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Extracted Species of Rare Earth Elements Using Bis(1,1,3,3-tetramethylbutyl)phosphinic Acid as an Extractant and Their Effective Mutual Separation by High-Performance Extraction Chromatography

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The possible extracted species of rare earth elements (REE) in bis(1,1,3,3-tetramethylbutyl)phosphinic acid (Hmbp)/cyclohexane–HNO_3 system was proposed by a log–log plot analysis and a saturated extraction method as being $[M(mbp)_3(Hmbp)_3]$ (M = REE). It was also verified by IR, ^{1}H NMR spectra and element analysis of lutetium–Hmbp extracted species. The effective mutual separation of REEs was achieved on the Hmbp modified C-18 column by a pH gradient elution. Moreover, the degree of the mutual separation of europium(III) from gadolinium(III) was remarkably improved by adding glycollic acid in the mobile phase. A fine concentrate of Sm_2O_3, Eu_2O_3, and Gd_2O_3 from a rare earths smeltery was analyzed by the present method with the spectrophotometric detection after postcolumn derivatization with Arsenazo III.

Rare earth elements (REEs) including lanthanides, yttrium, and scandium in the 3 group of the periodic table are known as one of the most difficult groups of elements to be separated due to the so-called lanthanide contraction. The methods for their mutual separation were recently reviewed by K. Robards and S. Clarke,[1] and K. Oguma et al.[2] Solvent extraction and extraction chromatography, in which the different extractive behavior of REEs on a selective extractant was utilized, took a very important role during the long practice in exploring their more effective mutual separation. Among many kinds of extractants used, the acidic phosphorus extractants such as 2-ethylhexylphenylphosphonic acid (HEHϕP),[3,4] bis(2-ethylhexyl)hydrogenphosphate (HDEHP),[5—7] 2-ethylhexyl hydrogen 2-ethylhexylphosphonate [HEH(EHP)],[8,9] bis(2-ethylhexyl)-phosphinic acid,[10] and bis(2,4,4-trimethylpentyl)phosphinic acid[11,12] have frequently been studied and applied. Bis(1,1,3,3-tetramethylbutyl)phosphinic acid (Hmbp) was recently synthesized, and successfully applied to the separation of Al^{III}, Ga^{III}, and In^{III}.[13] Moreover, the extractive behavior of REEs and their thermodynamic behavior during extraction process was also investigated in Hmbp–HNO_3 medium. The results indicated that the optimum acidity range for REEs extraction is much lower than that in the cases of HEHϕP, HDEHP, and HEH(EHP), owing to two alkyl substituents in its molecular structure.[14] Such a property of Hmbp allows it to be used for the mutual separation of REEs in a HPLC system.

In this paper, the extracted species in the Hmbp–HNO_3 medium was proposed by a log–log plot analysis and a saturated extraction method as being $[M(mbp)_3(Hmbp)_3]$ (M = REE); this was subsequently verified by Element Analysis, IR, and ^{1}H NMR. Combining the high selectivity of Hmbp to REEs and the high efficiency of a commercial C-18 column, the mutual quantitative separation of REEs was achieved by HPLC using a Hmbp modified C-18 commercial column, and a pH gradient elution. Furthermore, the degree of the mutual separation of Eu^{III} and Gd^{III} was remarkably improved by adding glycollic acid (Hglyc) in the mobile phase.

Experimental

Apparatus. Separatory funnels were shaken by an Iwaki SHK-101B shaker and the temperature was controlled by an Iwaki CTR-320 thermoregulator. A Shimadzu ICP-1000III sequential ICP atomic emission spectrometer was used for determining the contents of REEs. A Horiba F-16 pH meter was employed for pH measurement and correlation of pH and p[H^+]. A JASCO A-102 infrared spectrometer and a JEOL α-500 nuclear magnetic resonance spectrometer were used for measuring IR and ^{1}H NMR spectra.

A Varian Micro Pak SPC-18 column (5 μm, ϕ 4.6×150 mm) modified with Hmbp was used for the separation of REEs. The gradient elution was performed with two Waters 510 HPLC pumps through the control by the software Chrom 4.0 work station provided by Mr. Quan-sheng Liang. A Waters UK6 injection valve (20 μL) was used for sample injection. The effluent outlet from the column was delivered into a triplet device to mix with the Arsenazo III solution that was delivered by a CAS peristaltic pump. A 30-cm-length 0.1-mm-i.d. plastic tube was used as a delay for the coloring reaction between REEs and Arsenazo III. A Waters 484 tunable absorbance detector and a computer-386 installed with the software Chrom 4.0 were used for the spectral measurement of the color complex[15] and for recording of the chromatogram.

Reagents. Bis(1,1,3,3-tetramethylbutyl)phosphinic acid was obtained from Nippon Chemical Industrial Co., Ltd.; the purity is $\geq 99.99\%$. The standard solutions ($1\ \mathrm{mg\,cm^{-3}}$) of REEs were from Wako Pure Chemical Industry, Ltd. All rare earth oxides were offered by Prof. Chun-lin. Peng of Changchun Institute of Applied Chemistry of Chinese Academy of Sciences, the purity is $\geq 99.9999\%$. Arsenazo III was from Beijing Chemical Factory, and was purified before use.[16] All other chemicals used were of analytical grade, and deionized distilled water was used throughout.

Procedure. Solvent Extraction Experiment. At the temperature (298 K), an appropriate amount of REEs(III) as well as the buffer solution of chloroacetic acid–sodium chloroacetate for light REEs or dichloroacetic acid–sodium dichloroacetate for heavy REEs were added into a separatory funnel; the volume of the aqueous phase was adjusted to 20 cm^3 with the deionized distilled water in which sodium nitrate was added to maintain the ionic strength constant ($\mu = 0.1$) in the aqueous phase. The mixture was shaken for 10 min after the addition of 20 cm^3 of 5.0×10^{-2} mol dm^3 (Hmbp)$_2$/cyclohexane in spite of the extraction equilibrium being reached within 3 min. The REEs contents in the aqueous phase were determined by ICP-AES. The distribution ratio (*D*) of REEs could be obtained using

$$D = (w - w_{\mathrm{aq}})\cdot V_{\mathrm{aq}}/w_{\mathrm{aq}}\cdot V_{\mathrm{org}},$$

where w is the total amount of REEs originally added to the aqueous phase, w_{aq} is the amount of REEs left unextracted in the aqueous phase after extraction equilibrium, and V_{aq} and V_{org} denote the volume of the aqueous and organic phases, respectively.

Preparation of Lutetium–Hmbp Complex. An appropriate amount of lutetium nitrate was added into the separatory funnel which contained 1.5×10^{-3} mol Hmbp/cyclohexane solution and an equal volume of the aqueous phase at pH 3.0. In the aqueous phase there were $CH_2ClCOOH$–$CH_2ClCOONa$ buffer and the calculated amount of $NaNO_3$ for controlling pH and the ionic strength. The mixture was then shaken for achieving the extraction equilibrium. The content of lutetium in the aqueous phase was determined by EDTA titration using Arsenazo III as an indicator at pH 5, where pH was controlled by hexamethylenetetramine [$(CH_2)_6N_4$]. Such a procedure was performed many times until lutetium in the organic phase was saturated and the amount of lutetium left in the aqueous phase equaled that added. The saturated organic phase was then subjected to reduced-pressure distillation. The resulted colorless transparent viscous liquid (Lu–Hmbp complex) was dried over anhydrous diphosphorus pentaoxide (P_2O_5) in a desiccator.

^{1}H NMR ($CDCl_3$) $\delta = 1.01$ (s, 3×36 H), 1.39 (d, 3×24 H, $J = 15.0$ Hz), 1.75 (d, 3×8 H, $J = 10.0$ Hz), 5.54 (s, 3×1 H).

Separation Column Preparation. Hmbp/cyclohexane solution 50 mL of 1×10^{-5} mol dm^{-3} was pumped into a Varian Micro Pak SPC-18 column (5 μm, ϕ 4.6×150 mm) at the flow rate of 0.1 mL min^{-1} for modification. Before use, the modified column should be pre-equilibrated by a suitable mobile phase.

Preparation of the Synthetic REEs Sample. Each rare-earth oxide was ignited at 850 °C in an electric stove. The calculated amount of each rare-earth oxide was weighed, dissolved by 1 : 1 HNO_3, and evaporated to near dryness. Finally, the residue was dissolved and diluted by H_2O and a little bit of HNO_3 to get 1.00 mg ml^{-1} REE stock solution, pH = ca. 1. Each REE stock solution of 2.50 ml was added into a 100 ml beaker, and then it was evaporated slowly to near dryness at low temperature. The residue was dissolved and diluted into 10 ml (with a 10 ml volumetric flask) by H_2O to get the sample containing 0.25 mg ml^{-1} of each REE.

Results and Discussion

REEs Extraction Behavior and Possible Structure of REE–Hmbp Complex. REEs extraction behavior was investigated in Hmbp–HNO_3 system by the batch method described in our previous study.[14] The results showed that the distribution ratios (*D*) of REEs increased along with the increase both in p[H$^+$] value in the aqueous phase and the concentration of Hmbp in the organic phase. Moreover, it was also observed that the distribution ratios (*D*) of REEs increased along with the increase in their atomic number at the same extraction conditions. Since two types of the extracted species of REEs have been proposed in the system [M(mbp)$_3$] and [M(mbp)$_3$(Hmbp)$_3$] (M = REE), lutetium(III) was chosen as a representative of REEs for identifying the logical extracted species in this study. The solvent extraction experiment indicated that 44.31 mg (2.53×10^{-4} mol) lutetium(III) was needed to saturate 1.5×10^{-3} mol Hmbp in the organic phase, a 1 : 6 [Lu(mbp)$_3$(Hmbp)$_3$] extracted species was therefore thought to be formed in this case. Combining the results from the log–log plot analysis that both plots of $\log D\alpha$ vs. p[H$^+$] and $\log D\alpha$ vs. log [(Hmbp)$_2$] showed slopes of 3,[14] we found strong support for the conclusion that Hmbp exists as a dimer in the extracted species. Here, α is the side reaction coefficient, and it can be calculated as $\alpha = 1+\beta_1[\mathrm{L}]+\beta_2[\mathrm{L}]^2+\cdots$, where L indicates CH_2ClCOO^- or $CHCl_2COO^-$, and β_1 and β_2 are the successive stability constants of the complexes formed by REE and L, respectively. Furthermore, the elemental analysis data, IR and ^{1}H NMR spectra of Lu–Hmbp extracted species prepared were obtained to verify the possible structure of REE–Hmbp extracted species.

The elemental analytical data for Lu–Hmbp extracted species are listed in Table 1. The found values of %H and %C are in agreement with those calculated for [M(mbp)$_3$(Hmbp)$_3$] rather than for [M(mbp)$_3$], and these results also suggest that no water molecule exists in the extracted species.

The IR data for Hmbp and Lu–Hmbp extracted species showed (Table 2) that the stretching vibration of PO–H at 2600 cm^{-1} in Hmbp spectrum can also be observed at 2600 cm^{-1} in the extracted species spectrum, but the relative vibra-

Table 1. Results of Element Analysis for Lu–Hmbp[a)] Complex

	Calculated value		Found value
	[Lu(mbp)$_3$]	[Lu(mbp)$_3$(Hmbp)$_3$]	
%H	9.96	10.93	10.83
%C	56.25	60.82	59.61

a) Hmbp, $[(CH_3)_3CCH_2C(CH_3)_2]_2POOH$.

Table 2. IR Data of Hmbp and $[Lu(mbp)_3(Hmbp)_3]$

	Wavenumber/cm^{-1}	
	Hmbp	$[Lu(mbp)_3(Hmbp)_3]$
ν_{C-H}	2850	2850
ν_{PO-H}	2600	2600
$\delta_{C-H(methylene)}$	1470	1470
$\delta^{s}_{C-H(tert.butyl)}$	1358	1358
	1375	1375
$\nu_{P=O}$	1120	1120
		1080
ν_{P-OH}	920	920
		880

tion strength of PO–H is lower compared with that of pure Hmbp. The stretching vibration of P=O at 1120 cm^{-1} of Hmbp splits into two vibration at 1120 and 1080 cm^{-1} in the spectrum of the extracted species. Such a phenomenon indicates that there are two kinds of P=O groups in the extracted species: the oxygen in one P=O coordinates to lutetium, the P=O vibration peak is shifted to lower frequency at 1080 cm^{-1}; and the oxygen in the other P=O just associated with hydrogen in PO–H of another Hmbp molecule through the hydrogen bond; this P=O vibration is the same as that of pure Hmbp at 1120 cm^{-1}. A similar phenomenon was observed for the stretching vibration of P–OH in the extracted species; this vibration peak (920 cm^{-1}) also splits into 920 cm^{-1} which is assigned to –P–OH··· O=P–, and 880 cm^{-1}, assigned to –P–O–Lu. The above IR studies give the evidence that Hmbp as a dimer formed through the intermolecular (Hmbp) hydrogen bond participates in forming the extracted species. In the ^{1}H NMR spectrum of the extracted species, the proton of –P–OH··· O=P– also can be observed at 5.54 ppm as occurring in the ^{1}H NMR spectrum of the Hmbp molecule. This is a very important point to suggest that lutetium and Hmbp forms the extracted species of $[M(mbp)_3(Hmbp)_3]$. Thus, a reasonable extraction mechanism for REEs in Hmbp–HNO_3 system can be proposed as

$$M^{3+} + 3(Hmbp)_{2org} \rightleftharpoons [M(mbp)_3(Hmbp)_3]_{org} + 3H^{+}. \quad (1)$$

Separation Factor of Eu^{III} and Gd^{III} in Hmbp–Hglyc Acid–HNO_3 System. Among REEs, the 4f orbital of gadolinium(III) is half-filled—4f,[7] such a stable configuration leads to the effect from the coordinate field being weaker on gadolinium than that on the adjacent lanthanides, and the stability of gadolinium(III) complexes being somewhat lower than those of europium(III) in some cases such as $Eu(glyc)_3$ (β_3 6.52) and $Gd(glyc)_3$ (β_3 6.00).[17] Thus, the mutual separation of europium(III) from gadolinium(III) is more difficult than other adjacent pairs of lanthanides. Our previous study[14] showed that the separation factor ($S.F.^{Gd}_{Eu}$) of Gd^{III} and Eu^{III} in Hmbp–HNO_3 system was only 1.32 and was smaller than that of other adjacent pairs of REEs. Here Hglyc was added in the Hmbp–HNO_3 system, the reaction between Gd^{III} (or Eu^{III}) and Hglyc was considered as a side-reaction. $S.F.^{Gd}_{Eu}$ can be calculated by

$$S.F.^{Gd}_{Eu} = \frac{{}^{Gd}K'_{ex}(1+{}^{Eu}\beta_{1,glyc^-}[glyc^-]+{}^{Eu}\beta_{2,glyc^-}[glyc^-]^2+{}^{Eu}\beta_{3,glyc^-}[glyc^-]^3+\cdots)}{{}^{Eu}K'_{ex}(1+{}^{Gd}\beta_{1,glyc^-}[glyc^-]+{}^{Gd}\beta_{2,glyc^-}[glyc^-]^2+{}^{Gd}\beta_{3,glyc^-}[glyc^-]^3+\cdots)}, \quad (2)$$

and

$$Hglyc \rightleftharpoons H^{+} + glyc^{-}, \qquad pK_a \quad 3.63,$$

$$[glyc^{-}] = C_{Hglyc}\cdot K_a/([H^{+}] + K_a),$$

$$[H^{+}] = 10^{-(pH+\log \gamma_{H^+})},$$

where ${}^{Eu}K'_{ex}$ ($10^{-2.74}$) and ${}^{Gd}K'_{ex}$ ($10^{-2.62}$) are the overall equilibrium constant of Eu^{III} and Gd^{III} in Hmbp–HNO_3 system; the γ_{H^+} is the activity coefficient 0.86; and the successive stability constants of Eu^{III}–glyc and Gd^{III}–glyc complexes are ${}^{Eu}\beta_1$ $10^{2.93}$, ${}^{Eu}\beta_2$ $10^{5.07}$, ${}^{Eu}\beta_3$ $10^{6.52}$ and ${}^{Gd}\beta_1$ $10^{2.79}$, ${}^{Gd}\beta_2$ $10^{4.85}$, ${}^{Gd}\beta_3$ $10^{6.00}$, respectively. When $C_{Hglyc} = 0.50$ mol dm^{-3} and pH = 1.75, the $S.F.^{Gd}_{Eu}$ is 1.93. It is remarkably increased by adding Hglyc, and was close to that of Eu^{III} and Sm^{III} ($S.F.^{Eu}_{Sm} = 2.00$) in the Hmbp–HNO_3 system.[14] It should be noted, however, that the addition of Hglyc is not effective for the improvement of the mutual separation of REEs in this system except in the case of Eu and Gd, as the stability constant (β_3) of REE–glyc complex generally increases along with the atomic number of REE. This tendency results in somewhat smaller separation factors of other REEs.

Extraction Chromatographic Separation of REEs on a Hmbp Modified C-18 Column. The separation of REEs was performed on a Hmbp modified Varian Micro Pak SPC-18 column (5 μm, ϕ 4.6×150 mm). Hmbp was absorbed on the column through the hydrophobic interaction between its big alkyl groups [bis(1,1,3,3-tetramethylbutyl)] and the octadecyl of the stationary phase. At the same time the relative hydrophilic part [POOH] of Hmbp was mounted on the surface of the stationary phase. Such a column gains merits from the selectivity of Hmbp and from the high efficiency of the original column. On such a column prepared the extraction and back-extraction are performed many times[18] as described in Eq. 1. After being modified by Hmbp, the column was first equilibrated by a HNO_3 solution (pH 5). The synthetic REEs sample (20 μL) was injected, and then the pH gradient (pH 2.20—0.70) elution was carried out. A typical REEs separation chromatogram is shown in Fig. 1. Clearly, the mutual separation degree of REEs was remarkably improved by the present HPLC system, and the separation time was largely reduced compared with our previous results.[14,19] In this system, the quantitative mutual separation of REEs was achieved except that of europium(III) and gadolinium(III); La^{III} was much easier to be separated from other REEs, and the heavy REEs were easier to be separated from each other than the light ones. For the quantitative separation of Eu^{III} from Gd^{III}, therefore, 0.50 mol dm^{-3} Hglyc acid was added to the mobile phase.

Such a method was also applied to analyzing the sample of Nd_2O_3 (1%), Sm_2O_3 (41.5%), Eu_2O_3 (14%), Gd_2O_3 (41.5%), and Tb_4O_7 (2%) which was from a rare earths

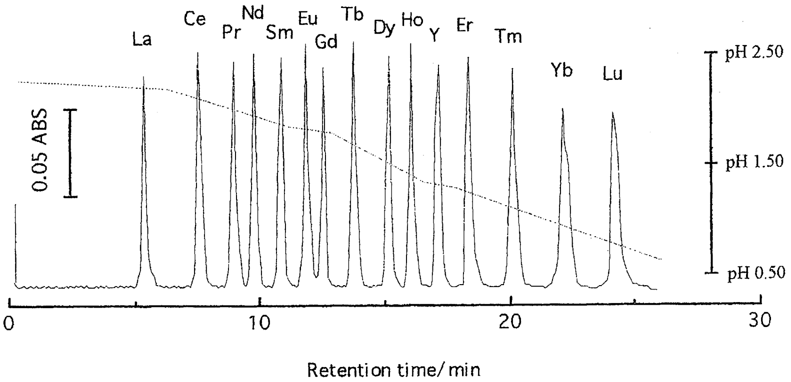

Fig. 1. Mutual separation of rare earth elements by Hmbp-extraction chromatography. Column, Varian Micro Pak SPC-18-5 (ϕ 4.6×150 mm) modified by Hmbp; mobile phase, HNO_3 [6.3×10^{-3} mol dm^{-3} (pH 2.20) to 0.21 mol dm^{-3} (pH 0.75) over 26 min by the gradient elution program]; flow rate, 0.5 mL min^{-1}; Column temperature, 298 K; sample, 20 μL containing 5 μg each of rare earth elements; detection after the post-column derivatization with Arsenazo III.

smeltery. The sample (0.2000 g) was first dissolved by 7 mol dm^{-3} nitric acid, and then was evaporated to almost dryness. At last the residue was diluted to 100 mL by H_2O. The separation chromatogram is shown in Fig. 2. The analytical result was in good agreement with the standard value for eachelement in the sample; the RSD of six duplicate runs for the above five rare earth elements is within ±5%.

In conclusion, the REEs extracted species as $[M(mbp)_3(Hmbp)_3]$ were formed in Hmbp–HNO_3 system. It is possible to separate rare earth elements quantitatively from each other by this high-performance extraction chromatographic system due to the selectivity of Hmbp to rare earth elements in such a low acidity. By adding Hglyc acid in the mobile phase, the mutual separation degree of europium(III) from gadolinium(III) could be remarkably enhanced. This method is also expected to be useful for the mutual separation of americium(III) and curium(III) in the future because of their chemical behavior is similar to that of europium(III) and gadolinium.

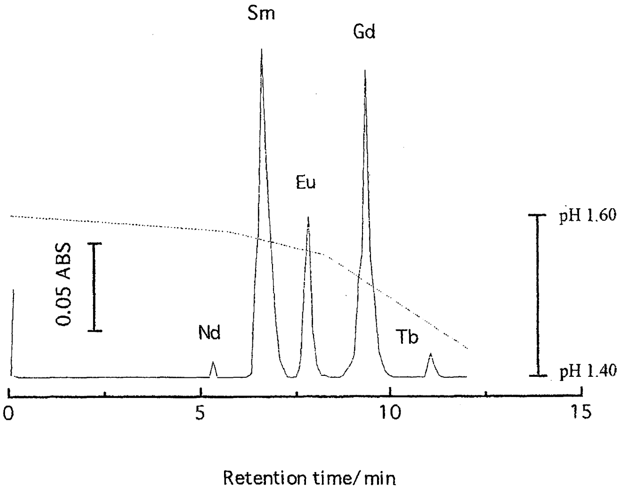

Fig. 2. Separation chromatography of Nd^{III}, Eu^{III}, Gd^{III}, and Tb^{III} in Hmbp–Hglyc–HNO_3 system. Mobile phase, 0.5 mol dm^{-3} Hglyc–HNO_3, pH gradient elution from pH 1.70 to 1.50; sample: the mixture of Nd_2O_3 (1%), Sm_2O_3 (41.5%), Eu_2O_3 (14%), Gd_2O_3 (41.5%), and Tb_4O_7 (2%). Other conditions were the same as those described in Fig. 1.

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References

1 K. Robards and S. Clarke, *Analyst*, **113**, 1757 (1988).

2 K. Oguma, T. Shimizu, and R. Kuroda, *Bunseki Kagaku*, **44**, 1 (1995).

3 D. F. Peppard, G. W. Mason, and I. Hucher, *J. Inorg. Nucl. Chem.*, **18**, 245 (1961).

4 I. Fidelis and S. Siekierski, *J. Chromatogr.*, **17**, 542 (1965).

5 D. F. Peppard, G. W. Mason, J. L. Maier, and W. J. Driscoil, *J. Inorg. Nucl. Chem.*, **4**, 334 (1957).

6 T. B. Pierce, P. E. Peck, and R. S. Hobbs, *J. Chromatogr.*, **12**, 81 (1963).

7 R. J. Sochacka and S. Siekierski, *J. Chromatogr.*, **16**, 376 (1964).

8 C. L. Peng, *Fenxi Huaxue*, **20**, 1242 (1992).

9 S. Nakamura, H. Hashimoto, K. Akiba, and Y. Saito, *Anal. Sci.*, **13**, 525 (1996).

10 S. X. Peng and C. L. Peng, *J. Rare Earths*, **11**, 64 (1993).

11 Y. Komatsu and H. Freiser, *Anal. Chim. Acta*, **227**, 397 (1989).

12 S. Muralidharan, G. Ma, and H. Freiser, in "Separation of f Elements," ed by K. L. Nash and G. R. Choppin, Plenum Press, New York (1995), p. 177.

13 Q. Wang, K. Tsunoda, H. Akaiwa, M. Sugiya, and T. Watanabe, *Anal. Sci.*, **12**, 931 (1996).

14 Q. Wang, K. Tsunoda, and H. Akaiwa, *Anal. Sci.*, **13** (Supplement), 153 (1997).

15 Q. Wang, F. Gao, L. Yang, T. Shi, and Q. Xie, *Microchem. J.*, **52**, 236 (1995).

16 Q. Luo, et al., in "Analytical Chemistry of Rare Earth Elements," ed by Wuhan University, Science Press, Beijing (1981), p. 336.

17 J. Cheng, in "Analytical Chemistry of Rare Earth Elements," ed by Wuhan University, Science Press, Beijing (1981), p. 63.

18 Q. Wang, K. Tsunoda, and H. Akaiwa, *Anal. Sci.*, **11**, 909 (1995).

19 Q. Wang, K. Tsunoda, H. Akaiwa, M. Sugiya, and T. Watanabe, "Extraction Chromatographic Behavior of Heavy Rare Earth Elements Using Bis(1, 1, 3, 3-tetramethylbutyl)phosphinic Acid as a Stationary Phase," "Proceeding of the 46th Annual Conference of Japan Society for Analytical Chemistry," Tokyo, Oct. 1997.