for separation of Er^{3+}/Yb^{3+}.(3) Accordingly chloroform was used in this work throughout.

Figure 1 shows the CPC diagrams of Sm^{3+}, Eu^{3+}, and Gd^{3+} obtained with aqueous mobile phase of 0.02 N HCl at 25°C. Almost complete CPC separation of Sm^{3+} and Gd^{3+} was observed under the condition. The separation between Sm^{3+} and Eu^{3+} was attained in a shorter time with lower HCl concentration than in the corresponding case where

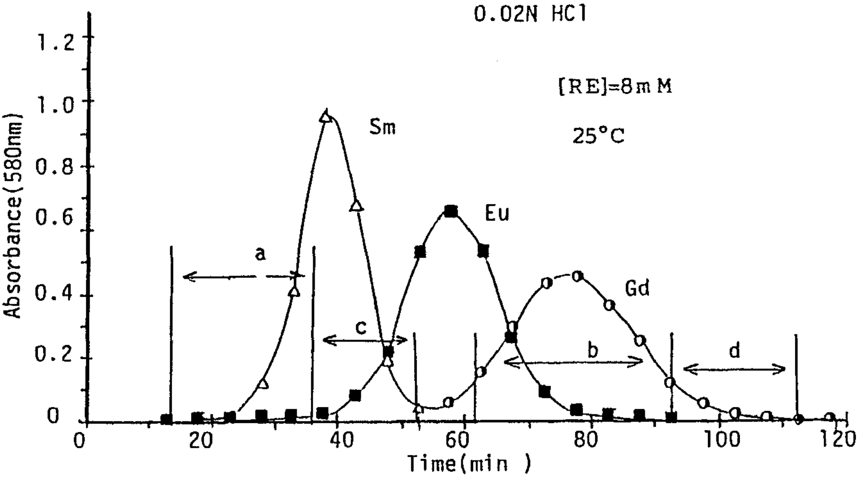

FIGURE 1. Chromatograms of Sm^{3+}, Eu^{3+} and Gd^{3+} at 25°C. Stationary phase: 0.1 M D2EHPA in $CHCl_3$. Mobile phase: 0.02 N aq. HCl.

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toluene stationary solvent and 0.03 N HCl mobile were used.(2)

The separation of Eu^{3+} and Gd^{3+} was partial but one can obtain high purity ions in the fraction ranges of c and d for Eu^{3+} and Gd^{3+}, respectively, from the 1:1 binary mixture.

Figure 2 shows the separation of Gd^{3+}, Tb^{3+}, and Dy^{3+} ions with 0.04 N HCl mobile phase at 25°C. In this case effective separations were observed for both pair of Gd^{3+}/Tb^{3+} and Tb^{3+}/Dy^{3+}. The Figure exemplifies that even when the concentration of Tb^{3+} is twice of Gd^{3+} and Dy^{3+}, mutual separations of these adjacent ions are attained.

As in Figure 3 shows, the use of mobile phase of slightly lower HCl concentration (0.03 N) suggests to attain almost complete mutual separation of the ternary

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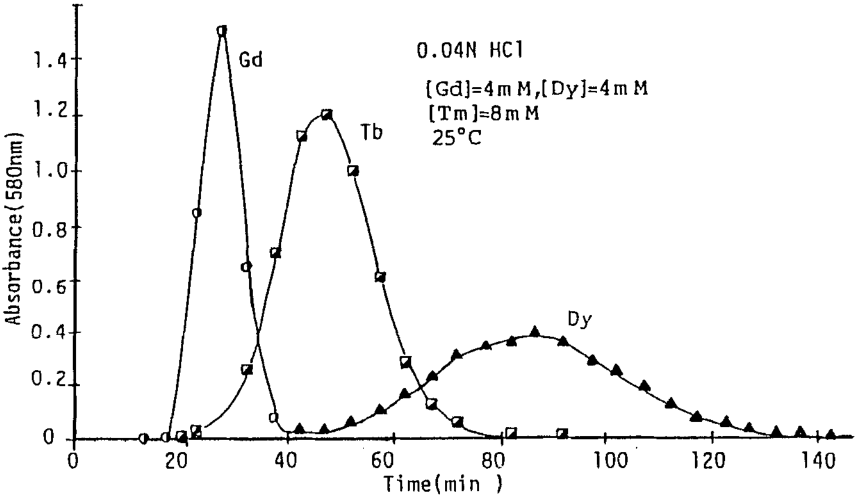

FIGURE 2. Chromatograms of Gd^{3+}, Tb^{3+} and Dy^{3+} at 25°C. Stationary phase: 0.1 M D2EHPA in $CHCl_3$. Mobile phase: 0.04 N aq. HCl.

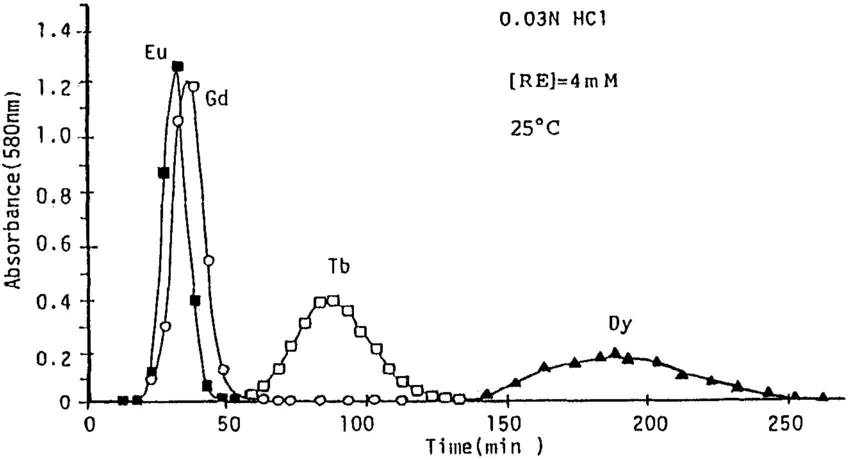

FIGURE 3. Chromatograms of Eu^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+} at 25°C. Stationary phase: 0.1 M D2EHPA in $CHCl_3$. Mobile phase: 0.03 N aq. HCl.

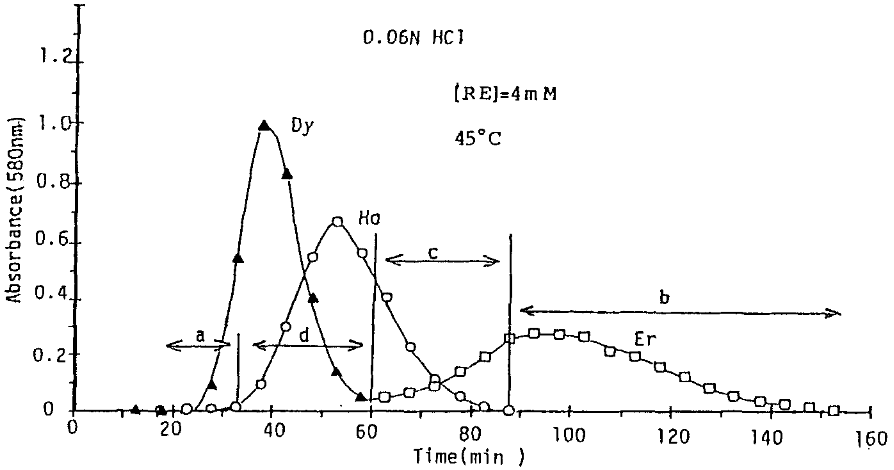

FIGURE 4. Chromatograms of Dy^{3+}, Ho^{3+} and Er^{3+} at 45°C. Stationary phase: 0.1 M D2EHPA in $CHCl_3$. Mobile phase: 0.06 N aq. HCl.

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mixture at the same time. Separation behaviors of the $Gd^{3+}/Tb^{3+}/Dy^{3+}$ set observed with D2EHPA separator are quite similar to those observed by Akiba et al.(5) with EHPA separator. This fact indicates that the basic roles of D2EHPA and EHPA are similar in view of phosphate salt formation with RE^{3+} ions and their trends of stability change for the ions are also identical. By comparing the chromatograms in Figures 2 and 3 one can find how HCl concentration affects the separation of Eu^{3+} and Gd^{3+} in the chloroform solvent system.

Separating behaviors of Dy^{3+} and Ho^{3+} ions in CPC have not been reported. These two adjacent ions were found to be rather difficult to separate under our experimental conditions at 25°C. However, by elevating temperature to 45°C these two peaks were partially sepa-

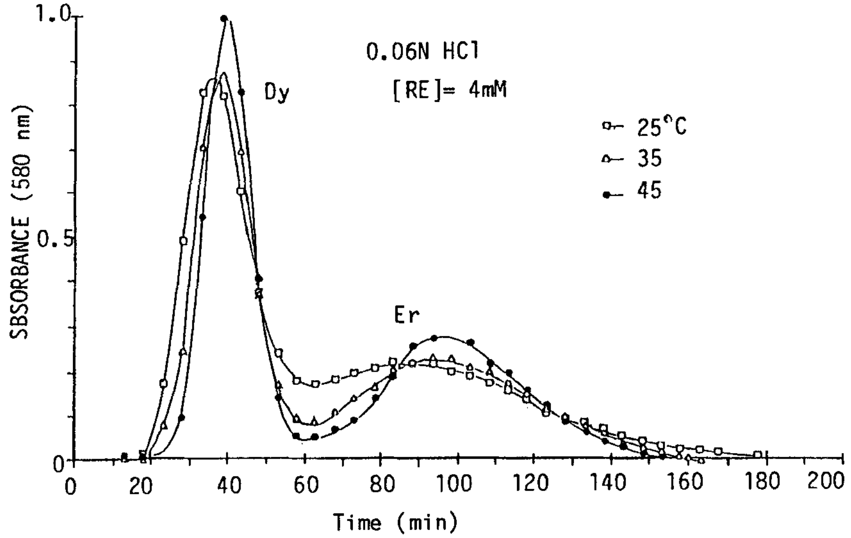

FIGURE 5. Effect of temperature on the behaviors of Dy^{3+} and Er^{3+} binary sample. Stationary phase: 0.1 M D2EHPA in $CHCl_3$. Mobile phase: 0.06 N aq. HCl.

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rated with 0.06 N HCl mobile phase as shown in Figure 4. Under this condition the separation of Ho^{3+} and Er^{3+} was almost satisfactory.

The effect of temperature was examined by using a binary mixture of Dy^{3+}/Er^{3+} pair (Figure 5) at 25°, 35° and 45°. Interestingly, the values of retention time (t_R) were not significantly changed with temperature, but the number of theoretical plate (n) especially for the component having higher t_R was considerably increased with temperature.

Chromatographic peaks of the RE ions having atomic numbers higher than that of Er^{3+} were highly broad at 25°C, and at this temperature no effective separations

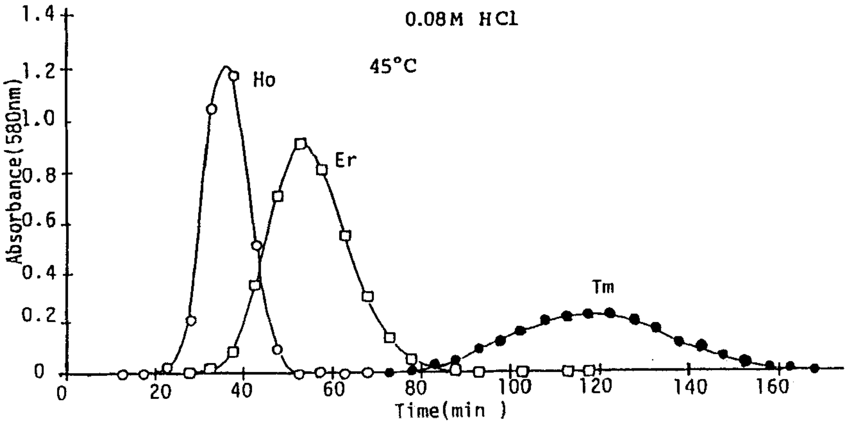

FIGURE 6. Chromatograms of Ho^{3+}, Er^{3+} and Tm^{3+} at 45°C. Stationary phase: 0.1 M D2EHPA in $CHCl_3$. Mobile phase: 0.08 N aq. HCl containing 20% ethyleneglycol.

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were observed as long as aqueous HCl solution was used as mobile phase. However, when 20% ethyleneglycol(5) was added to the 0.08 N aqueous HCl mobile phase at 45° C, considerably good chromatograms (Figure 6) were obtained for the separation of Er^{3+}, Tm^{3+} ions. Almost complete separation of Tm^{3+} and Yb^{3+} ions was attained with 0.10 N HCl as mobile phase containing 20% ethyleneglycol, though the separation of Er^{3+} and Tm^{3+} became unsatisfactory (Figure 7). For comparison, chromatograms of the same components obtained without ethyleneglycol were given in Figure 8.

Separation of Lu^{3+}, the heaviest RE ion, from Yb^{3+} was only partially attained with higher HCl concentration in mobile phase at 25°C (Figure 9). The main reason is the broadness of these peaks as in the case of EHPA system.(5) Attempt to obtain chromatogram upon

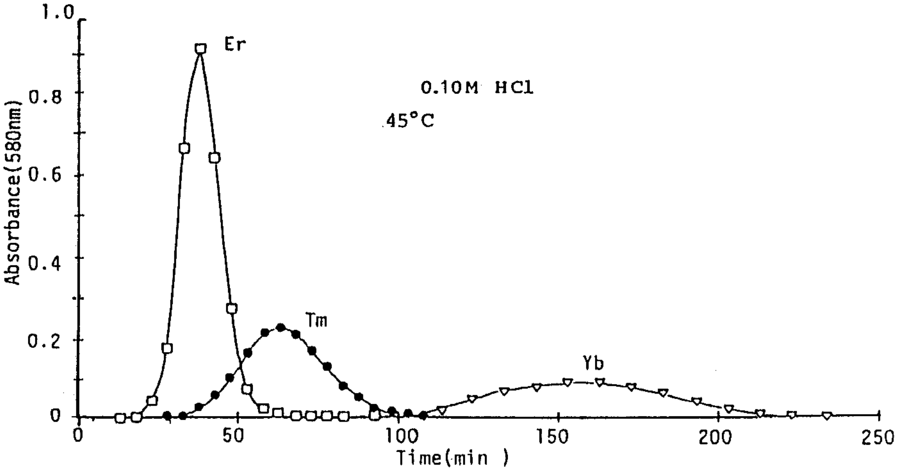

FIGURE 7. Chromatograms of Er^{3+}, Tm^{3+}, and Yb^{3+} at 45°C. Stationary phase: 0.1 M D2EHPA in $CHCl_3$. Mobile phase: 0.10 N aq. HCl containing 20% ethyleneglycol.

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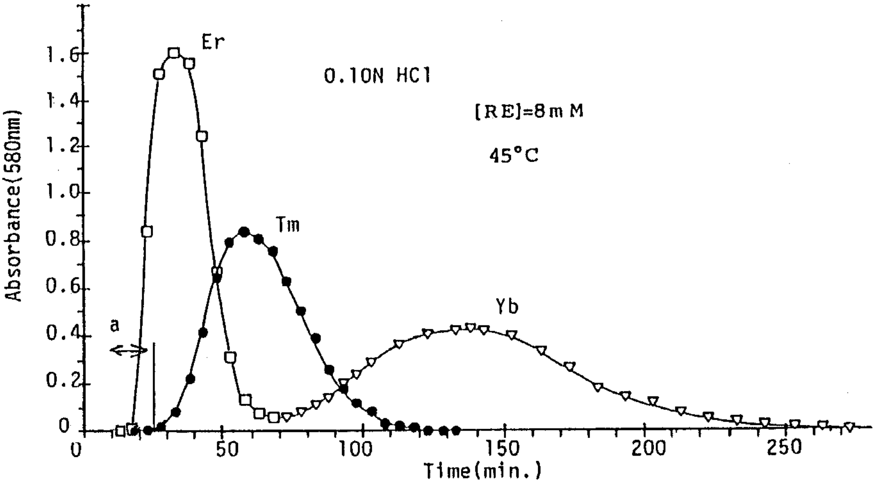

FIGURE 8. Chromatograms of Er^{3+}, Tm^{3+}, and Yb^{3+} at 45°C. Stationary phase: 0.1 M D2EHPA in $CHCl_3$. Mobile phase: 0.10 N aq. HCl alone.

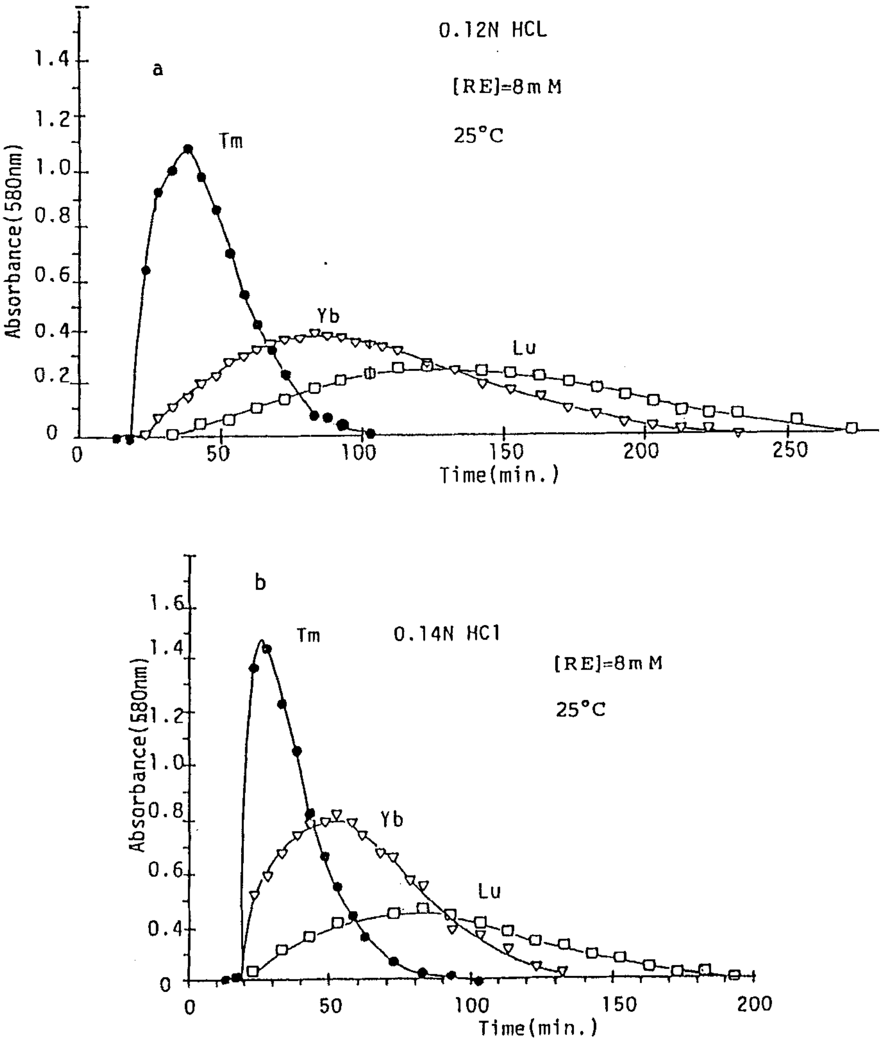

FIGURE 9. Chromatograms of Tm^{3+}, Yb^{3+}, Lu^{3+} at 25°C. Stationary phase: 0.1 M D2EHPA in $CHCl_3$. Mobile phase: (a) 0.12 N and (b) 0.14 N aq. HCl alone.

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TABLE 1. SEPARATION PARAMETERS.

RE_1	RE_2	[HCl] (N)	Temp. (°C)	n RE_1	n RE_2	Rs (RE_1/RE_2)	α
Sm	Eu	0.02	25	15	30	0.72	2.08
Eu	Gd	0.02	25	30	33	0.42	1.43
Eu	Gd	0.03	25	6	8	0.19	1.40
Gd	Tb	0.03	25	8	21	1.08	4.3
Gd	Tb	0.04	25	3	8	0.6	3.61
Tb	Dy	0.03	25	21	42	1.10	2.6
Tb	Dy	0.04	25	8	13	0.61	2.46
Dy	Ho	0.06	45	6	11	0.40	1.94
Ho	Er	0.06	45	11	15	0.65	2.43
Ho[a]	Er[a]	0.08	45	8	13	0.51	2.10
Er	Tm	0.10	25	1	3	0.35	4.06
Er[a]	Tm[a]	0.08	45	13	26	1.0	3.06
Er	Tm	0.10	45	3	7	0.4	2.4
Er[a]	Tm[a]	0.10	45	8	8	0.5	2.37
Tm	Yb	0.10	25	3	7	0.58	3.8
Tm	Yb	0.10	45	7	12	0.65	2.89
Tm[a]	Yb[a]	0.10	45	8	21	0.87	3.11
Tm	Yb	0.12	25	12	4	0.36	3.20
Tm	Yb	0.14	25	<1	1	0.28	5.60
Yb	Lu	0.12	25	4	5	0.22	1.35
Yb	Lu	0.14	25	1	3	0.20	2.02

a) 20% Ethyleneglycol was added to the mobile phase.

addition of ethyleneglycol at 45°C was failed because the presence of ethyleneglycol prevented the color development of Lu^{3+} ion by xylenol orange. However, when the systematic chromatographic behaviors of a series of intermediate or heavy RE^{3+} ions described above are considered, one supposes the separation of Yb^{3+} and Lu^{3+} should be attained by the use of experimental conditions around at 45°C with mobile phase of 0.12-0.14 N HCl containing 20% ethyleneglycol, and by employing a suitable detection method rather than color development with xylenol orange.

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The numerical chromatographic data for separation of heavier RE^{3+} ions obtained in this work are summarized in TABLE 1. Separation parameters are defined as follows:

$$\alpha = (t_{R,2} - t_0)/(t_{R,1} - t_0)$$

$$R_S = 2(t_{R,2} - t_{R,1})/(w_1 + w_2)$$

$$n = 5.54(T_R/w_h)^2$$

where , R_s, and n are separation factor, resolution and number of theoretical plate, respectively. Retention time and width of jth peak are denoted by $t_{R,j}$ and w_j, respectively. Half width of a peak and dead time are shown by w_h and t_0, respectively.

As mentioned above, the R_s values for Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, and Dy^{3+} can be improved by elevating temperature or by addition of ethyleneglycol in the mobile phase. It is notable that the trends and values of separation factor (α) observed for D2EHPA are almost comparable to the corresponding cases for EHPA,(5) though details of the chromatographic conditions differ each other. This fact suggests again that the essential roles of D2EHPA and EHPA are similar with respect to the phosphate salt formation as observed in extraction studies. Hence, both of D2EHPA and EHPA are almost equally useful for the CPC technique when suitable modification in the operation conditions is made.

ACKNOWLEDGMENTS

This work was supported partially by the Ministry of Education, Science, and Culture for Grant-in-aid for Scientific Research (Grant No. 61470026) and by Mitsui Inter-business Research Institute. The authors thank Professor Hiroshi Hashitani of Chemistry Department, Shimane University for kind gift of Tm_2O_3 and Lu_2O_3, and Dr. Yasuo Kubo of the same Department for his helpful discussions. Also thanks are given for Dr. Yoshio Hatanaka of Unocal Japan, Ltd. for kind gift of RE samples.

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