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Isotachophoretic separation behavior of rare-earth EDTA chelates and analysis of minor rare-earth elements in an iron ore by bidirectional isotachopheresis–particle-induced X-ray emission

Takeshi Hirokawa^{a,*}, Kazuhiro Nishimoto^{1,a}, Yang Jie^{2,a}, Kazuaki Ito^b,
Fumitaka Nishiyama^a, Natsuki Ikuta^a, Shinjiro Hayakawa^a

^aApplied Chemistry, Department of Chemistry and Chemical Engineering, Graduate School of Engineering, Hiroshima University,
1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

^bDepartment of Chemistry and Environmental Technology, School of Engineering, Kinki University, 1 Umenobe, Takaya,
Higashi-Hiroshima 739-2116, Japan

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Abstract

Mobilities of 16 anions of rare-earth–EDTA 1:1 chelate (RE–EDTAs) were isotachophoretically measured by using two leading electrolytes (pH 3.6 and 6.0) in order to assess their separation behavior. The leading electrolyte was 20 mM hydrochloric acid. The pH of the solution was adjusted to 3.6 by adding β -alanine and to 6.0 by adding histidine. The obtained mobilities were very close to each other in the range $20.1 \cdot 10^{-5}$ – $21.9 \cdot 10^{-5}$ cm² V⁻¹ s⁻¹ with the minimum mobilities for Pr–EDTA and Nd–EDTA for pH 3.6 and 6.0, respectively, and pH dependence was hardly observed. On the basis of the above knowledge, minor rare-earth elements in a standard iron ore sample were determined as RE–EDTAs by bidirectional isotachopheresis–particle-induced X-ray emission (PIXE), where the Fe(II) matrix digested by alkali fusion was separated as Fe(II)Phen₃²⁺ (phen=1,10-phenanthroline). Since 5% of the total iron was still detected as Fe(III)EDTA⁻ and might disturb PIXE analysis of RE–EDTA⁻, itaconic acid was used as the spacer for Fe(III)EDTA⁻ and RE–EDTA⁻. The fractions of RE–EDTA⁻ were successfully analyzed off-line by a multielemental analytical method, PIXE [analytical result (3.62% (w/w) as RE₂O₃); the nominal value was 3.37% (w/w) as RE_xO_y]. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Isotachopheresis; Particle-induced X-ray emission; Detection, electrophoresis; Metal chelates; Rare earth ions

1. Introduction

The mobility of a rare-earth–EDTA chelate anion (RE–EDTA⁻) in water is determined by the size of the hydrated chelate ion and its ionic charge. Since the ionic radius of a rare-earth cation is much smaller than that of its ligand EDTA, the size of the chelate anions is essentially equal to that of the ligand regardless of the small difference among ionic radii

*Corresponding author. Tel.: +81-824-24-7610; fax: +81-824-22-7192.

E-mail address: hiro77@hiroshima-u.ac.jp (T. Hirokawa).

¹Present address: MANAC Inc., 2-10-1 Nishi-machi, Fukuyama 720-0067, Japan.

²Present address: Analysis and Testing Center, Zhanjiang Ocean University, Zhanjiang, Guangdong, China.

of the central cations. The charge of RE–EDTA is uniquely -1 when the central RE ion is a trivalent cation. Consequently, the mobilities of RE–EDTAs are close to each other and simultaneous separation of all of them is difficult. In fact, the utility of RE–EDTAs in electrophoretic separation is limited to the low pH range where the chelate anions are very labile [1]. On the other hand, for alkaline-earth metal ions, Fe, Co, Ni, Pb, etc., the EDTA chelates were successfully utilized in the pH region where they are stable [2–7], suggesting significant differences among their mobilities.

We are developing a separation system using bidirectional isotachopheresis (bITP) [8] for metal ions, where several metal ions are detected as chelate anions and the others as free cations. Although the mobilities of RE–EDTAs are necessary for assessment of the separation behavior and its use for the determination of real samples, no mobility data have been reported yet [9]. Thus, firstly in this paper, the isotachopheretic mobilities were evaluated by analyzing quantitative indices and the assessment of the separability. Secondly, RE–EDTAs were utilized to bidirectional isotachopheretic analysis of trace rare-earth elements in a standard iron ore matrix [nominal value, 60.54% (w/w) as Fe, 86.56% (w/w) as Fe_2O_3 and 3.37% (w/w) as RE_xO_y]. Accurate analysis of minor components in a matrix component is difficult for any analytical method, and this situation is the same in isotachopheresis (ITP), as already reported previously [10]. For the determination of trace rare-earth elements in a iron ore, removal of the Fe matrix is necessary. Both Fe(II) ions and Fe(III) ions in the digested sample can be separated from RE^{3+} under proper electrolyte conditions [11]. However, a large amount of electric charge is necessary to separate RE^{3+} from the Fe(II) ion matrix due to its similar mobility. Furthermore Fe(III) ions may form a colloid and some of the target components may be included [11]. In this paper therefore most of the iron matrix was electrophoretically on-line separated from the minor RE ions by differentiating respective ionic charge using two complexing agents 1,10-phenanthroline (phen) and EDTA: that is, the major iron ions were converted into Fe(II) and formed Fe(II)phen_3^{2+} complex and the minor RE ions formed RE(EDTA)^- . An operational electrolyte system for bITP was used,

because not only RE ions but also iron ions were determined. Anionic and cationic components were fractionated by using a laboratory-made preparative isotachopheretic analyzer, considering migration behavior of RE–EDTA chelate anions. The fractions were analyzed off-line by particle-induced X-ray emission (PIXE) (ITP–PIXE method [12,13]). The practical aspect of such a bITP analysis was detailed and analytical results for the ore were reported.

2. Experimental

2.1. Test mixtures

For the mobility measurements, several solutions containing one to three RE–EDTAs were used as the sample. These test mixtures were prepared by stoichiometrical mixing of stock solutions of the chlorides (5 mM) and that of EDTA (10 mM). The former was prepared by dissolving the chlorides in purified water and the latter by dissolving EDTA in purified water by adding ammonia water (pH 4.8).

For the analytical study of the iron ore, stock solutions 20 mM of $\text{Fe(II)SO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Fe(III)Cl}_3 \cdot 6\text{H}_2\text{O}$, EDTA and 1,10-phenanthroline hydrochloride were prepared by using purified water. A 2.0% (w/w) solution of hydroxylamine hydrochloride was prepared just before usage. The pH of the stock solutions of $\text{Fe(II)SO}_4(\text{NH}_4)_2\text{SO}_4$ and Fe(III)Cl_3 were adjusted to 2 by adding H_2SO_4 and HNO_3 , respectively. The pH (4.8) of EDTA was same as the mobility measurements. The pH of 20 mM 1,10-phenanthroline hydrochloride was 3.1 as prepared. Test mixtures of Fe(II) and Fe(III) chelates were prepared by mixing these three stock solutions appropriately just before usage.

2.2. Chemicals

All the above chemicals were obtained from Katayama (Osaka, Japan) and Tokyo Kasei (Tokyo, Japan). Hydroxypropylcellulose (HPC) (extra pure) was obtained from Tokyo Kasei. The viscosity of a 2% (w/w) HPC aqueous solution was 1000–4000 cP at 20°C according to the specification.

2.3. An iron ore sample

The RE ore analyzed in this study was a standard iron ore sample (code R-715) from Bao Tou of the Ministry of Metallurgical Industry, China. The other components with reported abundance over 1% were CaO (5.17%), F (3.25%), and P₂O₆ (1.054%) except for Fe and RE_xO_y. The ore sample was digested according to the recommended alkali fusion method with iron-content reducing procedure. A sample for bITP–PIXE was prepared by mixing the ore solution obtained by alkali fusion with the same volume of three solutions appropriately before usage. The ore content was therefore 0.5 g/l in the final sample.

2.4. Alkali fusion of the ore sample

A 0.2-g amount of ore sample powder was mixed in an alumina crucible with sodium peroxide, and heated to a high temperature of 700°C for 30 min (in an oven). After cooling down in air (after it was taken out from the oven), 90°C hot water was poured onto it. We waited until the end of reaction, and then left the sample alone until it was cool. Then a mixture of 20 ml triethanolamine (TEA), 2 ml 5% EDTA, 2 ml 30% H₂O₂, and 0.5 g Na₂CO₃ was added to the sample solution (1:1), and the sample was transferred to a beaker. Then, 1 ml of 10% MgCl₂ was added to form a white precipitate. After a while, it was filtered out and the solid substance was washed with 2% NaOH solution. At this stage, a considerable amount of Fe(III) was removed as Fe-TEA in the filtrate. The solid substance was dissolved in another beaker by a mixture of 100 ml 10%

HCl and 1 ml 30% H₂O₂. After evaporation to 20 ml by using an infrared lamp, the solution was placed in a 100-ml measuring flask and purified water was added to the mark to give a 2 g/l sample solution. The pH was 2.1.

2.5. Operational electrolyte system

The operational electrolyte systems used for mobility measurements are summarized in Table 1. The leading electrolyte was 20 mM hydrochloric acid. The pH of the solution was adjusted to 3.6 by adding β-alanine and to 6.0 by adding histidine. The terminating electrolytes shown in Table 1 were those for bITP [8]. The real anionic terminator was acetate ion.

For the analysis of the iron ore, the catholyte was the same as the terminating electrolyte in Table 1 (pH buffer, β-alanine) except for pH 3.75. The anolyte was also the same as the leading electrolyte in Table 1 (pH buffer, acetic acid). All the electrolytes contained 0.1% (w/w) HPC to suppress electroosmotic flow. A Horiba Model F7-AD expanded pH meter (Tokyo, Japan) was used for pH measurements.

2.6. Isotachophoretic apparatus and R_E measurement

For mobility measurement, a high-frequency contactless conductivity detection (HFCCD) system developed by Gas and improved by Zuska [14] was used in combination with the separation unit of a Labeco ZKI-001 isotachophoretic analyzer (Sp.

Table 1
Operational electrolyte system for isotachopheresis

Leading electrolyte	20 mM hydrochloric acid
pH buffer	(1) β-Alanine (2) Histidine
pH	(1) 3.60 ^a (2) 6.00
Additive	0.1% (w/w) hydroxypropylcellulose (HPC)
Terminating electrolyte	20 mM ammonia solution
pH buffer	Acetic acid
pH	4.80
Chelating agent	0.1 mM EDTA
Additive	0.1% (w/w) HPC

^a pH 3.75 for the analysis of the iron ore.

Nova Ves, Slovak Republic). The separation column was a PTFE capillary (30 cm×0.32 mm I.D.). The amount of electric charge applied until the detection of terminating zone was 0.13 C in the blank run. The high-voltage power supply was that for a Shimadzu IP-2A (Kyoto, Japan). The measurement was carried out at 25°C in a temperature controlled room.

The qualitative index used was R_E , which was defined as the ratio of the potential gradient ($E/V\text{ cm}^{-1}$) of the sample zones (E_S) to that of the leading zone (E_L) [15]. Considered from the isotachophoretic principle, R_E is equal to the ratio of the effective mobility of the leading ion (m_L) to that of the sample ion (m_S). When a conductivity detector is used, it is equal to the ratio of specific resistance of each zone. Since the HFCCD output signal showed a nonlinear response to the specific resistance of the zones [14], the signal obtained was converted to the specific resistance using a fifth-order polynomial expression of the output voltage. The expression was obtained using KCl solutions with known specific resistances. Picrate ion was used as the internal standard to the correct slight drift of the HFCCD signals. The simulated R_E value was 2.644. The used HFCCD system was very stable and the reproducibility of the thus obtained R_E values was very high and the error was less than 1%.

The separation behavior of RE–EDTA chelates was also measured by ITP–PIXE: the preparative isotachophoretic analyzer made in our laboratory [12] with a pre-separation capillary (40 cm×1 mm I.D.) and a main capillary (16 cm×0.5 mm I.D.) was used. The amount of electric charge applied to the sample 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 a Nuclepore filter (thickness 5 μm and pore size 0.1 μm ; Nuclepore., USA) supported by an aluminum flame. The volume of one fraction was 5 μl and it contained a few nmol of rare-earth elements.

For the analysis of the iron ore, the preparative isotachophoretic analyzer made in our laboratory [16] was used. HFCCD was used to monitor separation and migration. The separation column used comprised a pre-separation capillary (100 cm×1 mm I.D.) and a main capillary (50 cm×0.5 mm I.D.). The analysis time was 2 h and the amount of electric

charge applied during separation was 7.5 C. The zones of the separated and preconcentrated RE components were collected as dropwise fraction (5 μl) for PIXE analysis in the same manner as the above method.

The other isotachophoretic apparatus used for analytical purposes, of which the separation unit was that of a Labeco ZKI-001 isotachophoretic analyzer and detection was by HFCCD. 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 qualitative index used was R_E and Na^+ , Li^+ and picrate were used as the internal standards: the simulated R_E values were 1.495, 1.963 and 2.644, respectively.

2.7. PIXE analysis

For the PIXE measurement [13], the Van de Graaff accelerator at our faculty was used (Nisshin High Voltage, Model AN-2500, Tokyo, Japan). The energy of the H^+ beam was 2 MeV, the beam current 50–80 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 amount of the RE was determined by comparing the X-ray counts with those (1 g/l) of the reference standards for atomic absorption spectrometry. Laboratory-made software (PIXS) was used for spectrum analysis utilizing an X-ray relative-intensity database [17].

3. Results and discussion

3.1. RE–EDTA anions

3.1.1. Mobilities of RE–EDTA anions

Table 2 shows the R_E values of EDTA and rare-earth–EDTA chelate anions observed by using two operational electrolyte systems (pH 3.6 and 6.0). The R_E values are the averaged values of two observed ones. Table 2 and Fig. 1a show the absolute mobilities determined by the least-squares method to give best-fitted R_E values. The mobilities of EDTA anions were given for the divalent anion which was

Table 2

Observed R_E values and absolute mobilities of EDTA and rare-earth–EDTA chelate anions (25°C)

	pH 3.6		pH 6.0		
	R_E (obs.)	Mobility ^a	R_E (obs.)	Mobility ^a	
H ₄ Y	2.26	44.2 ^b	H ₄ Y	2.01	60.7 ^c
LaY ⁻	4.23	20.6	LaY ⁻	4.21	20.7
CeY ⁻	4.23	20.6	CeY ⁻	4.30	20.3
PrY ⁻	4.27	20.4	PrY ⁻	4.34	20.1
NdY ⁻	4.27	20.4	NdY ⁻	4.34	20.1
SmY ⁻	4.25	20.5	SmY ⁻	4.30	20.3
EuY ⁻	4.21	20.7	EuY ⁻	4.23	20.6
GdY ⁻	4.16	20.9	GdY ⁻	4.16	20.9
TbY ⁻	4.10	21.2	TbY ⁻	4.10	21.2
DyY ⁻	4.08	21.3	DyY ⁻	4.08	21.3
HoY ⁻	4.08	21.3	HoY ⁻	4.05	21.4
ErY ⁻	4.08	21.3	ErY ⁻	4.03	21.5
TmY ⁻	4.05	21.4	TmY ⁻	4.03	21.5
YbY ⁻	4.05	21.4	YbY ⁻	4.01	21.6
LuY ⁻	4.05	21.4	LuY ⁻	4.01	21.6
ScY ⁻	3.94	21.9	ScY ⁻	3.99	21.7
YY ⁻	4.05	21.4	YY ⁻	4.05	21.4

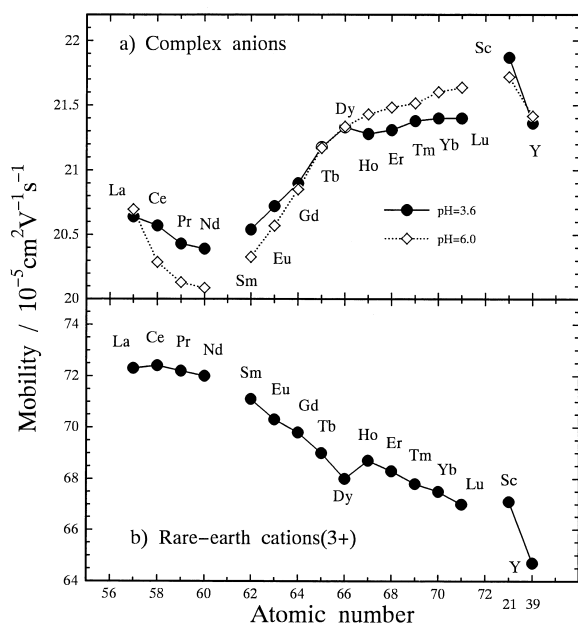
^a Absolute mobility at 25°C ($10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^b Mobility of EDTA dianion (see footnote “c”).^c Mobility of EDTA trianion (these values were obtained simultaneously by least-square method considering coexistence). The used pK_a values for EDTA were $pK_1=2.11$, $pK_2=3.01$, $pK_3=6.73$, $pK_4=11.07$. Original values [21] were corrected to ionic strength=0 using activity coefficients estimated by the Debye–Huckel equation.

Fig. 1. Absolute mobilities of RE–EDTA monoanions (a) and RE trivalent cations (b).

the major component at pH 3.6 and for the trivalent anion which coexisted with the divalent one at pH 6.0.

Obviously, the absolute mobilities of RE–EDTAs were very close to each other in the range $20.4 \cdot 10^{-5}$ – $21.9 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at pH 3.6 and $20.1 \cdot 10^{-5}$ – $21.7 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at pH 6.0. The differences between the mobilities of RE–EDTAs were so small that simultaneous separation of all chelate anions was impossible.

For comparison, absolute mobilities of trivalent rare-earth cations (RE^{3+}) are shown in Fig. 1b [18]. They were in the range $64.2 \cdot 10^{-5}$ – $72.2 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The atomic number (Z) dependence of the absolute mobilities of Fig. 1a was inverted in comparison with that in Fig. 1b. That is, in the case of the chelate anions the mobilities of light lanthanide were smaller than those of heavy lanthanide contrary to the case of the trivalent lanthanide cations.

The decrease of the absolute mobilities of RE^{3+} with the increase of Z is caused by the increase of the hydration number and subsequent increase of the ionic radius [18]. In the case of chelate anions, the

increase of the absolute mobilities with Z might be understood as the result of the decrease of the ionic radii of RE–EDTA anions caused by the decrease of those of central RE ions. However, the existence of the mobility minimum in Fig. 1a could not be explained by the above. A possible explanation was that coexisting ions in the ITP steady state zone might interact with RE–EDTAs to form labile chelates or ion pairs: The addition of the counter cation to RE–EDTA anion may cause the decrease of the anionic charge and the anionic mobility depending on the stability constant of RE–EDTA–counter ion ternary complex.

3.1.2. Separation behavior of RE–EDTA chelates by ITP–PIXE

In order to test the validity of the evaluated mobilities of RE–EDTA anions summarized in Table 2, a mixture of six kinds of complexes (RE=La, Nd, Ho, Er, Tm, Sc, the amount of a sample component was 8.3 nmol) was separated and the fractions were analyzed by PIXE.

Fig. 2 shows the analytical results of the fractions. The separation behavior observed for these six RE–EDTAs was consistent with the mobility data in Table 2. Since the mobility differences between the three RE–EDTAs (RE=Ho, Er, Tm) was only 0.1·

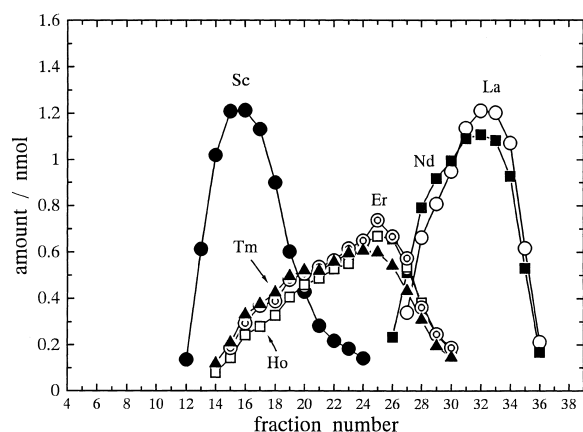


Fig. 2. Analytical results of the fractions for a test mixture of RE–EDTAs (RE=La, Nd, Ho, Er, Tm, Sc) by ITP–PIXE. The concentration of an RE component was 0.417 mM and the injected volume was 20 μ l. The amount of a sample component was 8.3 nmol. The pH of the leading electrolyte was 3.6 (see Table 1).

$10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or less, it is very natural that they formed a mixed zone. The mobility difference between the Sc–EDTA and the above mixed zone was $0.5 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which was enough to allow the Sc–EDTA forming ITP steady state zone. The mobility of Nd–EDTA was smaller than that of La–EDTA by $0.2 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This might be supported by Fig. 2 where the abundance of Nd–EDTA was a little greater than that of La–EDTA in fractions 27–29.

Sample recoveries of six RE–EDTAs were regarded as 100%. As discussed previously [16], the recovery depends on the effective stability constants of samples at the operational condition and the concentration of EDTA coexisting with central metal ions.

Thus high separability cannot be expected for RE–EDTA anions, however they can be utilized in bidirectional ITP for the separation of the anions from the other matrix cations. We have applied this technique to the analysis of an RE ore sample containing Fe matrix, which is reported in the next section.

3.2. Determination of trace rare-earth elements in an iron ore

3.2.1. Separation behavior under the used operational electrolyte system

Fig. 3 shows the separation behavior of bidirectional isotachophoretic separation in the present system. The catholyte simultaneously plays the role of the leading electrolyte for anions and that of the terminating electrolyte for cations. On the other hand, the anolyte is the leading electrolyte for cations and the terminating electrolyte for anions. The anionic leading ion is Cl^- and the cationic one is NH_4^+ . The pH-buffering ion in the catholyte is acetate (AcO^-) and that in the anolyte is β -alanine ($\beta\text{-ala}^+$). AcO^- and $\beta\text{-ala}^+$ also play the role of terminators for anions and cations, respectively.

EDTA in the catholyte was added to suppress the zone bleeding effect of the EDTA complex [19,20]. If no EDTA was contained in the catholyte, as already described [16], the isotachophoretic zone of RE–EDTA $^-$ gradually liberates RE cations during migration in the acidic pH region. Consequently, the recovery of the rare-earth elements may be less than

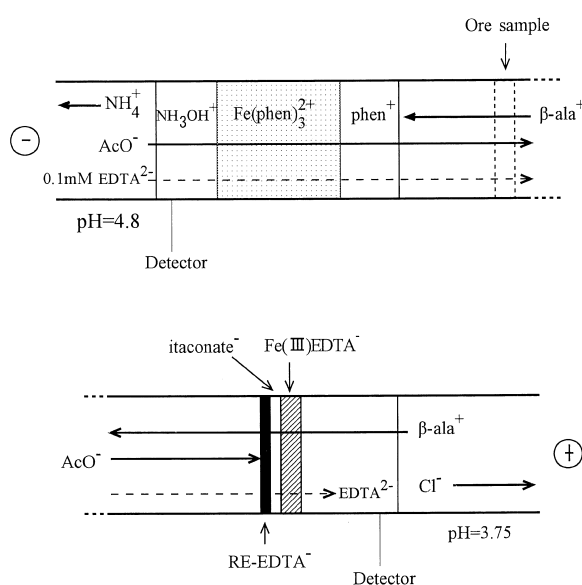


Fig. 3. Schematic diagram of bidirectional isotachopheresis of the ore sample at the steady state. For the electrolyte conditions, see Table 1.

100% depending on the stability constant of the complex anion. 0.1 mM EDTA was enough to suppress the zone-bleeding phenomena.

As shown in Fig. 3, the mobility of EDTA^{2-} is greater than that of RE-EDTA^- , therefore RE-EDTA^{2-} migrates just behind the leading zone. The zone length of EDTA^{2-} zone gradually increases during migration due to continuous supply from the catholyte: that is, the zone does not reach the steady state. Although the RE-EDTA^- zone was continuously passed by EDTA^{2-} from the catholyte, the bleeding effect was suppressed due to that and the zone length of the RE-EDTA^- zone was constant. However, the velocity of the zone front is slightly smaller than the anionic ITP velocity of the present electrolyte system. In this sense, the RE-EDTA^- zone is at a quasi-ITP state.

Excess amounts of EDTA and phen were added to the ore sample for complex formation before ITP separation. NH_2OH was also added to keep iron ions as Fe(II) , since the stability constant of the Fe(II)phen_3^{2+} complex ($\log K=21.3$) is greater than that of the $\text{Fe(III)phen}_3^{3+}$ complex ($\log K=14.3$). On the other hand, stability constants of RE-EDTA^- complexes are in the range of $\log K=15.5$ (La^{3+})–

19.8 (Lu^{3+}) and those of Fe(II)EDTA^{2-} and Fe(III)EDTA^- are $\log K=14.3$ and 25, respectively. If Fe(III) ions exist in the ore sample, Fe(III)EDTA^- may disturb the detection of RE-EDTA^- .

Therefore, before analyzing the real sample, a test mixture of Fe(II) and phen (4 mM:16 mM) containing NH_2OH was analyzed. The calibration line for Fe(II)phen_3^{2+} zone in the examined range of 4–32 nmol showed good linearity with small negative intercept, suggesting the formation of Fe(III)EDTA_3^- during migration in the present electrolyte system. Actual ore sample was also tested. The obtained isotachopherograms are shown in Fig. 4a and b for anions and cations, respectively. It was found that most of Fe ions could be separated from the minor RE ions as Fe(II)phen_3^{2+} and small amount of Fe(III)EDTA^- was formed.

3.2.2. Spacer for Fe(III)EDTA^- and RE-EDTA^-

If the separation of Fe(III)EDTA^- and RE-EDTA^- zones is incomplete, PIXE analysis of fractionated RE ions may be deteriorated because the characteristic X-rays of Fe overlap with those of lanthanide. In fact, a preliminary ITP-PIXE experiment shows the amount of Fe(III)EDTA^- was greater than that of RE-EDTA^- . Fig. 4a shows the obtained anionic isotachopherogram. Therefore a spacer for the Fe(III)EDTA^- and RE-EDTA^- zones was necessary. Consequently we selected itaconic acid utilizing a computer simulation technique based on a mobility and $\text{p}K_a$ database for ca. 300 kinds of anions [15]. The observed R_E value of itaconate zone at $\text{pH}_L=3.6$ was 3.84 and it was just between Fe(III)EDTA^- ($R_E=3.70$) and RE-EDTA^- (≥ 3.93). The pH_L was finally increased to 3.75 taking into account the actual separability. Fig. 4c shows the observed isotachopherogram for a Model mixture of Fe(III) and RE with itaconic acid as the spacer.

3.2.3. Analytical results

Considering the above discussion, 400 μl of the sample solution (0.5 g ore/l) and 15 μl of a 10 mM itaconic acid solution were injected and isotachophoretically separated zones were fractionated. Analytical results by PIXE for anionic fractions are shown in Fig. 5. Obviously the use of itaconate spacer was successful to separate RE-EDTA^- and Fe(III)EDTA^- , and RE components were completely

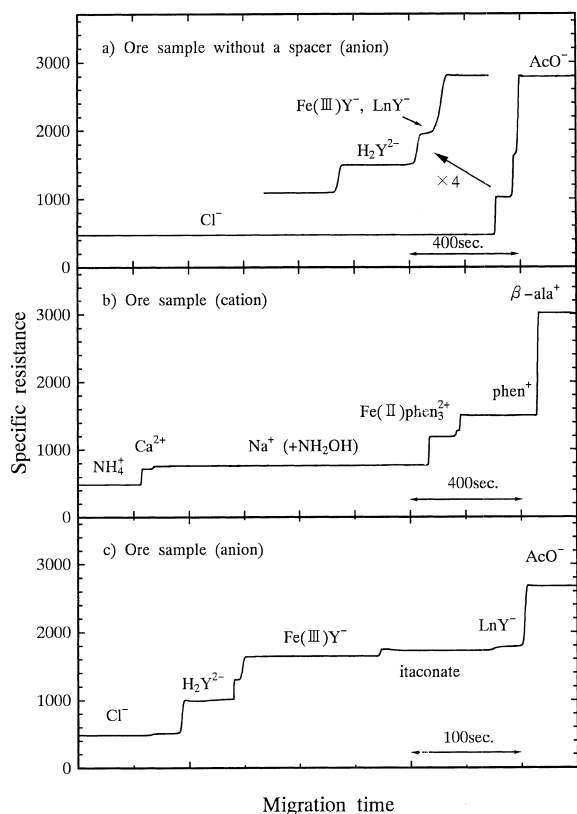


Fig. 4. (a) Anionic isotachopherogram of the real ore without adding the spacer. Injected sample=5 μ l of the 0.5 g/l solution (ore content=2.5 μ g). (b) Cationic isotachopherogram of the real ore corresponding to (a). (c) Anionic isotachopherogram of the model mixture of Fe(III) ion and RE ions with the itaconate spacer. Injected volume of the test mixture was 5 μ l and the concentration of Fe(III) was 3.7 mM and that of RE ions was 0.73 mM. Injected volume of 10 mM itaconic acid (10 mM) was 2 μ l. Migration current=40 μ A for (a), (b) and (c).

separated as RE-EDTA⁻ ions from major components. The mixed zone formation was natural because the mobility difference was small among them as studied in the former section. Although the analysis of the PIXE spectrum for the mixture of RE components was possible by using a spectrum-fitting technique, accuracy was limited depending on the amount of each component.

Table 3 also shows analytical results obtained by ITP-PIXE together with those by PIXE analysis. The determined RE by PIXE were La, Ce, Pr and Nd and the determination of minor RE was disturbed by Fe in the matrix. This is because that the K-X ray

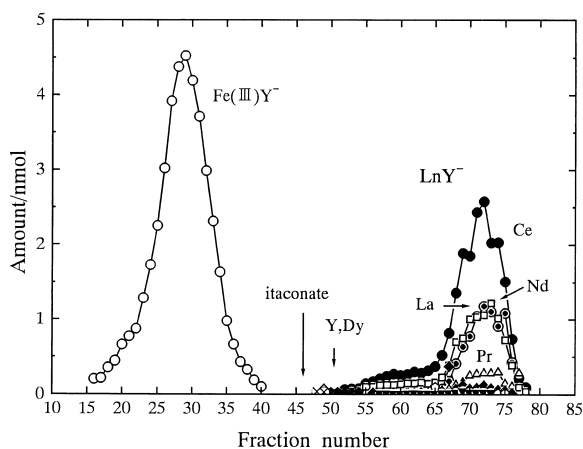


Fig. 5. Analytical results of anionic fractions by PIXE. Injected sample=400 μ l of the 0.5 g/l solution (ore content=200 μ g). Injected volume of 10 mM itaconic acid (10 mM) was 2 μ l. Applied charge=7.5 C.

lines of Fe overlapped with L-X ray lines of medium lanthanide. For bITP-PIXE, all RE was determined. Obviously, the total amount of RE in the 200 μ g ore sample was 6.21 μ g, which corresponded to 7.25 μ g of RE₂O₃. Using this value, abundance of RE₂O₃ was 3.63%, which agreed well with the nominal value of 3.30% as RE_xO_y. In Table 3, analytical errors for minor components Ho–Y were obtained from X-ray counts in PIXE analysis. However, when the found amount was less a few nanograms (abundance is less than 0.005%, w/w), the analytical error might be larger than the listed, since the amount was almost equal to the detection limit under the used experimental conditions. By comparing the abundance of each RE in the analyzed ore with typical ones, the RE in the present iron ore had similar constitution as the monazite.

The total recovered amount of iron was 37.7 μ g, and 93.8% (w/w) was in the form of Fe(II)phen₃²⁺ and 6.2% was Fe(III)EDTA⁻. As already discussed, the conversion from Fe(II)phen₃²⁺ to Fe(III)EDTA⁻ did not occur when no EDTA was contained in the catholyte, the recovery of RE-EDTA⁻ could not be 100%. The conversion rate may be improved more or less, if the EDTA concentration is optimized.

In conclusion, RE-EDTA⁻ was successfully used in ITP-PIXE analysis for the separation of minor RE components in the present iron ore from its major

Table 3
Analytical results by PIXE and bITP-PIXE

RE	PIXE			bITP-PIXE		
	RE	RE ₂ O ₃		RE	RE ₂ O ₃	
	(μg)	μg	% (w/w) ^a	(μg)	μg	% (w/w) ^b
Y	–	–	–	0.007	0.008	0.004
La	0.014	0.016	0.657	1.135	1.331	0.665
Ce	0.030	0.035	1.406	2.957	3.464	1.732
Pr	0.008	0.009	0.375	0.344	0.402	0.201
Nd	0.014	0.016	0.653	1.463	1.706	0.853
Sm	–	–	–	0.177	0.205	0.102
Eu	–	–	–	0.021	0.025	0.012
Gd	–	–	–	0.040	0.046	0.023
Tb	–	–	–	0.017	0.020	0.010
Dy	–	–	–	0.028	0.032	0.016
Ho	–	–	–	0.012	0.002	0.001
Er	–	–	–	0.001	0.001	0.000
Tm	–	–	–	0.005	0.006	0.003
Yb	–	–	–	0.002	0.002	0.001
Lu	–	–	–	0.001	0.001	0.001
RE total	0.066	0.077	3.090	6.209	7.250	3.625
Fe(+) ^c	–	–	–	35.370	50.569	25.285
Fe(–) ^d	–	–	–	2.354	3.366	1.683
Fe total	0.469	0.671	26.822	37.724	53.935	26.968

^a Mass % for the 2.5 μg ore sample.

^b Mass % for the 200 μg ore sample.

^c Fe detected as Fe(II)phen₃²⁺.

^d Fe detected as Fe(III)EDTA[–].

components. Although the isotachophoretic analysis of RE–EDTA[–] mixtures using a conventional detection method is severely limited due to similar electrophoretic mobilities of RE–EDTA[–], it can be very useful when a detection method like PIXE with high analyzability is combined.

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