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Study of isotachophoretic separation behaviour of metal cations by means of particle-induced X-ray emission

III. Analysis of a crude rare earth chloride from monazite

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ABSTRACT

A crude rare earth chloride produced from monazite was analysed by coupled isotachophoresis–particle-induced X-ray emission (ITP–PIXE). The sample was separated and fractionated by the use of a micro-preparative isotachophoretic analyser and the dropwise fractions containing nanomole amounts of rare earth elements were analysed off-line by PIXE. By means of ITP–PIXE, the minor elements (Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) co-existing with the other major lanthanoids (La, Ce, Pr and Nd) were determined accurately, because the "matrix effect" in X-ray analysis was reduced by isotachophoretic removal of the major elements. The maximum abundance found was for Ce at 47.4% with respect to total rare earths and the minimum abundance was 0.001% for Lu. The separation efficiency of the crude rare earth chloride was *ca.* 500 nmol/C. The method for the fractionation of minor elements and PIXE analysis is discussed in detail. The analytical results obtained by ITP–PIXE were confirmed by means of inductively coupled plasma atomic emission spectrometry.

INTRODUCTION

The accurate determination of minor components co-existing with major components is often difficult when the method used depends on a preliminary separation. In isotachophoresis (ITP), when the amount of electricity is not sufficient for separation, mixed zones remain, causing the errors in determination. We have pointed out that the errors would be serious for the determination of a minor component co-existing with a major component, as the mixed zones formed in such a sample system tend to be overlooked because of the similarity between the signal of the mixed zone and that of the major component zone [1]. Therefore, the study of separa-

tion efficiency is important to avoid overloading of the sample.

The separation efficiency of a pair of separands depends not only on the mobility difference between them [2,3] but also on the amount of co-existing ionic components [1,4]. Further, the mobility difference between the separands and the co-existing components also affects the separation efficiency. Therefore, the necessary amount of electricity for complete separation varies in relation to these factors even if the sample amount of interest is kept constant. Such an effect was called the composition effect on the separation efficiency [4].

A crude rare earth chloride, which is a primary product of rare earth elements after extracting

thorium from monazite [5], is a typical sample containing rare earth elements with various abundances. According to the analytical results evaluated by the manufacturer using atomic absorption spectrometry, etc., the major elements were La, Ce, Pr and Nd (total abundance *ca.* 95% of the total rare earth elements) and the minor elements were Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Y (total abundance *ca* 5%). The ratio of Ce with the maximum abundance to Yb with the minimum abundance was over 10^4. In order to determine the minor elements, it is difficult to obtain a highly separation efficiency of the crude rare earth chloride when ITP analysis is carried out in the usual manner. In our previous paper [6], we reported a study of the separation efficiency of a binary mixture of lanthanoids and clarified that the simulated separation efficiency agreed well with that observed and that the necessary amount of electricity for the separation of minor components can be estimated from the total amount of the whole sample using coupled isotachophoresis–particle-induced X-ray emission (ITP–PIXE), where isotachophoretically separated zones were fractionated and analysed off-line by means of PIXE.

In this work, first the separation efficiency of a model crude rare earth chloride was measured, then the minor rare elements contained in a real crude rare earth chloride sample were determined by means of ITP–PIXE. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was also applied in order to confirm the ITP–PIXE results.

EXPERIMENTAL

Chemicals

A crude rare earth chloride from monazite was obtained from Santoku Kinzoku (Tokyo, Japan). Lanthanoid chlorides ($LnCl_3 \cdot 6H_2O$), α-hydroxyisobutyric acid (HIB) and carnitine hydrochloride were obtained from Katayama Kagaku (Osaka, Japan). Two cationic dyes, toluidine blue (TB) and astrazon pink (AP), and hydroxypropylcellulose (HPC) were obtained from Tokyo Kasei (Tokyo, Japan). The lanthanoid chlorides and HPC were of Extra Pure grade and HIB and carnitine hydrochloride were of Guaranteed Reagent grade. The viscosity of a 2% HPC aqueous solution was 1000–4000 cP at 20°C according to the specification.

Samples

Crude rare earth solutions of 8.808, 0.8808 and 0.5872 g/l were prepared by dissolving the sample in high-purity water processed with an ion exchanger (Puric-R; Japan Organo, Tokyo, Japan). The specific resistance of the water used was $18.3 \cdot 10^6$ ohm cm.

A model mixture of the crude rare earth chloride from monazite was prepared by using the chlorides of rare earths according to the analytical results supplied by Santoku Kinzoku. Stock sample solutions were prepared by dissolution in high-purity water. The concentrations of the stock solutions of La, Ce, Nd, Y and the other rare earth elements were 27.90, 53.59, 50.00, 10.89 and 5.00 mM, respectively. Although the presence of Lu was not specified by Santoku Kinzoku, the same amount of Lu as the trace element Yb was added. The total concentration of the model mixture was 25 mM. Small amounts of TB and AP were added to the above samples to monitor the migration process and to determine the timing of fractionation.

Rare earth standard solutions (1000 ppm) for atomic absorption spectrometry (Tokyo Kasei) were used as analytical standards for PIXE and ICP-AES analysis.

Electrolyte system

The electrolyte system used is summarized in Table I. The leading electrolyte was 20 mM ammonia, which contained 10 mM HIB as the complex-forming reagent for the efficient separation of rare earth elements [7,8]. The utility of complex-forming reagents in ITP separations of inorganic ions including lanthanoids has been thoroughly reviewed by Bocek and Foret [9]. The pH was adjusted to 4.8 by adding acetic acid. pH measurements were carried using a Horiba (Tokyo, Japan) Model F7ss expanded pH meter. The terminating electrolyte was 10 mM carnitine hydrochloride. In order to make a clear interface between the leading and terminating electrolytes (no valves were used at the electrolyte interface), sucrose (20 wt.%) was added to the terminating electrolyte at the sample preseparation stage. The addition of sucrose was also effective in suppressing the convection of the terminating electrolyte. HPC (1.75%) was added to the leading electrolyte used for sample preseparation stage in order to suppress heat convection and 0.2%

TABLE I

ELECTROLYTE SYSTEM USED IN ISOTACHOPHORETIC SEPARATION

HIB = α-hydroxyisobutyric acid; CARH = carnitine hydrochloride; HPC = hydroxypropylcellulose.

Component	Stage I[a]	Stage II[b]
Leading electrolyte	20 mM NH$_3$	20 mM NH$_3$
Complex-forming reagent	10 mM HIB	10 mM HIB
pH buffer	Acetic acid	Acetic acid
pH of leading electrolyte	4.8	4.8
Terminating electrolyte	10 mM CARH	10 mM CARH
Additive to leading electrolyte	1.75% HPC	0.2% HPC
Additive to terminating electrolyte	20% sucrose	0.2% HPC

[a] Preseparation stage.
[b] Separation stage as shown in Fig. 1.

HPC in the separation and fractionation stages in order to suppress electroendosmosis.

Preparative isotachophoretic analyser

The preparative analyser and the method of fractionation used were reported in a previous paper [10]. A simplified diagram of the apparatus is shown in Fig. 1. The pre-separation tube was made of acrylic resin (I.D. 5 mm) and it was tapered off to 3 mm I.D. The preseparation tube was connected to the separation tube at the branch B1. The principle of fractionation was of the Arlinger type [11], except for the dropwise fractionation (*ca.* 5 μl). It was carried by applying a counter-flow of the leading electrolyte using a syringe pump. The separated zones were detected by potential gradient detection (PGD) and the fractions were analysed off-line by PIXE.

The load of leading electrolyte in the preseparation tube was made either 1.7 or 3.4 ml by extending the PTFE tube (55 cm × 2 mm I.D.) connecting the preseparation tube with the separation stage. This enabled *ca.* 10°C to be applied at the preseparation stage. In order to obtain the amount of electricity in the electrophoretic process, the migration current was integrated using a microcomputer with an analog–digital conversion interface (sampling rate 2.070 s per datum).

PIXE analysis

For the PIXE spectra measurements [12], a Van de Graaff accelerator was used (Model AN-2500,

Nisshin High Voltage, Tokyo, Japan). The energy of the H$^+$ beam was 2 MeV and the beam current was in the range 35–50 nA. A typical single run for an ITP fraction took 190–260 s. The detector used was a highly pure Ge detector (Ortec Model GLP-10180) and the multi-channel analyser used was a Laboratory Equipment (Tokyo, Japan) Model AMS-1000.
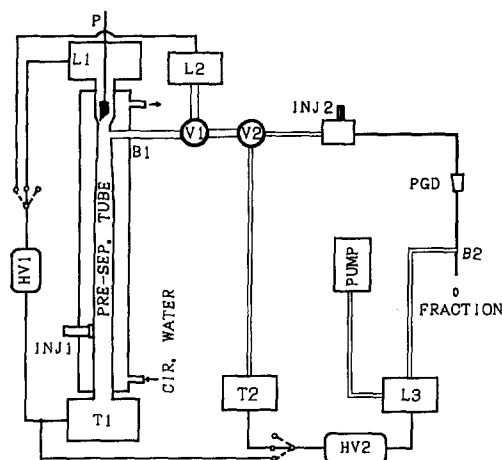
The Nuclepore filter used as the target backing

Fig. 1. Schematic diagram of the preparative isotachophoretic analyser. L1, L2, L3 = leading electrolyte compartment; T1, T2 = terminating electrolyte compartment; V1, V2 = valves to change the current path; INJ1, INJ2 = injection ports; P = PTFE plug to cut off L1 compartment; PRE-SEP. TUBE = preseparation tube; B1 = branch of preseparation tube; B2 = sample fractionating branch with a narrow-bore nozzle; PGD = potential gradient detector; HV1, HV2 = high voltage power supplies.

was of thickness 5 μm and pore size 0.1 μm and was mounted on an aluminium frame. The impurities were mainly Cr and Fe, and the abundance of Fe was one tenth of that of Cr. The fraction was dropped on the Nuclepore filter directly from the nozzle of the preparative isotachophoretic analyser (B2 in Fig. 1). The diameter of the sample spot was *ca.* 3 mm. After drying in a desiccator, it was used as the PIXE target. The amount of the rare earth element was determined by comparing its X-ray counts with those of the standard targets.

Our data reduction software PIXS was used with an option of spectrum deconvolution utilizing an X-ray relative intensity database [13]. It was useful for the X-ray spectral analysis from multi-elements containing in a target. Calculation was carried on an NEC (Tokyo, Japan) PC-9801RA microcomputer (CPU = 80 386, co-processor = 80 387, clock = 20 MHz).

The PIXE spectrum of the crude rare-earth chloride from monazite was measured and analysed in a similar manner. A 5-μl sample solution (0.5872 g/l, 2.936 μg) was spotted on the Nuclepore filter.

ICP-AES analysis

A Nippon Jarrel-Ash (Tokyo, Japan) Model ICAP-575 Mark II ICP-AE spectrometer equipped with a Fassel-type high salt concentration torch was operated with an input power of 1.4 kW at 27.12 MHz. The nebulizer argon flow-rate was 0.47 l/min at 1.5 kg/cm^2 and the sample aspiration rate was 2.4 ml/min. The emission from the plasma was observed at 15 mm above the load coil and detected with a Model R-500-01 (above 300-nm range) and a Model R-427-08 (below 300 nm) photomultiplier manufactured by Hamamatsu Photonics (Hamamatsu, Japan). An NEC PC-9801 UX21 microcomputer was used for data acquisition and processing. Quantitative analysis was carried out by comparing the strength of one or two emission lines of an element with that of a standard sample. The wavelengths of the lines used for the determination of each rare-earth element are shown in Table II.

RESULTS AND DISCUSSION

Separation efficiency of the model mixture of the crude rare earth chloride

In order to evaluate the separation efficiency of

TABLE II

WAVELENGTHS USED FOR THE DETERMINATION OF RARE EARTH ELEMENTS BY ICP-AES

Z	Element	Wavelength (nm)
57	La	(i) 379.478 × 1
		(ii) 408.672 × 1
58	Ce	(i) 399.924 × 1
		(ii) 413.38 × 1
59	Pr	(i) 422.535 × 1
60	Nd	(i) 406.109 × 1
		(ii) 430.358 × 1
62	Sm	443.388 × 1
63	Eu	272.778 × 3
64	Gd	(i) 310.05 × 2
		(ii) 336.223 × 2
65	Tb	350.917 × 2
66	Dy	353.602 × 2
67	Ho	345.6 × 1
68	Er	337.271 × 2
69	Tm	346.22 × 2
70	Yb	211.667 × 3
71	L	(i) 261.542 × 2
		(ii) 219.554 × 3
39	Y	(i) 324.228 × 1
		(ii) 377.433 × 1

the crude rare earth chloride, first a model mixture of the crude rare earth chloride was separated and fractionated (sample volume = 200 μl, total concentration = 25 mM, 5000 nmol, *ca.* 700 μg). The sample constituents are shown in Table III. The zones of the major components (La, Ce, Pr and Nd) were removed at the preseparation stage. The integrated amount of electricity at the preseparation stage was 5.2 C (30 min). A further 0.92 C was added during 90 min at the separation stage.

Table III also summarizes the zone lengths of the minor components detected by the use of PGD and the recovery evaluated by means of PIXE. A mixed zone of Y and Dy was not completely resolved, although the effective mobility of Y was slightly larger than that of Dy. The time-based zone lengths of Sm, Eu, Gd and Tb were 186, 15, 141 and 13.5 s (coulomb-based zone lengths: 28, 2.25, 21.45 and 2.10 mC, respectively). The individual zone lengths of Ho, Er, Tm, Yb and Lu could not be observed owing to their low abundances (less than 0.9 nmol). Eighteen fractions were obtained in 525 s (29.2 s per

TABLE III

RECOVERY OF MINOR RARE EARTH ELEMENTS IN THE MODEL MIXTURE OF CRUDE RARE EARTH CHLORIDE BY ITP–PIXE

For experimental conditions, see text.

Rare earth	Injected amount		5.2 C[a]		10.0 C[a]	
	μg	nmol	Recovery (%)	ZL (mC)[b]	Recovery (%)	ZL (mC)[b]
La	163.6	1168	—[c]	—	—	—
Ce	331.9	2369	—	—	—	—
Pr	39.19	278.1	—	—	—	—
Nd	133.3	924.2	—	—	—	—
Sm	18.57	123.4	63	28.0	100	45.45
Eu	1.196	7.9	78	2.25	97	1.8
Gd	10.85	68.9	79	21.45	100	25.2
Tb	0.791	5.0	83	2.10	96	2.25
Y	3.753	42.2	101 ⎫	15.3	102 ⎫	15.75
Dy	0.770	4.7	97 ⎭		101 ⎭	
Ho	0.141	0.9	96 ⎫		94 ⎫	
Er	0.139	0.8	98 ⎪		97 ⎪	
Tm	0.063	0.4	97 ⎬	0.45	98 ⎬	0.45
Yb	0.039	0.2	107 ⎪		107 ⎪	
Lu	0.039	0.2	107 ⎭		97 ⎭	
Total[d]	704.3	5000	—	—	—	—

[a] Amount of electricity integrated at preseparation stage.
[b] Zone length (mC) of separated zones (current: 150 μA).
[c] –, Removed at preseparation stage or not detectable.
[d] Total amount of rare earth elements.

fraction) and were analysed by PIXE. In the last fraction Ho, Er, Tm, Yb and Lu were detected.

As shown in Table III, the recovery of Sm, Eu, Gd and Tb was incomplete, suggesting that the amount of electricity applied (5.2 C) at the preseparation stage was not enough for the complete separation of Sm, Eu, Gd and Tb from the major light lanthanoids (La, Ce, Pr and Nd).

Almost all of the major lanthanoids were removed at the preseparation stage and apparently part of the Sm, Eu, Gd and Tb was not recovered because the mixed zone was not completely resolved owing to an insufficient amount of electricity. As we have already confirmed a 100% recovery of the equimolar lanthanoids under the electrolyte conditions used [9,14], when the recovery is imperfect it can be correlated with the amount of electricity applied as follows:

$$\text{Recovery} (\%) = \frac{\text{separable amount (nmol)}}{\text{injected amount (nmol)}} \cdot 100$$

= (applied amount of electricity per unit sample amount/necessary amount of electricity per unit sample amount) · 100

In order to obtain a 100% recovery, the necessary amount of electricity (Q) for the separation of a 5000-nmol sample was estimated from the minimum recovery of Sm (63%) in Table III:

$$Q = 5.2/0.63 = 8.3C$$

Consequently, the separation efficiency of the crude rare earth chloride was estimated as 602 nmol/C (= 5000/8.3).

The integrated amount of electricity was then increased to ca. 10 C by using the preseparation tube with a larger load of leading electrolyte. The 5000-nmol sample was fractionated and 23 fractions were obtained in 648 s (28.2 s per fraction). As summarized in Table III, the recovery of Sm–Lu was 100%, as expected, suggesting that 10 C were sufficient for

the separation of Sm–Lu from the major light lanthanoids. The zone length of Tb was almost unchanged (15 s) but that of Eu became shorter (12 s). From the PIXE analysis of the fractions, this was confirmed to be the result of the incomplete separation of the mixed zone between Eu and Gd.

From the above experimental results with the model mixture, it became evident that the separation efficiency of the crude rare earth chloride was at least 500 nmol/C ($=5000/10$) for the separation of the medium to heavy rare earth elements Sm–Lu from major light lanthanoids.

ITP–PIXE analysis of real sample

Before determining minor elements, the major elements were determined in order to obtain the abundance of total rare earth elements in the actual sample. A 6.5-μl sample (8.808 g/l, 57.3 μg) was separated and whole zones were fractionated. The preseparation stage was not used as the sample amount was small. The integrated amount of electricity was 0.603 C. The coupled tubes used were 16 cm $\times$ 1 mm I.D. $\times$ 2 mm O.D. and 32 cm $\times$ 0.5 mm I.D. $\times$ 1 mm O.D., respectively. Fig. 2 shows the observed isotachopherogram for the 57.3-μg sample, where La, Ce, Pr, Nd, Sm, Gd and Y were detected. Twenty-three fractions were obtained in 420 s (19.1 s per fraction) and were analysed by PIXE. Fig. 3 shows the analytical results. In addition to the elements detected by means of ITP, the minor elements Eu, Tb and Dy were also detected.
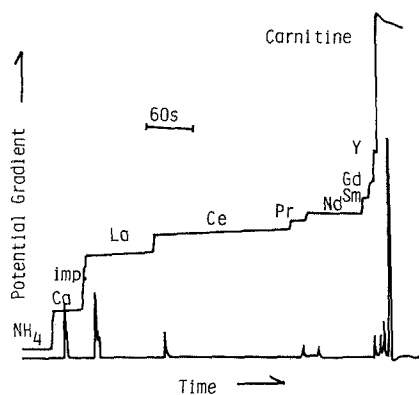

Fig. 2. Observed isotachopherogram of the crude rare earth chloride. The injected sample amount was 57.3 μg. For electrolyte conditions, see the Table I. Migration current = 150 μA. Separation stage was used (see Fig. 1). The integrated amount of electricity was 0.603 C.
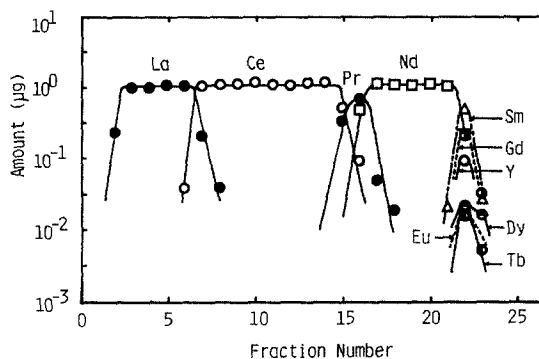

Fig. 3. Analytical results for the 23 fractions by means of PIXE. The corresponding isotachopherogram is shown in Fig. 2. For the operating conditions, see Table I.

The abundances evaluated from PIXE analysis are listed in Table IV.

In order to detect the other trace rare-earth elements, Ho, Er, Tm, Yb and Lu, the sample amount was increased to 1761.6 μg (sample solution = 200 μl, total amount of rare earth elements = 638 μg, *ca.* 4500 nmol). The amount of electricity applied during the separation was *ca.* 10 C. After removing the major elements La, Ce, Pr and part of the Nd zone, the zones containing the other minor elements were fractionated. Fig. 4 shows the observed isotachopherogram. Twenty fractions were obtained in 582 s (29.1 s per fraction). Fig. 5 shows the constituents of the fractions and the amounts evaluated by PIXE. As shown in Fig. 5, even the ultra-trace element Lu was determined. The abundances are summarized in Table IV. As discussed in the previous section, an integrated amount of electricity of 10 C was sufficient to separate Sm–Lu from major light lanthanoids (total $\approx$ 4500 nmol), although six elements from Dy to Lu were found in the last fraction (No. 20) only.

In order to separate these elements, a 1000-μl sample solution (total $\approx$ 8808 μg, 22 500 nmol) was injected at the preseparation stage. After removing the La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and part of the Dy zones, the remaining zones were fractionated. The abundances of Ho, Er, Tm, Yb and Lu are given in Table IV; these elements were found in the last four fractions.

PIXE analysis of real sample

The limitation of the PIXE analysis itself was

TABLE IV

ABUNDANCE (%) OF THE CRUDE RARE EARTH CHLORIDES EVALUATED BY ITP–PIXE AND COMPARISON WITH OTHER METHODS

Rare earth	ITP–PIXE			PIXE: 2.936 μg^a	ICP-AES
	57.3 μg^a	1762 μg^a	8808 μg^a		
TRE^b	36.20 ± 0.34^c	36.20 ± 0.34	—	37.4 ± 1.36	—
La/TRE	23.08 ± 0.11	—	—	22.8 ± 0.43	23.1 ± 0.4
Ce/TRE	47.43 ± 0.28	—	—	47.0 ± 0.71	47.8 ± 0.4
Pr/TRE	5.54 ± 0.06	—	—	5.40 ± 0.21	5.68 ± 0.13
Nd/TRE	19.57 ± 0.15	—	—	18.5 ± 0.43	19.7 ± 0.3
Sm/TRE	2.78 ± 0.04	2.61 ± 0.01	—	2.74 ± 0.16	2.74 ± 0.16
Eu/TRE	$0.07 \pm 5 \cdot 10^{-3}$	$0.026 \pm 1 \cdot 10^{-3}$	—	0.64 ± 0.08	$0.022 \pm 1 \cdot 10^{-3}$
Gd/TRE	1.19 ± 0.024	$1.12 \pm 7 \cdot 10^{-3}$	—	1.46 ± 0.13	1.07 ± 0.01
Tb/TRE	$0.10 \pm 5 \cdot 10^{-3}$	$0.082 \pm 1 \cdot 10^{-3}$	—	0.41 ± 0.07	$0.15 \pm 3 \cdot 10^{-3}$
Dy/TRE	0.18 ± 0.01	$0.20 \pm 7 \cdot 10^{-3}$	—	0.27 ± 0.06	$0.23 \pm 5 \cdot 10^{-3}$
Ho/TRE	—	$0.019 \pm 7 \cdot 10^{-4}$	$0.016 \pm 3 \cdot 10^{-4}$	—	$0.029 \pm 1 \cdot 10^{-3}$
Er/TRE	—	$0.022 \pm 2 \cdot 10^{-4}$	$0.019 \pm 6 \cdot 10^{-5}$	—	$0.025 \pm 5 \cdot 10^{-4}$
Tm/TRE	—	$0.002 \pm 3 \cdot 10^{-4}$	$0.002 \pm 6 \cdot 10^{-5}$	—	$0.015 \pm 2 \cdot 10^{-3}$
Yb/TRE	—	$0.006 \pm 5 \cdot 10^{-4}$	$0.004 \pm 2 \cdot 10^{-4}$	—	$0.006 \pm 3 \cdot 10^{-4}$
Lu/TRE	—	$0.001 \pm 2 \cdot 10^{-4}$	$0.001 \pm 6 \cdot 10^{-5}$	—	$0.001 \pm 5 \cdot 10^{-4}$
Y/TRE	0.45 ± 0.08	0.507 ± 0.02	—	—	0.438 ± 0.021

^{a} Analysed sample amount.
^{b} Total amount of rare earth elements.
^{c} PIXE standard deviation estimated from counts.

demonstrated with the present sample. A PIXE spectrum was obtained for 2.936 μg of crude rare earth chloride (5 μl, 0.5872 g/l). By analysing the spectra using the computer program PIXS [13], La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Y were

determined. The other minor rare-earth elements could not be detected owing to the limitation of deconvolution technique. The quantitative results are given in Table IV. The evaluated abundances of La, Ce, Pr, Nd, Sm and Gd agreed well with the
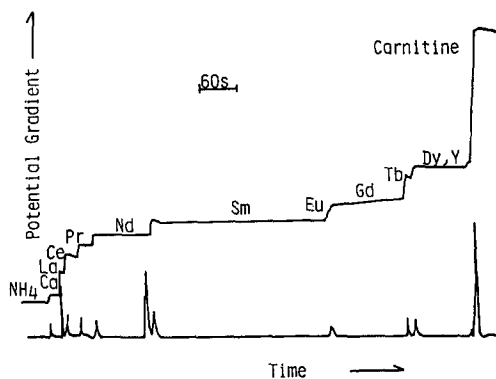

Fig. 4. Observed isotachopherogram of the crude rare earth chloride (1762 μg). The total amount of rare earth elements was 638 μg. Preseparation stage was used. For the operating conditions, see Table I.
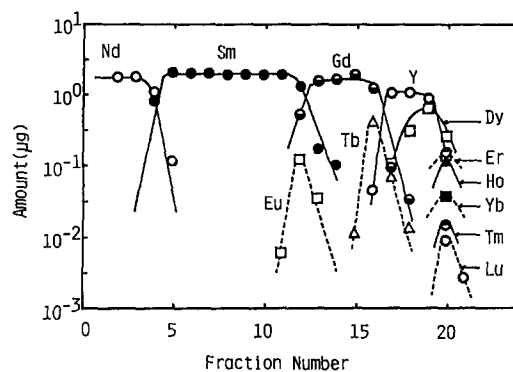

Fig. 5. Analytical results for the 21 fractions by means of PIXE. The corresponding isotachopherogram is shown in Fig. 4. The integrated amount of electricity was *ca.* 10 C.

values obtained by ITP–PIXE, except for Eu, Tb and Dy. Apparently from the results, it was necessary to remove the major elements by ITP in order to determine subsequently these elements, the abundances of which were lower than 1%.

Analytical results by ICP-AES and comparison between ITP–PIXE and ICP-AES methods

Table IV also summarizes the abundances of the lanthanoids evaluated by ICP-AES. The total concentration of sample solution was 8.808 g/l for the determination of ultra-trace Lu, 3.523 g/l for Yb, 0.8808 g/l for Eu, Gd, Tb, Dy, Ho, Er, Tm and Y, 0.1762 g/l for Sm, 0.04404 g/l for La, Pr and Nd, and 0.01762 g/l for Ce. Good agreement was obtained between the values obtained by ITP–PIXE and ICP-AES, except for Tb, Ho and Tm. The latter slight disagreement might be due to the overlap of the analysed spectral lines with weak lines of the major elements. Boumans *et al.* [15,16,17] have described the mutual interference among rare earth elements in ICP-AES analysis.

Fig. 6 shows the distributions of rare earth elements contained in the crude rare earth chloride from monazite which were determined by ITP–PIXE and ICP-AES. The abundances were normalized to the Ce abundance being 100%. It is well known that the natural abundance of the earth elements in their ores such as monazite should contain the whole range of rare earth elements except for the radioactive element Pm, even though some elements are present in extreme trace amounts. Also, the abundance of the elements with even atomic number should be greater than those of the neighbouring elements with odd atomic number [5]. The present results confirmed the higher accuracy of ITP–PIXE than ICP-AES, suggesting that a pre-separation technique would also be necessary to obtain a higher accuracy in ICP-AES analysis.

This work confirms the analytical utility of the ITP–PIXE method. The method combines the high separability of ITP and the high sensitivity, multi-element capacity and small sample size of PIXE [12]. More complex mixtures can be analysed by ITP–PIXE. Another application to a model solution of nuclear fuel cycle waste will be published in due course.
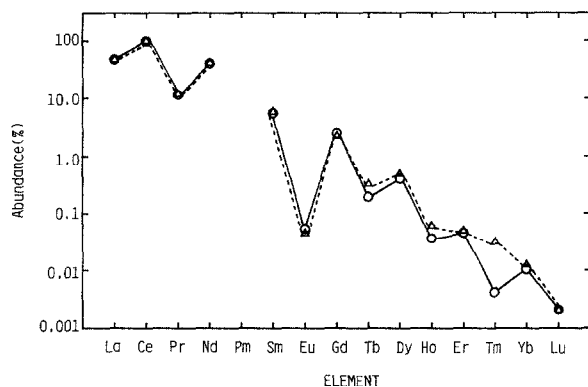

Fig. 6. Distribution of rare earth elements contained in the crude rare earth chloride from monazite. The Ce abundance was normalized as 100%. Solid line, results obtained by ITP–PIXE; dashed line, results obtained by ICP-AES.

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