Analysis of Some Rare-Earth Ores by the Isotachophoresis-Particle Induced X-Ray Emission Method

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Rare-earth ores (monazite, ion-adsorption type and xenotime) were analyzed using a coupled analytical method, isotachophoresis-particle induced X-ray emission (ITP-PIXE). The detection limit for each minor rare-earth element in the ores was *ca.* 0.01 mass% of the total rare-earth elements (TREE), when 200 µg of monazite was analyzed. Since yttrium was the major component in ion-adsorption type and xenotime ores, the use of a leading electrolyte containing α -hydroxyisobutyric acid and tartaric acid as complexing agents was effective for the separation of yttrium ion from lanthanide ions.

Keywords Rare-earth element, isotachophoresis, particle induced X-ray emission (PIXE), isotachophoresis-PIXE

The analysis of rare-earth ores, which include fourteen lanthanide elements and yttrium with very different abundances, is one of the difficult problems for any analytical method. Especially when the minor components in the ores are analyzed, an accurate analysis may be disturbed by inherent disadvantages of the employed method, for example, spectrum interference in atomic emission spectroscopy, isotope interference in mass spectroscopy and a matrix effect in X-ray analysis.

In such instances chromatographic analysis may be useful. However, since the separation column used for analytical chromatography is easily overloaded, a large amount of sample can not be applied. Therefore, the detection method should be sufficiently sensitive to analyze minor components in the applied sample. As long as conventional detection methods are used, however, the necessary sensitivity is not always available. A coupled analytical method for rare-earth ores, HPLC-ICP-AES, as reported by Yoshida and Haraguchi¹, is one possible solution, where ICP-AES plays the role of an HPLC detector with high sensitivity and discriminating ability.

On the basis of the same strategy, we have developed isotachophoresis-particle induced X-ray emission (ITP-PIXE). Ionic components in a sample solution are first preconcentrated and separated by ITP, and zones of the separated components are fractionated utilizing the counterflow of a leading electrolyte. Dropwise fractions are then analyzed off-line by PIXE. By using this

coupled method, a crude rare-earth chloride from monazite ore² and a model solution of high-level waste from the nuclear fuel cycle^{3,4} were analyzed with high accuracy.

The leading electrolyte used contained α -hydroxyisobutyric acid (HIB) as the complex-forming agent. The separation of fourteen lanthanide ions using the electrolyte is one of the typical applications of ITP.^{5,6} However, since Y and Dy could not be separated by using the electrolyte, ITP was not useful for analyzing rare-earth ores containing both Y and Dy. In order to improve this defect we have recently developed a new leading electrolyte by adding tartaric acid to the previous leading electrolyte as a helping complexing agent.⁷

This paper aims to confirm the utility of the above-mentioned electrolyte system in the analysis of rare-earth ores containing Y as one of the major components. For that purpose, three rare-earth ores (monazite, ion-adsorption type and xenotime) were selected. Monazite contains almost no Y; its main component is light lanthanide elements. Ion-adsorption type ore contained light lanthanide and Y as the major components, and the abundance of medium and heavy lanthanide was much larger than monazite. The major component of xenotime was Y, and lanthanides comprised the minor components.^{8,9} In this study, these ores were analyzed by the ITP-PIXE method. Compared with ITP-PIXE, they were also analyzed by ITP and PIXE, respectively.

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Experimental

Samples

Solutions of a monazite ore and an ion-adsorption type ore (each 2 g/l) were prepared, respectively, as follows: 0.5 g of the ore fine powder was dissolved in a PTFE vessel by adding 5 ml of concentrated hydrochloric acid. It was then evaporated to dryness using a 500-W lamp to remove excess hydrochloric acid. Subsequently, 5 ml of water was added and then dried up. Finally, the chloride residue was dissolved in deionized water to be 250 ml. The pH of the prepared sample solution was 2.6.

Since it was estimated that the isotachophoretic analysis of xenotime was most difficult among the ores treated, due to the large abundance of Y³⁺, a model mixture of known composition was used instead of a real xenotime ore. It was prepared from stock sample solutions of rare-earth chlorides (RECl₃), considering typical compositions^{8,9}, which are tabulated in a later section. The concentration of the model solution was 3.233 g/l as the chloride; the rare-earth content was 49.5% (mass%, throughout this paper).

Slight amounts of Toluidine Blue and Astrazon Pink were added to the above-mentioned samples to monitor the isotachophoretic migration process and to determine the timing of fractionation.

Operational electrolyte system for isotachopheresis

Two leading electrolytes were used. One was a 20 mM (mM=10⁻³ mol dm⁻³) ammonia solution containing 10 mM HIB; the other was a 20 mM ammonia solution containing 8 mM HIB and 0.5 mM tartaric acid. The pH of both solutions was adjusted to 4.80 by adding acetic acid. These leading electrolytes were used in combination with a terminating electrolyte, a 10 mM solution of carnitine hydrochloride.

The electrolyte system containing only HIB as the complexing agent is referred to as the HIB system, and that containing both HIB and tartaric acid (Tar) is referred to as the HIB-Tar system in this paper. All of the electrolytes contained 0.1% hydroxypropylcellulose (HPC) to suppress electroendosmosis. A HORIBA (Model F7-AD) expanded pH meter (Tokyo, Japan) was used for the pH measurements.

Chemicals

Fine powders of a monazite ore and an ion-adsorption type ore (rare-earth oxides) were provided by Nippon Kogyo Co. (Tokyo, Japan). The rare-earth chlorides used were of guaranteed grade (GR) obtained from Katayama Chemical Co. (Osaka, Japan). Hydrochloric acid was of ultrapure grade from E. Merck (Darmstadt, Germany). Complexing agents (α -hydroxyisobutyric acid (GR) and tartaric acids (GR)), and HPC (extra pure) were obtained from Tokyo Kasei Co. (Tokyo, Japan). The viscosity of a 2% HPC aqueous solution was 1000–4000 cP at 20°C according to the specification. The

water used was obtained by a purifier (Japan Organo Co. Ltd., Model PURIC-R, Tokyo, Japan). The resistivity of the deionized water was 18.3×10⁶ Ω/cm. Rare-earth standard solutions for atomic absorption spectroscopy (1 mg/l, Tokyo Kasei Co.) were used as reference standards in PIXE analysis.

Isotachophoretic analyzers

The separation unit of the preparative isotachophoretic analyzer used was made in our laboratory.¹⁰ The separation column used comprised a pre-separation capillary (40 cm×1 mm i.d.) and a main capillary (16 cm×0.5 mm i.d.). The apparatus and its operation was detailed in ref. 10. The analysis time was 1 h and the amount of electric charge applied during separation was 1.2 C. The zones of the separated and preconcentrated RE components were fractionated by applying the counter flow of the leading electrolyte. The dropwise fraction was separately sampled on the Nuclepore filter (thickness 5 μm and pore size 0.1 μm, Nuclepore Co., USA) supported by an aluminum frame. The volume of one fraction was 5 μl; it contained a few nanomoles of REE.

The other isotachophoretic apparatus was used for analytical purposes. Its detector was a high-frequency contactless conductivity detector (HFCCD) developed by Gas *et al.*¹¹, which was used in combination with the separation unit of a LABECO ZKI-001 isotachophoretic analyzer (Sp. Nova Ves, Slovakia). The separation column comprised a pre-separation capillary (20 cm×0.5 mm i.d.) and a main capillary (20 cm×0.25 mm i.d.). The migration current in the pre-separation stage was 125 μA; it was reduced to 50 μA while detecting zones. The amount of electric charge applied until detecting the terminating zone was 0.37 C in a blank run. Measurements were carried out at 25°C in a temperature-regulated room.

PIXE analysis

For the PIXE measurement¹², the van de Graaff accelerator at our faculty was used (Nisshin High Voltage Co., Model AN-2500, Tokyo, Japan). The energy of the H⁺ beam was 2 MeV, the beam current 50 nA, and the beam diameter 6 mm. The detector was a high purity Ge detector (an ORTEC Model GLP-10180, USA), which was used in combination with a Laboratory Equipment (Tokyo, Japan) Model AMS-1000 multi-channel analyzer. A typical single run for an ITP fraction took 200 s (10 μC).

The PIXE spectra of the rare-earth ore samples were also measured and analyzed for the 5 μl sample solution spotted on the Nuclepore filter by using an Eppendorf 4700 pipette (Hamburg, Germany). The sample solution was appropriately diluted to contain a few micrograms or less in 5 μl. The diameter of the sample spot was 3 mm.

The amount of the rare-earth element was determined by comparing the X-ray counts with those of the reference standards. Data-reduction software (PIXS)

Fig. 1 Isotachopherograms of an equimolar mixture of fifteen rare-earth ions (0.33 mM, 5 μ l) obtained using HFCCD: a) the HIB system, b) the HIB-Tar system. imp, electrolyte impurity; C_{Tar} , concentration of tartaric acid; C_{HIB} , concentration of HIB; migration current, 50 μ A.

was used with an option of spectrum deconvolution utilizing an X-ray relative-intensity database.¹³

Results and Discussion

ITP analysis of rare-earth ores

Figures 1a and 1b show isotachopherograms of an equimolar mixture of 15 rare-earth ions (1.7 nmol each; sample concentration, 0.33 mM; injected volume, 5 μ l) obtained by using the HIB system and the HIB-Tar system, respectively. Obviously from these figures, Y^{3+} and Dy^{3+} could not be separated to form a mixed zone when the HIB system was used. On the other hand, although Y^{3+} and Dy^{3+} were separated, Eu^{3+} and Gd^{3+} were not when the HIB-Tar system was used. Since a leading electrolyte for the simultaneous separation of 15 REE is not presently known, the above two leading electrolytes should be selectively used according to analytical purposes. In this study, a monazite sample was analyzed using the HIB system because of a small abundance of Y; the others were analyzed using the HIB-Tar system.

The averaged zone-passing time of 1.7 nmol of rare-earth ions was *ca.* 15 s (see Fig. 1). Accordingly, the sensitivity of the present analytical system (the amount of lanthanide ion/the zone passing time) was 0.11 nmol/s,

Fig. 2 ITP-PIXE analysis of a monazite ore: a) observed isotachopherogram of the ore sample (concentration=2 g/l, 8 μ l); b) PIXE analysis of the ITP fractions (sample volume=11 μ l); c) PIXE analysis of the ITP fractions (sample volume=100 μ l); the HIB system was used as an operational electrolyte system.

and the values were almost equal to each other. Since the minimum zone-passing time which could be measured precisely was 2–3 s in the present experiments, the detection limit of ITP was *ca.* 0.3 nmol (ex. 50 ng of Gd).

Figures 2a, 3a and 4a show the isotachopherograms observed for the monazite ore (concentration, 2 g/l; injected volume, 8 μ l), the ion-adsorption type ore (2 g/l, 5 μ l), and the xenotime model (3.2 g/l, 5 μ l), respectively. On the basis of the observed isotachopheric qualitative indices⁷ the elements shown in these figures could be assigned. The existence of the other minor REE (shown in parentheses) could not be confirmed without qualitative information by PIXE.

Since the separabilities (separable sample amount per unit amount of charge) of adjacent lanthanide pairs are different from each other², the separability of the ores depends on the composition. The values observed for monazite, ion-adsorption type and xenotime ores were 42 μ g (280 nmol)/C, 24 μ g (155 nmol)/C and 19 μ g (100 nmol)/C, respectively, which were obtained by

Table 1 Analytical results of a monazite ore

RE	ITP		PIXE		ITP-PIXE			
	sample vol. 5 μ l wt. 10 μ g		5 μ l ^a 1 μ g		11 μ l 22 μ g		100 μ l 200 μ g	
	μ g	% ^b	μ g	%	μ g	%	μ g	%
La	2.168	28.73	0.215	28.3	4.850	29.50	nf ^c	
Ce	3.465	45.91	0.342	45.0	7.379	44.88	nf	
Pr	0.389	5.16	0.044	5.8	0.881	5.36	nf	
Nd	1.406	18.63	0.130	17.1	2.957	17.99	pf ^d	
Sm	0.085	1.13	0.018	2.3	0.221	1.34	2.124	1.44
Eu	—	—	0.005	0.7	0.061	0.37	0.427	0.29
Gd	—	—	0.007	0.9	0.076	0.46	0.712	0.49
Tb	—	—	—	—	0.006	0.04	0.077	0.05
Dy	—	—	—	—	0.009	0.05	0.173	0.12
Ho	—	—	—	—	—	—	0.024	0.01
Er	—	—	—	—	—	—	0.022	0.01
Tm	—	—	—	—	—	—	0.006	0.004
Yb	—	—	—	—	—	—	—	—
Lu	—	—	—	—	—	—	—	—
Y	—	—	—	—	0.026	—	0.395	0.24
Total	7.547 μ g		0.761 μ g		16.466 μ g		150.02 μ g ^e	

a. 1/10 diluted sample. b. Mass%=(mass of REE/total mass of REE)×100. c. Not fractionated. d. Partly fractionated. e. Sample amount for not fractionated and partly fractionated were assumed.

Table 2 Analytical results of an ion-adsorption type ore

RE	ITP		PIXE		ITP-PIXE			
	sample vol. 5 μ l wt. 10 μ g		5 μ l ^a 1 μ g		14 μ l 28 μ g		50 μ l 100 μ g	
	μ g	% ^b	μ g	%	μ g	%	μ g	%
La	2.378	27.87	0.211	25.3	6.161	27.1	nf ^c	
Ce	0.229	2.68	0.024	2.9	0.564	2.48	nf	
Pr	0.467	5.47	0.061	7.3	1.506	6.62	nf	
Nd	2.004	23.49	0.190	22.8	5.161	22.7	pf ^d	
Sm	0.374	4.38	0.037	4.4	1.067	4.69	3.576	4.40
Eu	0.471 ^f	5.52	0.015	1.8	0.221	0.97	0.767	0.94
Gd	—	—	0.043	5.2	1.037	4.56	3.555	4.38
Tb	—	—	0.010	1.2	0.134	0.59	0.535	0.66
Dy	0.334	3.92	0.028	3.4	0.892	3.92	3.107	3.83
Ho	0.052	0.61	0.005	0.6	0.201	0.88	0.613	0.75
Er	0.177	2.07	0.014	1.7	0.419	1.84	1.531	1.89
Tm	—	—	0.002	0.2	0.084	0.37	0.216	0.27
Yb	0.147	1.72	0.015	1.8	0.329	1.45	1.129	1.39
Lu	—	—	0.002	0.4	0.037	0.16	0.171	0.21
Y	1.898	22.2	0.175	21.0	4.928	21.7	pf	
Total	8.531 μ g		0.833 μ g		22.741 μ g		80.629 μ g ^e	

a – e. As in Table 1. f. Eu and Gd.

plotting a calibration line (sample amount vs. zone passing time) for each zone; when the separation tube was overloaded, the component zones reached the detector before complete separation; this caused a point of inflection in the calibration lines.¹⁴ If an ITP analysis was carried over that point, accurate results could not be obtained. The most difficult pair to separate among the

major components was La–Ce for monazite and Dy–Y for ion-adsorption type and xenotime ores, respectively.

The analytical results given in Tables 1, 2 and 3 for 5 μ l samples were evaluated while taking into account the separability. The mass% values in these tables were the averages of 2 – 5 runs for a sample (injected volume, 2 – 10 μ l). Obviously, ITP was useful for analyzing the RE

Table 3 Analytical results of a xenotime model ore

RE	Nominal %	ITP		PIXE		ITP-PIXE	
		sample vol. 5 μ l wt. 16 μ g		5 μ l ^a 1.6 μ g		11 μ l 35.6 μ g	
		μ g	% ^b	μ g	%	μ g	%
La	0.54	—	—	0.005	0.6	0.105	0.58
Ce	5.17	0.464	5.7	0.046	5.3	0.939	5.23
Pr	0.72	—	—	0.009	1	0.143	0.80
Nd	2.33	0.187	2.3	0.021	2.4	0.442	2.46
Sm	2.00	0.165	2.0	0.016	1.8	0.388	2.16
Eu	0.22	—	—	0.003	0.3	0.046	0.26
Gd	4.33	0.403	5.0	0.041	4.7	0.791	4.41
Tb	1.06	—	—	0.014	1.6	0.133	0.74
Dy	9.28	0.673	8.3	0.080	9.1	1.593	8.87
Ho	2.22	0.201	2.5	0.027	3.1	0.467	2.60
Er	5.78	0.505	6.2	0.056	6.4	1.070	5.96
Tm	0.94	—	—	0.008	0.9	0.179	1.00
Yb	6.67	0.575	7.1	0.060	6.9	1.291	7.19
Lu	0.44	—	—	—	—	0.083	0.46
Y	58.30	4.915	60.8	0.482	55.1	10.284	57.28
Total		8.088 μ g		0.875 μ g		17.954 μ g	

a. and b. As in Table 1.

components with an abundance of 1% or more. The smallest abundance obtained by ITP was 0.6% for Ho in an ion-adsorption type ore. The determination of an Ho zone was barely possible by applying 8–10 μ l of the sample. In the case of xenotime, the major component (Y) easily formed mixed zones with adjacent minor components (Tb and Dy). REE with an abundance of 2% or more were analyzable by ITP. The found abundances of the xenotime model agreed with the nominal values within errors of a few percent for the major components and *ca.* 10% for the minor components.

PIXE analysis of rare-earth ores

Although the sensitivity of PIXE analysis is much higher than that of ITP, the sensitivity varies according to the atomic number. The sensitivity of La ($Z=57$) and Lu (71) was 11496 and 3685 counts/ μ g/ μ C, respectively, when L X-rays were analyzed. That of Y (39) was smallest among REE (397 counts/ μ g/ μ C) when K X-rays were analyzed. The minimum detectable amount in the routine analysis is a few nanograms.

The analytical results obtained by analyzing the spectra are given in Tables 1, 2 and 3. Although the L X-ray spectrum deconvolution technique has been successfully used in the analysis of samples containing lanthanide^{13,15,16}, the analytical accuracy depends on the accuracy of the detector response function used in the deconvolution process, the relative intensity database, and the abundance of lanthanide components in the sample. As shown in Tables 1, 2 and 3, the components with *ca.* 1% abundance were determined by PIXE analysis. As revealed by ITP-PIXE (subsequent sec-

tion), however, the analytical result for Eu (abundance, 0.7%) and Gd (0.9%) in the monazite sample (Table 1) contained a considerable error due to spectrum deconvolution. As in an ICP-AES analysis, spectrum interference is serious in a PIXE analysis. To analyze these minor components accurately, it is necessary to remove the major elements. Then, the rare-earth ore solutions were analyzed by the ITP-PIXE method.

ITP-PIXE analysis of rare-earth ore

Monazite ore. Figure 2b shows the analytical result of ITP-PIXE for a 11 μ l sample (22 μ g). The separated sample zones were fractionated into *ca.* 50 fractions, and analyzed by PIXE. Table 1 summarizes the analytical results. In addition to the elements determined by ITP, Eu, Gd, Tb and Dy were detected. Their abundances were in the 0.5–0.04% range.

To find the heavier lanthanide in monazite ore, the sample volume was increased to 100 μ l (a 200 μ g of the ore). The amount of electric charge applied in the separation process was increased to 2.5 C by using a longer separation tube. After removing the La, Ce, Pr and a part of the Nd zones, the zones of trace elements were selectively fractionated. Figure 2c and Table 1 show the analytical results. By increasing the sample amount, additional trace elements (Ho, Er and Tm) were determined. Er and Tm are not shown in Fig. 2c so as to avoid complexity. The most minor element found in this experiment was 6 ng (30 ppm) of Ho. Its abundance was less than 0.01% of the total rare-earth elements (TREE).

The quality of separation was not very good for fractions No. 9–19 in Fig. 2c, suggesting that the applied

Fig. 3 ITP-PIXE analysis of an ion-adsorption type ore: a) observed isotachopherogram of the ore sample (concentration, 2 g/l, 5 μ l); b) PIXE analysis of the ITP fractions (sample volume, 14 μ l); c) PIXE analysis of the ITP fractions (sample volume, 50 μ l); the HIB-Tar system was used as the operational electrolyte system.

amount of charge was not sufficient for completely separating *e.g.* Eu–Gd pairs. It should be noted that the method previously described to evaluate the isotachophoretic separability cannot be applied to the minor components of which calibration lines cannot be easily available.

Since the volume of one fraction was *ca.* 5 μ l, adjacent sample zones were mixed during fractionation, even if they were separated in the separation tube. Although such mixing is not problematic, because of the multi-elemental analyzability of PIXE, it may cause a small analytical error during spectrum deconvolution. In comparison with a simple PIXE analysis, this error is not serious, because the major components are separated.

Ion-adsorption type ore

Figure 3b shows the analytical result of ITP-PIXE for a 14 μ l sample: fourteen lanthanide ions and Y^{3+} were detected. Table 2 summarizes the analytical result. Eu (abundance, 0.97%), Tb (0.59%), Tm (0.37%), and Lu (0.16%), which could not be detected by ITP, were determined by ITP-PIXE. The abundance of heavy

Fig. 4 ITP-PIXE analysis of the model mixture of a xenotime ore: a) observed isotachopherogram of the ore sample (concentration, 3.2 g/l, 5 μ l); b) PIXE analysis of the ITP fractions (sample volume, 11 μ l); c) PIXE analysis of the ITP fractions (sample volume, 100 μ l); the HIB-Tar system was used as the operational electrolyte system.

lanthanide elements in this ore was much higher than that of the monazite ore. The most minor element was Lu; its abundance was 0.2% of TREE.

Although the injected sample amount was sufficient to analyze the minor element of such abundance, a 50 μ l sample was analyzed again by ITP-PIXE in order to confirm isotachophoretic separability, analytical accuracy and reproducibility. The applied charge was 2.7 C and fractionation was started at the end of the Nd zone. The Y^{3+} zone was partly fractionated. Figure 3c and Table 2 show the analytical results. The abundances of the light lanthanide in a 50 μ l sample were assumed from the analytical results of a 14 μ l sample. Based on Fig. 3c, the separation of Y^{3+} and Dy^{3+} was good, thus confirming the utility of the newly developed electrolyte system. The separation of Eu^{3+} and Gd^{3+} was impossible, as estimated from Fig. 1. A PIXE analysis revealed that the zone was a homogeneous mixed zone. Obviously from Table 2, the analytical results for a 14 μ l sample and a 50 μ l sample agreed within the errors.

Xenotime model ore

Finally, the xenotime model ore was analyzed by ITP-PIXE. Figure 4b shows the analytical result for isotachophoretic fractions of a 11 μ l (35 μ g) sample. The amount of charge applied was 1.8 C. Table 3 summarizes the analytical result. The most minor element was Lu and the found abundance was 0.4% of TRE, which agreed well with the prepared value, as did the other elements.

A PIXE analysis revealed that the separation of Y^{3+} and Dy^{3+} was not very good compared with the case of the ion-adsorption type ore. Moreover, the separation of Y^{3+} and Tb^{3+} was incomplete, suggesting that the amount of electric charge was not sufficient. Since the characteristic X-ray energies of these elements were quite different, the analytical accuracy was not affected by the mixing. Therefore, the analytical error given for Tb in Table 3 might be due to statistics, that the X-ray counts of Tb in each fraction were small.

As exemplified by the analysis of rare-earth ores, the advantages of ITP-PIXE can be summarized as follows: (1) the detection limit is as low as 1 ng by using PIXE as a detection method of ITP. This means that the necessary sample amount is small. (2) Isotachophoretic pre-separation reduces the matrix effect in an X-ray analysis and spectrum interference, which enables an accurate analysis of a complex sample. Since PIXE has multielemental analyzability, complete separation is not necessary. To obtain accurate results, however, good quality separation is necessary.

By applying a ten-times larger amount of ore samples, the heavier lanthanide ions with an order of 0.001% or less may be analyzed. For this purpose, a preparative ITP apparatus with a large-bore separation tube (ex. 5 mm i.d.) could be necessary.¹⁰

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