



ELSEVIER

Journal of Chromatography A, 802 (1998) 203–210

JOURNAL OF
CHROMATOGRAPHY A

Separation of rare-earth ions by isotachopheresis and capillary zone electrophoresis

Qinglu Mao, Yoshio Hashimoto, Yuuki Manabe, Natsuki Ikuta, Fumitaka Nishiyama, Takeshi Hirokawa*

Applied Physics and Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama 1, Higashi-hiroshima 739, Japan

Abstract

The simultaneous separations of 15 rare-earth (RE) ions including yttrium and lanthanide both by isotachopheresis (ITP) and by capillary zone electrophoresis (CZE) were achieved by using the developed electrolyte systems containing α -hydroxyisobutyric acid (HIBA) as main complexing agent and malonic acid as the assistant one. The successful separation of Y^{3+} from Dy^{3+} without loss of the separation of Eu^{3+} and Gd^{3+} was briefly summarized. Based on the assumed equilibria existed in steady state zone while using such an electrolyte system with binary complexing agents, the effective mobilities of the RE complex ions and the qualitative indicies (R_E , the ratio of the specific conductivity of the sample zone to that of the leading zone) for the RE complex zone were theoretically simulated. The reason for the successful separation was clarified from the view of complex formation, and the simulated isotachopherogram for an optimum electrolyte system was then obtained. The validity of the simulation was checked by comparison of the simulated R_E with the observed ones. Furthermore, the historic sample didym prepared from a RE ore by Brauner was analyzed by ITP–particle-induced X-ray emission as well as by CZE, where the supporting electrolyte for CZE analysis is 30 mM creatinine containing 4 mM HIBA and 0.4 mM malonic acid buffered by 2-ethylbutyric acid to pH 4.8. © 1998 Elsevier Science B.V.

Keywords: Isotachopheresis; Buffer composition; Complexation; Rare-earth ions; Inorganic cations; Hydroxyisobutyric acid; Malonic acid

1. Introduction

The separation of rare-earth ions plays an important role in the analytical determination of the rare-earth samples, especially of the ores. However, this separation is very difficult due to the highly similar properties of RE ions. In such cases, electrophoresis including isotachopheresis (ITP) and capillary zone electrophoresis (CZE) has proved to be very powerful for the separation of lanthanide ions by employing α -hydroxyisobutyric acid (HIBA) as a complex-forming agent [1–3]. While recognizing the

importance of separation of yttrium from lanthanide ions, binary complexing agents containing HIBA as the main complexing agent and tartaric acid as the assistant one was used for the analysis of several RE ores [4,5]. The weak point of this electrolyte system is that the simultaneous separation of yttrium together with lanthanide ions was not achieved. For this reason, recently, an electrolyte system containing HIBA as the main complexing agent and malonic acid as an assistant one was successfully developed for the simultaneous separation of yttrium and lanthanide ions by ITP [6].

On the other hand, theoretical simulation has been widely accepted as a powerful method for optimizing

*Corresponding author.

the separation conditions and simulating electropherograms. Especially in isotachopheresis, the pH and ionic strength of the separated zones are different from each other and, no practical separability assessment is possible without a theoretical approach when the sample has a complex constitution. Theoretical approach regarding separation optimization in ITP utilizing a computer simulation technique can at least limit the range of experimental survey [7]. The separation of RE ions, especially of lanthanide ions, has served as a typical example for elucidating the ITP separation theory in the past decades. However, due to the limitation of the electrolyte system employing HIBA as complexing agent, only the separation of fourteen lanthanide ions was theoretically optimized and simulated [8]. In this paper, theoretical simulation for ITP separation of the fifteen RE ions was given on the basis of the assumed equilibria occurring in the steady state sample zones while HIBA and malonic acid were used as the binary complexing agents. The main complex equilibria which control the simultaneous separation are clarified. Then, the analytical results of the didym sample, by ITP–particle-induced X-ray emission (PIXE) using the developed electrolyte and by CZE using a similar electrolyte are reported and compared.

2. Experimental

2.1. Samples, chemicals and operational electrolyte system

For ITP separation, a standard sample with a concentration of 0.33 mM for each RE ion (Y^{3+} , La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} and Lu^{3+}) was prepared from 5 mM stock solutions of the chlorides. The real sample is 2 g/l $[Di_2(SO_4)_3 \cdot H_2O]$ which was prepared by dissolving didym into diluting H_2SO_4 solution. The didym sample was prepared by Brauner (1855–1935) about 100 years ago and kept by the Inorganic Chemistry Laboratory at Charles University (Prague, Czech Republic). Li^+ was used as the internal standard (I.S.) for the analysis of didym. To suppress electroendosmosis, 0.1% hydroxypropylcellulose (HPC) was added into the

electrolytes. The operational conditions for ITP separation are listed in Table 1.

For CZE separation and analysis, RE standard samples as well as those for the calibration line with a concentration range from 2.5 mg/l to 200 mg/l were prepared from the 3200 mg/l RE stock solutions. Real sample is 1.0 g/l didym solution and Li^+ was used as I.S. The supporting electrolyte was 30 mM creatinine, 4 mM HIBA, 0.4 mM malonic acid buffered by 2-ethylbutyric acid to pH 4.8 where creatinine served as the UV visualizing agent. An expanded pH meter of Horiba Model F7-AD (Tokyo, Japan) was used for pH measurement. All the chemicals used in this work are as specified in [6].

2.2. ITP and CZE analysis

For ITP separation, the detector was a high frequency contactless conductivity detector (HFCCD) [9] in which a fused-silica capillary was used and thermostatted to 25°C by a Peltier device. The detector was combined with the separation unit of an ITP analyzer (Labeco Zki-001, Slovakia). The separation column was a PTFE tube (25 cm×0.32 mm I.D.). The high voltage power supply was that for a Shimadzu IP-2A (Kyoto, Japan).

CAP1-3100 (Otsuka electronics) was used for CZE separation and analysis of the didym sample. The fused-silica capillary was 40 cm (27.7 cm effective length for detection)×75 μm I.D. The applied voltage was 10 kV. Sample siphoning lasted 30–120 s with a height difference of 20 mm. Analysis was

Table 1
Operational electrolyte systems used for ITP analysis of the RE ores

Leading electrolyte	20 mM ammonia water
Complexing agent	(1) 7.5 mM HIBA (2) 2.0 mM malonic acid
pH buffer	2-Ethylbutyric acid (pH 4.80)
Additive	0.1% HPC
Terminating electrolyte	20 mM carnitine hydrochloride
Additive	0.1% HPC
Electric charge amount	8.8 C
Pump speed	~10 s/fraction
Sample	Didym $[Di_2(SO_4)_3 \cdot 8H_2O]$ 2.0 g/l Internal standard, Li^+
Injection amount	(a) 5 μl (b) 40 μl (c) 120 μl

performed at 25°C with an indirect UV detection at 220 nm.

For theoretical simulation, a program called *sips* [7,10,11] was performed on a personal computer after a modification for treating the present binary complexing agent system.

2.3. PIXE analysis

To improve the detection limit, the off-line combination of ITP with PIXE, which is a multi-elemental method with high sensitivity [12], was used for analyzing didym. For the PIXE spectra measurement, a Van de Graaff accelerator at our faculty was used (Nisshin High Voltage Co. Model AN-2500, Tokyo, Japan). The detector was a high pure Ge detector (an ORTEC model GLP-10180, USA) and the multi-channel analyzer was a Laboratory Equipment Model AMS-1000 (Tokyo, Japan).

Nuclepore filter (Nuclepore, USA) used as the target backing was of thickness 5 μm with a pore size 0.1 μm . The fraction was dropped on the Nuclepore filter directly from the nozzle of the preparative isotachopheretic analyzer [13]. After drying in a desiccator, it was used as the PIXE target. The amount of each RE element was determined by comparing its X-ray counts with those of the standard targets.

3. Results and discussion

3.1. Simultaneous separation of yttrium and lanthanide ions

As detailed in our previous paper [6], several organic acids having similar structures, such as malonic, malic, tartaric and glycolic acid, have been tried as an assistant complexing agent to HIBA system for the simultaneous separation of yttrium and lanthanide ions. While using tartaric acid as assistant, Y^{3+} was successfully separated from lanthanide ions, however, the separation of Gd^{3+} – Eu^{3+} was lost [5]. According to our investigation, only malonic acid is successful for the separation. A leading electrolyte of 20 mM ammonia solution containing 2 mM malonic acid and 7.5 mM HIBA (pH 4.8, 2-ethylbutyric acid buffer) and a terminating

one of 20 mM carnitine hydrochloride was found to be an optimized operation electrolyte system for the simultaneous separation. Fig. 1 shows the isotachopherogram of fifteen RE ions in a standard samples using the operational electrolyte system.

The reason for the successfully simultaneous separation, on one hand, can be attributed to the molecular structures of the complexing agents. The bite distance of HIBA formed by two oxygen atoms from an OH and a COOH group, and that of malonic acid formed from two COOH groups recognized the complexing difference between yttrium and lanthanide ions. This difference in complexation results in a sufficient mobility difference between Y^{3+} and Dy^{3+} without decreasing that between Eu^{3+} and Gd^{3+} as confirmed by checking the effective mobility of RE ions in the electrolyte system. From another viewpoint, by evaluating the stability constants of RE–malonate complexes where 2-ethylbutyric acid

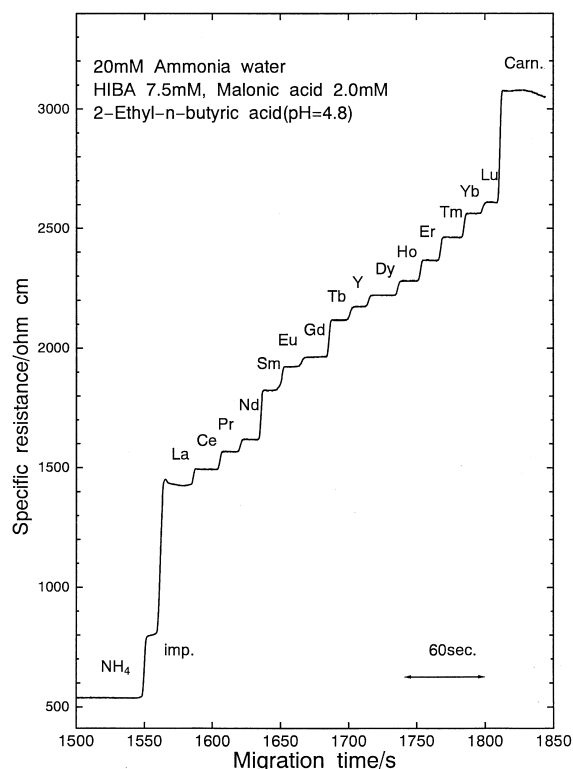


Fig. 1. Observed isotachopherogram for the 15 RE ions by using the developed electrolyte system. Sample injection: 5 μl , migration current: 40 μA .

was used as the pH buffer, it was observed that the successful separation was due to the smaller stability constants of Y^{3+} –malonate complexes over those of the medium lanthanide elements to be separated.

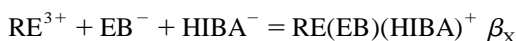
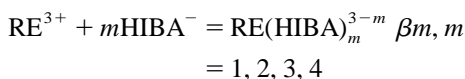
We have investigated the ITP behavior of Sc^{3+} in detail though RE ores seldom contain Sc^{3+} . It was observed that Sc^{3+} cannot be detected in the cation side of ITP due to its much lower effective mobility than the actual terminator (protons) in our developed electrolyte system for ITP separation. It can be detected on the anion side while EDTA was employed as the complexing agent. As a result, it is difficult to simultaneously separate Sc^{3+} together with yttrium and lanthanide ions by ITP.

Following the successful ITP separation, a similar electrolyte to the leading one of ITP for CZE separation of the 15 RE ions was also developed. Fig. 2 gives the complete separation of the fifteen RE ions in a standard sample while using 30 mM creatinine solution containing 8 mM HIBA, 0.7–0.9

mM malonic acid buffered by 2EA (pH 4.8). By the way, it has been observed that Sc^{3+} can be detected together with other RE ions in CZE separation.

3.2. Theoretical simulation of ITP separation of RE ions in the developed electrolyte system

For the above developed electrolyte system, it is practically important to simulate out the qualitative and quantitative indices of such a separation so that the complex formations which determine the successful separation can be clarified. To simulate the ITP separation, a function describing the effective mobilities of RE ions is necessary. The function depends on the complex-forming equilibria in the steady state sample zone. Since the equilibria occurring in the real sample zones are estimated to be very complicated, a simplified model was then used for our simulation where the considered complex species were RE–HIBA, RE–malonic acid (MAL), RE–2EB and the cross ones of RE ions with HIBA and 2EB. All of the equilibria included in our model were as follows:



All other equilibria including those of some cross complexations in the system such as RE(HIBA) (MAL) were ignored due to the fact that we have no data of mobilities and stability constants. Consequently, the effective mobility (\bar{m}) of RE ions concerning with the above equilibria can be expressed as:

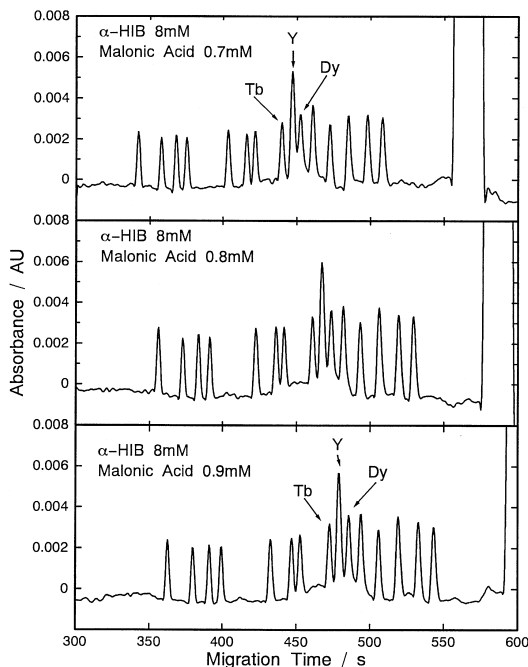


Fig. 2. CZE separation of 15 RE ions with indirect UV detection by using the developed supporting electrolyte. Sample concentration: 50 mg/l for each RE ion. Sample siphoning: 20 mm for 30 s.

$$\bar{m}_{RE} = \frac{m_{RE}[RE^{3+}] + m_n[RE(EB)_n^{3-n}] + m_m[RE(HIBA)_m^{3-m}] + m_k[RE(MAL)_k^{3-2k}] + m_X[RE(EB^-)(HIBA^-)]}{[RE^{3+}] + [RE(EB)_n^{3-n}] + [RE(HIBA)_m^{3-m}] + [RE(MAL)_k^{3-2k}] + [RE(EB^-)(HIBA^-)]}$$

$$= \frac{m_{RE} + m_n\beta_n[EB^-]^n + m_m\beta_m[HIBA^-]^m + m_k\beta_k[MAL^{2-}]^k + m_X\beta_X[EB^-][HIBA^-]}{1 + \beta_n[EB^-]^n + \beta_m[EB^-]^m + \beta_k[MAL^{2-}]^k + \beta_X[EB^-][HIBA^-]}$$

where $n=1, 2$ for the RE complexes with 2EB; $m=1, 2, 3, 4$ for those with HIBA; $k=1, 2$ for those with MAL; subscript X represents the cross complex of RE ion with 2EB and HIBA. The concentrations of $2EB^-$ and $HIBA^-$ are determined by the total concentration of 2EB and HIBA and the pH in the sample zone through the mass balance equations [8,11,12], respectively.

Mobilities and stability constants in the above equations were mainly taken from the literature and part of them were obtained by our isotachopheric method. Table 2 shows the physicochemical constants of La^{3+} , Tb^{3+} , Y^{3+} , Dy^{3+} and Lu^{3+} used in the present simulation. The stability constants of RE–HIBA complexes obtained by Powell et al. [14] were used after correcting them to the infinite dilution. The mobilities of RE–HIBA complexes in Table 2 were determined by the least squares method to get best-fitted RE values, while the stability constants were fixed to the literature-cited values.

Iterative calculation is then performed by varying the pH of a sample zone to find the pH at which all of ITP steady state conditions are satisfied. Under this steady state pH, based on the equations included in the ITP conditions, the concentrations of the sample and pH buffer, the effective mobilities, the

conductivities of the zones can be calculated [7,10,11,15]. Although the separability depends upon the mobility difference in the mixed zone, the mobility difference at the steady state, or the difference of the R_E values, was used as a criterion for separation optimization, since simulation of the transient mixed zone [16] is practically impossible for such a complex system. The qualitative index (the ratio of potential gradient (E) or specific conductivity (κ) of the separated zone to that of the leading zone in the steady state, R_E) was obtained through $R_E = E_S/E_L = \kappa_L/\kappa_S = \bar{m}_L/\bar{m}_S$.

Table 3 listed the simulated R_E values and the observed ones, and Fig. 3 shows the simulated isotachopherogram for the separation of 15 RE ions using the simulated R_E values and zone passing time. Obviously present separation of fifteen REEs were successfully simulated, although the simulated R_E values were significantly underestimated ($\sim 10\%$) in comparison with the observed ones. However, this was not surprising because of the simplicity of our model. As described in Section 3.1, the real complex-forming equilibria might not be so simple and some additional cross complexes such as RE–(HIBA)(MAL) complex should be taken into account.

Table 2
Physicochemical constants of La^{3+} , Tb^{3+} , Y^{3+} , Dy^{3+} and Lu^{3+} used for simulation (25°C)

Complex ions	La^{3+}		Tb^{3+}		Y^{3+}		Dy^{3+}		Lu^{3+}	
	m^a	$\log K^b$	m^a	$\log K^b$	m^a	$\log K^b$	m^a	$\log K^b$	m^a	$\log K^b$
Ln^{3+}	72.3	6.00 ^c	69.0	6.00 ^c	64.7	6.00 ^c	68.0	6.00 ^c	67.0	6.00 ^c
$LnHIB^{2+}$	48.0	3.145	36.1	3.637	33.6	3.731	35.0	3.802	30.1	4.195
$Ln(HIB)_2^+$	24.0	5.308	18.1	6.520	16.8	6.680	17.5	6.788	15.1	7.362
$Ln(HIB)_3^0$	0.0	6.645	0.0	8.517	0.0	8.597	0.0	8.955	0.0	9.907
$Ln(HIB)_4^-$	–24.0	6.913	–18.1	9.690	–16.8	9.370	–17.5	9.820	–15.1	11.06
$LnMal^+$	18.7	4.955	15.9	5.448	16.4	5.409	15.8	5.464	15.3	5.517
$Ln2EB^{2+}$	39.3	2.07	38.1	2.190	42.8	1.900	38.0	2.220	37.3	2.33
$Ln(2EB)_2^+$	17.0	3.43	16.7	3.970	18.0	3.860	16.6	3.880	16.4	4.19
$Ln(2EB)HIB^+$	17.2	5.29	16.9	5.934	18.3	5.978	16.8	6.011	16.6	6.35

^a Mobility ($10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

^b Overall stability constants.

^c pK_a , assumed value.

Table 3
Comparison of observed and simulated R_E values

REEs	R_E , obs	R_E , sim	Error (%)	REEs	R_E , obs	R_E , sim	Error (%)
La	2.73	2.49	-8.8	Y	4.26	3.86	-9.4
Ce	2.85	2.68	-6.0	Dy	4.38	3.96	-9.6
Pr	2.98	2.81	-5.7	Ho	4.56	4.10	-10.1
Nd	3.08	2.92	-5.2	Er	4.73	4.18	-11.6
Sm	3.49	3.23	-7.4	Tm	4.94	4.43	-10.3
Eu	3.68	3.35	-7.0	Yb	5.02	4.66	-7.2
Gd	3.75	3.46	-7.7	Lu	5.17	4.81	-7.0
Tb	4.06	3.77	-7.1				

Although it is certain that the successful separation depends on the difference of the abundances among the complex ions, this was not so clearly verified in spite of the simulation of the steady state zone: Table 4 shows several steady state zone parameters, the total concentration (C^tS), the abundances of the complex ions (%c), and the contribution of each complex ion to the effective mobility (%m) calcu-

lated for La^{3+} , Tb^{3+} , Y^{3+} , Dy^{3+} and Lu^{3+} . In summary, from this table, $\text{RE}(\text{HIBA})_n^{3-n}$ ($n=1,3$) complex ions, $\text{RE}(\text{MAL})$ and $\text{RE}(\text{HIBA})(2\text{EB})^+$ should be taken into account for the simulation and, the complex ions of $\text{RE}(\text{HIBA})_4^-$ and $\text{RE}(2\text{EB})_2^+$ could be neglected due to their low abundance. Table 4 also shows the percent contribution of each complex ions to the effective mobility. From these parameters, we found that the contribution of $\text{RE}(\text{HIBA})_2^{2+}$ to the mobility is almost the same among Tb^{3+} , Y^{3+} and Dy^{3+} , but $\text{RE}(\text{HIBA})_2^{2+}$ increased in that order, while the contribution of $\text{RE}(\text{MAL})^+$ is almost the same between Y^{3+} and Dy^{3+} . This may be closely related with the successful separation of Y^{3+} from the others.

The quantitative indices of zone lengths can be easily obtained according to total concentration of the sample in the sample zone. The simulated values agreed with the observed values with deviations of less than a few percent. For example, the observed zone lengths for 10 nmol Gd, Tb and Dy at a migration current of 40 μA were 87.2, 83.3, and 82.1 s while the simulated ones were 87.0, 88.8 and 88.8 s with deviations of -0.2%, +6.6% and +7.5%, respectively. It is obvious that the simulation gives a precise isotachopherogram to that of the observed one for the sample in Fig. 2.

3.3. Analysis of didym by ITP-PIXE and CZE analysis

Brauner's didym, a valuable sample in the history of finding RE elements, was served as the example for checking the applicability of the developed electrolytes. Using spectroscopic analysis, Brauner

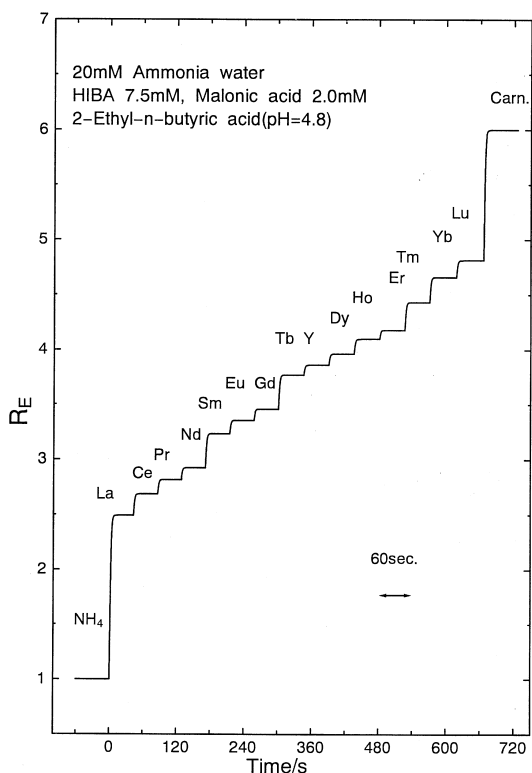


Fig. 3. Simulated isotachopherogram of the 15 RE ions under the same electrolyte system as in Fig. 1.

Table 4

Steady state zone parameters, total concentrations, abundances of the complex ions, and contribution of each complex ion to the effective mobility for La³⁺, Tb³⁺, Y³⁺, Dy³⁺ and Lu³⁺

		La ³⁺		Tb ³⁺		Y ³⁺		Dy ³⁺		Lu ³⁺	
R_E		2.51		3.77		3.86		3.95		4.81	
Mobility ($10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)		27.8		18.5		18.1		17.7		14.5	
Passing time (s)		85.5		88.8		89.8		88.8		95.5	
$C^1 S$ (mM)		7.97		7.67		7.59		7.68		7.14	
		%c	%m	%C	%m	%C	%m	%C	%m	%C	%m
RE(HIBA)	2	27.5	41.5	19.0	31.9	20.1	32.0	19.4	33.4	20.3	36.0
RE(HIBA)2	1	11.0	8.4	26.4	22.4	31.0	24.9	30.2	26.2	34.2	30.7
RE(HIBA)3	0	0.8	.0	5.6	.0	5.2	.0	8.3	.0	15.8	.0
RE(HIBA)4	-1	0.0	.0	.2	.1	.1	.0	.1	.1	.3	.3
RE(MAL)	1	27.7	15.2	26.3	19.3	23.0	17.9	22.8	17.6	14.2	12.9
RE(2EB)	2	3.9	4.5	1.6	2.8	.7	1.5	1.4	2.5	1.0	2.1
RE(2EB)2	1	0.4	.2	.4	.3	.3	.2	.2	.2	.3	.2
RE(HIB)(2EB)	1	19.9	11.0	17.6	13.8	16.7	14.8	15.3	12.2	12.6	12.7
C_{RE}^1 (free)		8.6		2.8		2.7		2.2		1.3	

%C: Abundance of complex ion (%).

%m: Contribution of each complex ion to the effective mobility (%).

(see [17]) found that didym, discovered by Mosander (1842) and assumed to be one of the RE elements at that time (see [18]), was not a pure element but a mixture of Pr, Nd and Sm. Here, interest is paid to analyze Brauner's didym sample by ITP-PIXE and CZE.

In ITP-PIXE analysis, ITP fraction was analyzed by PIXE. For CZE analysis, the calibration line was made by analyzing the standard samples. Fig. 4a, b and c show the isotachopherogram of didym as well as the analytical results of the fractions by PIXE. Table 5 summarises the abundances of the RE elements in didym analyzed by ITP-PIXE and CZE as well as ion chromatography (IC), and ion chromatography-neutron activation analysis (IC-NAA) performed in our laboratory. Obviously, the ITP-PIXE analytical results are in good agreement with those from CZE, IC and IC-NAA. It is shown that the detection limit for ITP-PIXE reaches as low as 0.01% for the analysis of didym while the injection amount sample for ITP is 120 μl . Also, it is obvious that the major components of didym are Nd and La while Pr, Sm and Gd are the minor ones. It is interesting that a considerable amount of La was found to be contained in didym sample. Comparison with the constituents of some standard RE ore

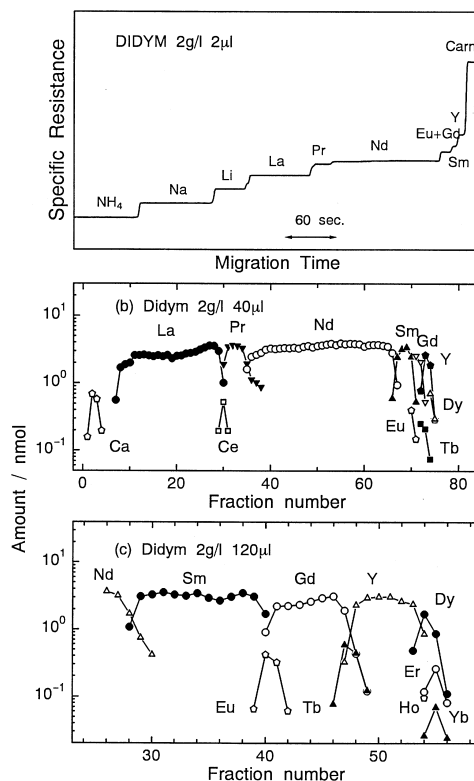


Fig. 4. Isotachopherogram and PIXE analytical results of didym for different injection amounts.

Table 5
Analytical results of didym by ITP–PIXE and CZE

RE	ITP–PIXE		CZE	IC	IC–NAA ^a
	40 μ l	120 μ l			
La	10.1		11.3	11.3	9.94
Ce	0.16		0.18		0.24
Pr	4.47		4.49	6.70	4.86
Nd	19.2		20.7	17.4	18.4
Sm	2.38	2.37	2.41	2.37	2.14
Eu	0.082	0.055			0.049
Gd	1.02	1.11	1.24	1.10	1.22
Tb	0.11	0.082		0.074	0.087
Y	0.62	0.64	0.76	0.64	
Dy	0.21	0.21			0.21
Ho					0.021
Er		0.032			0.026
Tm					0.022
Yb					0.006
Lu					0.006

^a IC–NAA: ion chromatography–neutron activation analysis.

samples suggested that Brauner's didym sample was prepared from a Monazite ore.

For ITP separation, the detection sensitivity can be improved by increasing the injection amount and the applied charge to some extent. For CZE separation, a more suitable concentration of malonic acid, for example, 0.45 mM, can be used to improve the separation of Y³⁺ and Dy³⁺ so that the abundance of Y³⁺ can be determined more accurately. In general, it was confirmed that both ITP and CZE are very convenient methods for the analysis of RE ore samples.

4. Conclusion

One of the keys to the successful simultaneous separation of RE ions is attributed to the developed electrolyte system both for ITP and CZE. The electrolyte systems containing HIBA as main complexing agent and malonic acid as an assistant one are very suitable for simultaneously separating 15 RE ions both by ITP and by CZE. Based on the electrolyte condition and the assumed equilibria occurring in the steady state zone, the ITP separation as well as the main complex formations which control the separation was successfully traced by using theoretical simulation. The good agreement

between the simulated isotachopherogram and the observed one confirmed the validity of such a simulation. Quantitative results of an ore sample, didym, demonstrated the applications of the developed electrolytes for the separation of RE ions both by ITP and by CZE.

Acknowledgements

The authors thank Professor Bohuslav Strauch of Charles University in Prague for kindly providing the didym sample and Professor Bohuslav Gas for providing the high-frequency contactless conductivity detector used in this work.

References

- [1] I. Nukatsuka, M. Taga, H. Yoshida, *J. Chromatogr.* 205 (1981) 95.
- [2] F. Foret, S. Fanali, A. Nardi, P. Bocek, *Electrophoresis* 11 (1990) 780.
- [3] Y. Shi, J.S. Fritz, *J. Chromatogr.* 640 (1993) 473.
- [4] T. Hirokawa, W. Xia, F. Nishiyama, H. Takemi, K. Ito, E. Shoto, *Anal. Sci.* 11 (1995) 801.
- [5] T. Hirokawa, W. Xia, Y. Kiso, *J. Chromatogr. A* 689 (1995) 149.
- [6] T. Hirokawa, Y. Hashimoto, *J. Chromatogr. A* 772 (1997) 357.
- [7] T. Hirokawa, Y. Kiso, *Anal. Sci.* 8 (1992) 737.
- [8] T. Hirokawa, N. Aoki, Y. Kiso, *J. Chromatogr.* 312 (1984) 11.
- [9] B. Gas, J. Zuska, J. Vacik, *J. Chromatogr.* 470 (1989) 69.
- [10] T. Hirokawa, Y. Kiso, *J. Chromatogr.* 242 (1982) 227.
- [11] T. Hirokawa, Y. Kiso, *J. Chromatogr.* 248 (1982) 341.
- [12] S.A.E. Johansson, J.L. Campbell, *PIXE: A Novel Technique for Elemental Analysis*, Wiley, New York, 1988.
- [13] T. Hirokawa, J. Hu, K. Umeda, G. Kimra, H. Ikeda, F. Nishiyama, Y. Kiso, *J. Chromatogr.* 513 (1990) 297.
- [14] J.E. Powell et al., in: K.S. Vorres (Editor), *Rare Earth Research II*, Gordon and Breach, New York, 1964, p. 509.
- [15] F.M. Everaerts, J.L. Beckers, T.P.E.M. Verheggen, *Isotachopheresis: Theory, Instrumentation and Applications (Journal of Chromatography Library, Vol. 6)*, Elsevier, Amsterdam, 1976, p. 62.
- [16] T. Hirokawa, K. Nakahara, Y. Kiso, *J. Chromatogr.* 470 (1989) 211.
- [17] M. Vobecky, *The Czechoslovak Spectroscopic Society by the Czechosl. Acad. Sci. 1949–1984* (1984).
- [18] N.E. Topp, *Chemistry of Rare-Earth Elements*, Elsevier, Amsterdam, 1965.