

Application of electrokinetic supercharging capillary zone electrophoresis to rare-earth ore samples

Hikaru Okamoto, Takeshi Hirokawa*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama 1, Higashi-Hiroshima 739-8527, Japan

Abstract

Capillary zone electrophoresis (CZE) using electrokinetic injection (EKI) with transient isotachopheresis, which was named “electrokinetic supercharging-CZE” (EKS-CZE), was applied to model samples of rare-earth ores (xenotime and monazite) and a real sample of monazite ore, the abundance of the components being greatly different among samples. When simple EKI was applied, separation and detection of rare-earth ions with smaller mobilities than the major component became difficult with an increase of the content of the major component. In contrast, when EKS-CZE was applied, the minor components (Er, Tm, Yb) with contents less than 0.025% (rare-earth/total rare-earth) could be analyzed. The analytical results for minor components in monazite ore agreed with those obtained by isotachopheresis–particle-induced X-ray emission (ITP–PIXE) and inductively coupled plasma atomic emission spectrometry (ICP–AES) with errors less than 17%. The sample amount required for analysis was 9 μg which is 200-fold smaller than that used in ITP–PIXE analysis. Analytical sensitivity of EKS-CZE was comparable with that of ICP–AES.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Electrokinetic supercharging; Injection methods; Rare earth ions

1. Introduction

On-line preconcentration methods such as field-enhanced sample stacking [1–3], transient isotachopheresis (tr-ITP) [3–7], and electrokinetic injection (EKI) [8] have been widely used to improve concentration sensitivity of capillary electrophoresis (CE), which is inherently low due to geometrical restriction. Recently we have proposed EKI with tr-ITP for preconcentration, and the approach was named “electrokinetic supercharging” (EKS) [9]. Although the method is virtually a combination of two already-known techniques, we found it was quite

powerful for capillary zone electrophoresis (CZE) analysis. The procedure of EKS-CZE is as follows: after filling the separation capillary with supporting electrolyte, appropriate amount of a leading electrolyte was filled and electrokinetic injection was performed. After sampling, terminating electrolyte was filled subsequently and separation voltage was applied. This procedure enabled introduction of a large amount of sample components from a dilute sample without deteriorating separation. Consequently, we could analyze 15 rare-earth ions (0.5 $\mu\text{g}/\text{l}$ for each) and the found low limit of detectable concentration was 0.3 $\mu\text{g}/\text{l}$ (1.2 nM for Er, $S/N=3$) [9], which is comparable or even better than that of ion chromatography or inductively coupled plasma atomic emission spectrometry (ICP–AES).

In our previous studies [9–13], preconcentration

*Corresponding author. Tel.: +81-824-227-1111; fax: +81-824-227-192.

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

and separation behavior was investigated for the samples containing rare-earth components with equal concentrations. However, abundances of components in real samples are sometimes significantly imbalanced. For example, in the typical rare-earth ore monazite treated in this paper, the major component was Ce with the abundance of 47.8% (rare-earth/total rare-earth), and the most minor component was Lu with the abundance of 0.001% (rare-earth/total rare-earth). The abundance of Lu was therefore ca. 5×10^4 times smaller than that of Ce. It was interesting to study how EKS-CZE works for the determination of such minor components in real samples.

In the present paper, firstly, preconcentration and separation behavior of EKS-CZE was studied for two model samples: in one model sample, the abundance of Y was changed and the separation behavior was studied for the analysis of xenotime (an yttrium ore) where Y was the major component. In the other model sample, the abundance of La was changed for the analysis of monazite ore, where La and adjacent Ce were the major components. Secondly, on the basis of basic study, EKS-CZE was applied for the trace analysis of two rare-earth ores (xenotime and monazite). We have already analyzed the latter sample by isotachopheresis–particle-induced X-ray emission (ITP–PIXE) and ICP–AES [14] and accurate analytical results have been obtained. Comparative study by EKS-CZE was carried out to clarify its utility in trace analysis in matrix component.

2. Experimental

2.1. Samples, operational systems and chemicals

The model samples were a chloride mixture of 18 cations, alkali–metal ions (K, Na, Li) and trivalent rare-earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y). Model samples were prepared from the stock solutions of the chlorides. The concentration of each component in the samples was in the range from 20 $\mu\text{g}/\text{l}$ to 200 mg/l . Xenotime model sample (1 and 10 mg/l) was prepared from stock solutions of the chlorides according to its typical composition. The used supporting electrolyte (SE) was summarized in Table 1

Table 1
Operational electrolytes used in experiments

L:	100 mM aq. NH_3 , 7.5 mM 2-hydroxyisobutyric acid (HIBA), 2.0 mM malonic acid, 2-ethyl- <i>n</i> -butyric acid (pH 4.8)
T:	1 M HCl
SE:	(1) 30 mM creatinine, 4 mM HIBA, 0.4 mM malonic acid, 2-ethyl- <i>n</i> -butyric acid (pH 4.8) (2) 10 mM 4-methylbenzylamine, 4 mM HIBA, 0.4 mM malonic acid, 2-ethyl- <i>n</i> -butyric acid (pH 4.8)

together with the leading and terminating electrolytes.

The chlorides (analytical grade), malonic acid (analytical grade), 1 M hydrochloric acid (for volumetric analysis) were obtained from Katayama Kagaku (Osaka, Japan), creatinine (extra pure grade) was from Sigma–Aldrich Japan (Tokyo, Japan), 4-methylbenzylamine (>97%,GC) was from Fluka (Buchs, Switzerland), α -hydroxyisobutyric acid (HIBA) and 2-ethyl-*n*-butyric acid (>99%,GC) were from Tokyo Kasei (Tokyo, Japan). Ammonium solution (1 M) was obtained from Nacalai Tesque (Kyoto, Japan). A mixture of rare-earth chloride prepared from monazite was offered by Santoku Kinzoku Kogyo (Tokyo, Japan). Water purified with a Milli-Q Gradient A10 (Nihon Millipore, Tokyo, Japan) was used throughout this work.

2.2. Capillary electrophoresis

The used apparatus was a CAPI-3100 (Otsuka Electronics, Osaka, Japan). Indirect UV absorption was used to obtain electropherograms [$\lambda=220$ nm for creatinine system (SE-1 in Table 1), 214 nm for 4-methylbenzylamine system (SE-2)]. The fused-silica capillary (Otsuka Electronics) with 100 cm length (87.7 cm effective length) \times 75 μm I.D. was used. Analyzed sample volume was 100 μl for all runs. The applied voltage was 20 kV for both electrokinetic injection and separation. The capillary chamber was thermostatted at 25 $^\circ\text{C}$.

Operational procedure of EKS-CZE was as follows: (1) leading electrolyte (L) was injected by negative pressure, (2) the sample solution was

electrokinetically introduced (+20 kV/1 m), (3) terminating electrolyte (T) was injected by negative pressure (typical injection times were 1 and 5 s, estimated plug length was 11 and 55 mm, respectively), and (4) migration started after replacing both reservoirs of SE.

2.3. Determination of trace rare-earth in monazite by standard addition method

Standard addition method was used to determine the concentration of trace rare-earth ions (Er, Tm, Yb) in rare-earth chlorides from monazite. The concentration of the chlorides was 90 mg/l and the concentrations of the added Er, Tm and Yb were 0, 4, 8, 12 and 16 $\mu\text{g/l}$ for Er, 0, 0.5, 1.0, 1.5 and 2.0 $\mu\text{g/l}$ for Tm, and 0, 1, 2, 3 and 4 $\mu\text{g/l}$ for Yb, respectively. The concentration of Er, Tm and Yb were determined from the extrapolations of resulting linear plot (for Er, Tm, Yb) of peak area against additive concentration.

3. Results and discussion

3.1. Choice of co-ion in SE and preconcentration effect in EKI

When EKI is used, the relation of effective mobilities among the UV-visualizing reagent (co-ion) and the sample components is important. This is obvious from the fact that the co-ion can play the role of the leading ion for the sample components whose mobilities are smaller than that of the co-ion. Fig. 1 shows two electropherograms for a cation sample (concentration of rare-earth is 20 $\mu\text{g/l}$) obtained by using different SEs (SE-1 and SE-2 in Table 1).

Obviously from the peak profiles of rare-earth ions in Fig. 1 b, Sm was concentrated but Nd was not, which suggests that the effective mobility of creatinine (co-ion in SE-1) was between Nd and Sm. In order to preconcentrate light rare-earths (La–Nd), it is necessary to inject a leading electrolyte with higher mobility ions than the analyte ions before EKI process. EKS is just such a requested operational procedure.

On the other hand, from Fig. 1b, the effective

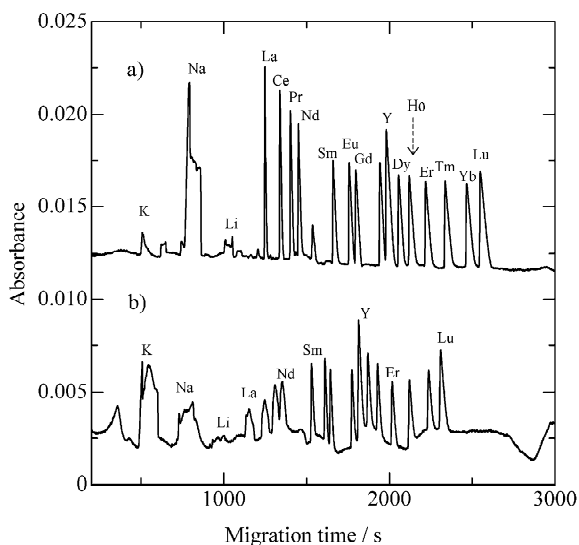


Fig. 1. Effect of the effective mobility of co-ion on preconcentration behavior in EKI. Sample: K (26 μM), Na (34 μM), Li (47 μM) and trivalent rare earth (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y, 20 $\mu\text{g/l}$ for each), (a) supporting electrolyte, SE-2; (b) supporting electrolyte, SE-1. See Table 1 for supporting electrolytes. EKI time: 150 s (+20 kV/1 m).

mobility of 4-methylbenzylamine (abbreviated as 4-MB hereafter, the co-ion in SE-2) was between those of Li and La. In the following discussion SE-2 was used, since we could expect better separation behavior when using the electrolyte.

3.2. Effect of major components on EKI-CZE

Separation behavior of La, Sm, Y, Dy, Ho and Er (20 $\mu\text{g/l}$ for each) in EKI-CZE was studied when concentration of coexisting Y was increased up to 20 mg/l (1:1000). Fig. 2 shows the obtained electropherograms. Obviously, both resolution and peak profiles were deteriorated with increasing the Y concentration. Although the effective mobility of the co-ion 4-MB was greater than all of the treated rare-earth ions, the separation of Dy, Ho, and Er was insufficient. This might be explained as the result of two phenomena: the decrease of the transference number of the minor components at high Y concentrations and the tr-ITP state being too short for the complete separation of Y from the minor components (insufficient electric charge during the tr-ITP process). Although the former factor equally affects

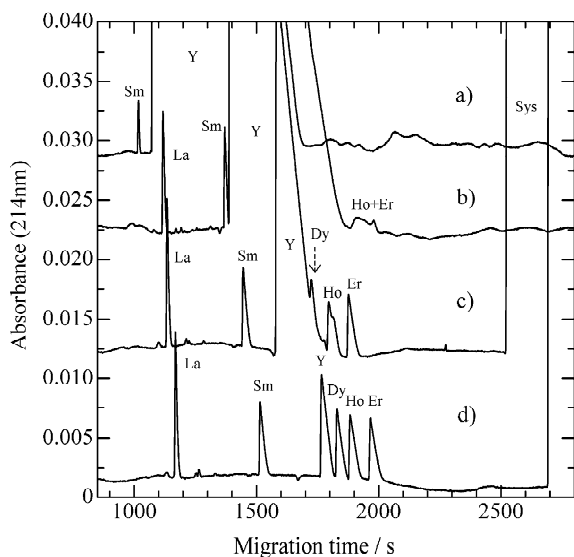


Fig. 2. Effect of excess of Y on electropherograms obtained by EKI-CZE for model mixtures containing six rare-earth ions. Original sample: La, Sm, Y, Dy, Ho and Er (20 $\mu\text{g/l}$ for each), (a) +20 mg/l (Y), (b) +2 mg/l (Y), (c) +0.2 mg/l (Y), (d) original sample, EKI condition: 200 s (+20 kV/1 m).

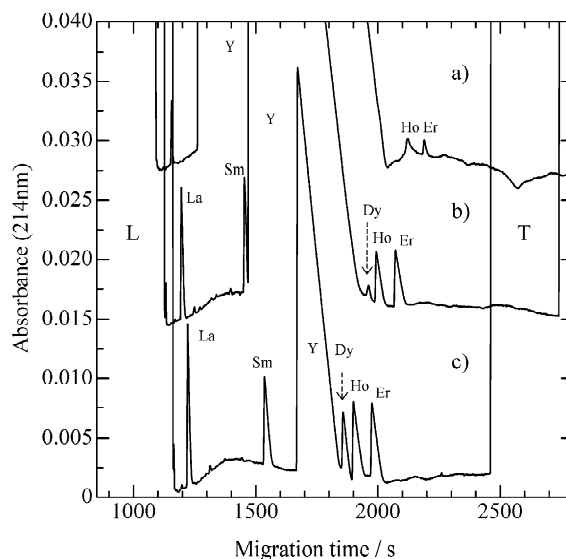


Fig. 3. Effect of excess of Y on electropherograms obtained by EKS-CZE for model mixtures containing six rare-earth ions. Samples as in Fig. 2. (a) +20 mg/l (Y), (b) +2 mg/l (Y), (c) +0.2 mg/l (Y), L and T were injected by negative pressure. L: 5 s. EKI, T: 1 s, EKI conditions were as in Fig. 2.

EKS-CZE, the tr-ITP conditions could be improved in EKS-CZE.

3.3. Effect of major components on EKS-CZE

Next, EKS-CZE was applied for the same samples as in Fig. 2. Fig. 3 shows electropherograms obtained. Although the peaks of 20 $\mu\text{g/l}$ Dy, Ho and Er were not observed by EKI-CZE in the presence of 2 mg/l Y (Fig. 2b), they could be observed by applying EKS-CZE (Fig. 3b). This suggests that EKS-CZE is more effective for trace analysis from samples with uneven distribution of analytes in comparison with EKI-CZE. The smaller peak of Dy was due to insufficient electric charge during the tr-ITP process. The situation regarding limited detectability was the same as in Fig. 3a.

Similar experiments were carried out for a model mixture where La was the major component (2 mg/l) and the others were at a 2 $\mu\text{g/l}$ level (1000:1). Fig. 4 shows the obtained electropherograms. When EKI-CZE was used, only Er was detected as shown in Fig. 4b. However, all peaks due to Ce, Pr, Nd, Sm and Er were successfully observed when EKS-CZE

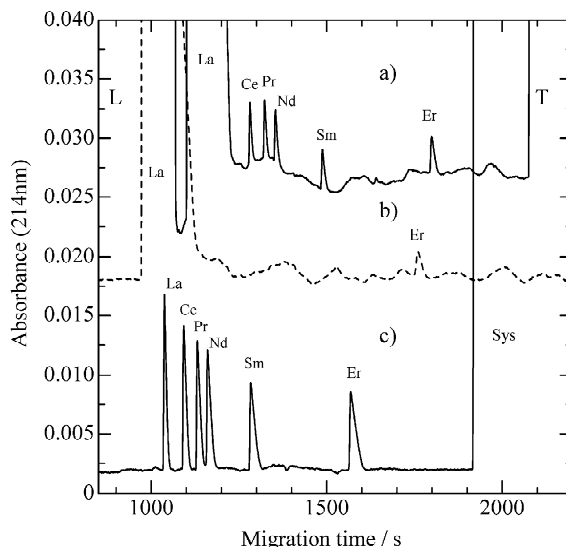


Fig. 4. Effect of excess of La on electropherograms obtained by EKS-CZE and EKI-CZE for model mixtures containing six rare-earth ions. Original sample: La, Ce, Pr, Nd, Sm and Er (20 $\mu\text{g/l}$ for each), (a) +20 mg/l (La), (b) +2 mg/l (La), (c) original sample. Method: (a) EKS (L: 5 s, EKI: 200 s, T: 1 s), (b) EKI: 200 s, (c) EKI: 200 s; other conditions as in Fig. 3.

was used, again proving its high analytical potential for analyzing trace components.

3.4. Analysis of xenotime model sample by EKI-CZE and EKS-CZE

The abundances of RE in xenotime model sample (rare-earth/total rare-earth) are shown in Table 2. Fig. 5 shows typical electropherograms for the 1 and the 10 mg/l samples. The sample was overloaded on the purpose to observe the minor peaks. Since the abundance was not so much different among the components (e.g., Er:Y=1:10, Lu:Y=1:133), there was no substantial difference in resolution EKI-CZE and EKS-CZE, when the 1 mg/l sample was analyzed (cf. Fig. 5a and b). However, even in this case Dy could not be separated from Y by EKI-CZE (Fig. 5b), and moreover all of the heavy rare-earth ions (Dy–Lu) could not be separated when the 10 mg/l sample was used (Fig. 5d). Obviously from the peak shapes in Fig. 5d, the heavy rare-earth reached the detector still in the tr-ITP state. Contrarily, the peak profiles in EKS-CZE remained sharp in spite of high sample-load (Fig. 5c). Thus, it is apparent that a comparatively large amount of sample could be introduced by EKS-CZE without deterioration of separation. In other words, the dynamic range of EKS-CZE was wider than that of EKI-CZE as a consequence of high preconcentration ability of the former process.

3.5. Analysis of monazite ore by EKS-CZE

Finally a real sample (a mixture of rare-earth chlorides prepared from monazite ore) was analyzed. As shown in Table 2, the abundances of the light rare-earth ions (La–Nd) were over 20% but those of the heavy rare-earth ions (Ho, Er, Tm, Yb, Lu) were less than 0.025%. Fig. 6 shows an electropherogram

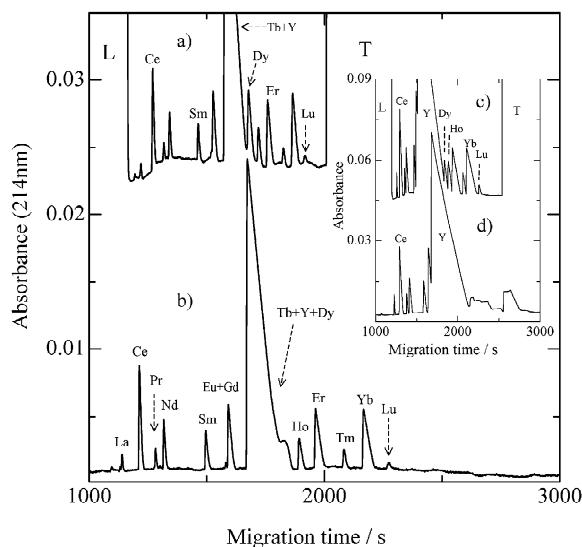


Fig. 5. EKS-CZE and EKI-CZE analysis of xenotime. Sample: (a,b) 1 mg/l (sample: 100 μ l, 0.1 μ g), (c,d) 10 mg/l (sample: 100 μ l, 1 μ g). Method: (a,c) EKS (L: 5 s, EKI: 50 s, T: 1 s), (b,d) EKI: 50 s; other conditions as in Fig. 3.

for a 90 mg/l sample. Although the light rare-earths (La–Nd) were obviously overloaded so that they formed a huge merged peak (see Fig. 6), Sm, Gd and Y could still be separated. No peaks of Sm, Gd and Y were found when EKI-CZE was applied (data not shown). The insert shows a close-up of the electropherogram in the region of heavy rare-earth ion migration. The peaks therein were identified as Ho, Er, Tm and Yb by standard additions; however, Lu could not be observed as its peak was probably merged with the terminator. The shoulder peak at the peak of Y was due to unresolved Dy.

Concentration of the trace components (Er, Tm, Yb) was estimated using standard addition method. The obtained results are summarized in Table 3, together with the analytical data of ITP-PIXE and

Table 2

Abundances (rare-earth/total rare-earth %) of rare-earth elements in xenotime and monazite

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Xenotime ^a	0.54	5.17	0.72	2.33	2.00	0.22	4.33	1.06	9.28	2.22	5.78	0.94	6.67	0.44	58.3
Monazite ^b	23.1	47.8	5.68	19.7	2.74	0.022	1.07	0.15	0.23	0.019 ^c	0.025	0.002 ^c	0.006	0.001	0.438

^a Model sample (prepared abundance) [15].

^b Analytical results obtained by ICP-AES and ITP-PIXE [14].

^c Rare-earth/total rare-earth obtained by ITP-PIXE, others were obtained by ICP-AES.

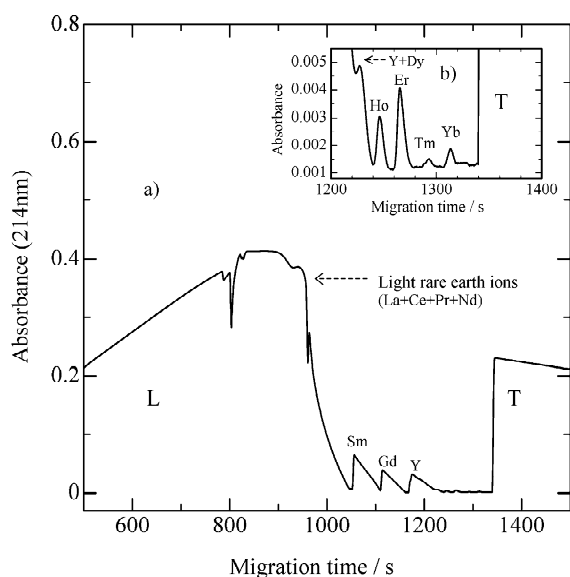


Fig. 6. EKS-CZE analysis of monazite. Sample: 90 mg/l (100 μ l, 9 μ g), (a) EKS (L: 5 s, EKI: 500 s, T: 1 s); (b) close-up; other conditions as in Fig. 3.

ICP-AES [14]. The concentrations (μ g/l) for ITP-PIXE and ICP-AES in Table 3 were recalculated values for the 90 mg/l sample. The results obtained by EKS-CZE were in good agreement with data of independent methods within experimental errors ($<17\%$). It should be emphasized that the sample amount used in EKS-CZE analysis was only 9 μ g, whereas from 1.8- to 8.8-mg samples were required for ITP-PIXE. Since high sensitivity of EKS-CZE is obvious from the present study, quantitative analysis

for light rare-earth ions was not done. For that purpose, EKI time should be reduced and optimized.

4. Conclusion

EKS-CZE is a powerful technique to analyze trace constituents coexisting with major components. Limitation of EKI-CZE was obvious because transition from the initial ITP state to the CZE state could not be controlled after the EKI process. This means that after the EKI process, the ITP process (exactly speaking, a moving boundary process) begins to turn to the CZE process due to the migration of co-ion from the SE reservoir. Injection of the terminating electrolyte in EKS-CZE is crucial to change the moving boundary process to the ITP process and maintain the ITP state for a while. This is essential not to deteriorate the separation of sample components that are electrokinetically introduced.

References

- [1] J.P. Quirino, S. Terabe, J. Chromatogr. A 902 (2000) 119, and references cited therein.
- [2] J.L. Beckers, F.M. Everaerts, J. Chromatogr. 508 (1990) 19.
- [3] J.L. Beckers, P. Bocek, Electrophoresis 21 (2000) 2747.
- [4] P. Gebauer, W. Thormann, P. Bocek, J. Chromatogr. 608 (1992) 47.
- [5] F. Foret, E. Szoko, B.L. Karger, J. Chromatogr. 608 (1992) 3.
- [6] P. Gebauer, W. Thormann, P. Bocek, Electrophoresis 16 (1995) 2039.

Table 3

Concentration (μ g/l) of trace rare-earth elements in the rare-earth chlorides from monazite (90 mg/l) evaluated by ITP-PIXE, ICP-AES and EKS-CZE

Rare-earth	ITP-PIXE 1 ^a	ITP-PIXE 2 ^b	ICP-AES	Average ^c	EKS-CZE	Error (%)	Rare-earth/total rare-earth (%)
Ho	6.19 \pm 0.23	5.21 \pm 0.10	9.45 \pm 0.33	6.95 (5.70)	–	–	0.019 \pm 3 \times 10 ⁻⁴ ^d
Er	7.17 \pm 0.07	6.19 \pm 0.02	8.15 \pm 0.17	7.16	7.6 \pm 0.67	6.1	0.025 \pm 5 \times 10 ⁻⁴
Tm	0.65 \pm 0.10	0.65 \pm 0.02	4.9 \pm 0.7*	0.63	0.73 \pm 0.14	15.7	0.002 \pm 3 \times 10 ⁻⁴ ^d
Yb	2.0 \pm 0.2	1.3 \pm 0.1	2.0 \pm 0.1	1.74	1.45 \pm 0.32	16.6	0.006 \pm 3 \times 10 ⁻⁴

^a Analysed sample amount: 57.3 μ g (La–Dy), 1762 μ g (Ho–Lu, Y) [14].

^b Analysed sample amount: 8808 μ g [14]; EKS-CZE: 9 μ g.

^c Averaged values for ITP-PIXE 1, 2 and ICP-AES [14]. The value * was not included, because it was accompanied by large error due to spectral disturbance.

^d Rare-earth/total rare-earth obtained by ITP-PIXE 1. Others were obtained by ICP-AES.

- [7] L. Krivankova, P. Pantuckova, P. Bocek, J. Chromatogr. A 838 (1999) 55.
- [8] Z. Krivacky, A. Gelencer, J. Hlavay, G. Kiss, Z. Sarvari, J. Chromatogr. A 834 (1999) 21.
- [9] T. Hirokawa, H. Okamoto, B. Gas, Electrophoresis (2003) in press.
- [10] T. Hirokawa, N. Ikuta, T. Yoshiyama, H. Okamoto, Electrophoresis 22 (2001) 3444.
- [11] T. Hirokawa, H. Okamoto, N. Ikuta, Electrophoresis 22 (2001) 3483.
- [12] T. Hirokawa, H. Okamoto, N. Ikuta, B. Gas, Anal. Sci. 17 (2001) i185.
- [13] H. Okamoto, N. Ikuta, T. Hirokawa, Anal. Sci. 17 (2001) i925.
- [14] J. Hu, T. Hirokawa, F. Nishiyama, Y. Kiso, K. Ito, E. Shoto, J. Chromatogr. 594 (1992) 371.
- [15] T. Hirokawa, W. Xia, F. Nishiyama, H. Takemi, K. Ito, E. Shoto, Anal. Sci. 11 (1995) 801.