

Study of isotachophoretic separation behaviour of metal cations by means of particle-induced X-ray emission VI. Selective separation of twenty metal cations using tartaric acid as a complexing agent

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Abstract

The selective isotachophoretic (ITP) separation of twenty metal ions that form kinetically labile complexes with tartaric acid was investigated. The leading electrolyte was 20 mM ammonia solution buffered by adding acetic acid (pH 4.8) and the concentration of tartaric acid (C_{Tar}) was varied in the range 0–5 mM. The terminator was 20 mM carnitine hydrochloride solution. Isotachophoretic qualitative indices (R_E) of the metal ions were measured by using a high-frequency contactless conductivity detector. An equimolar test mixture was separated by using a micro-preparative apparatus and the fractions were analysed off-line by particle-induced X-ray emission method (ITP-PIXE). When $C_{\text{Tar}} = 1$ mM, the separability was good on average. The migration order was Ba^{2+} , (Sr^{2+} , Na^+), Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Cd^{2+} , (Ni^{2+} , Li^+), Zn^{2+} , La^{2+} , (Ce^{3+} , Pb^{2+}), Y^{3+} , Gd^{3+} , Lu^{3+} , Cu^{2+} , where the ions in parentheses were not separated. $\text{Zr}^{\text{IV}}\text{O}^{2+}$ was not detected. With increase in C_{Tar} , the number of detectable elements decreased owing to the decrease in the effective mobilities of the separands. When $C_{\text{Tar}} = 5$ mM, the migration order was Na^+ , Ba^{2+} , Sr^{2+} , Mg^{2+} , Li^+ , Ca^{2+} , Mn^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} . A model waste from a nuclear fuel was successfully analysed using the electrolyte system.

1. Introduction

Isotachopheresis (ITP) has been applied to analyses for many kinds of inorganic ions such as metal ions and also organic ions [1]. The separation of metal ions usually utilizes complex-

forming equilibria between the metal ions and suitable complexing agents. The separation behaviour of metal ions in such a system depends on the complexing agent selected, its concentration and the pH of the operational electrolyte system [2,3], because these factors directly affect the effective mobilities of metal ions. The appropriate use of complexing agents permits the selective separation of metal ions from a complex mixture.

Gebauer and Boček [4] have reviewed the

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utility of complex-forming equilibria in ITP separations and presented a table of complexing reagents and inorganic ions separated by using the reagents. Although various reagents have been used for ITP analysis, only a few systematic approaches have been made to describe the separability of metal cations [5]. This situation is presumably related to the fact that there have been no convenient detection methods with high detectability for metal ions: when similar qualitative indices are obtained for different separands by using universal detectors (*e.g.*, a potential gradient detector), separability assessment of the separands is almost impossible. Even if the same values of the qualitative indices are obtained for separands at the isotachophoretic steady state, suggesting the same effective mobilities, it does not always mean an imperfect separation [6]. That is, the separability of adjacent samples depends on the difference between the separand mobilities in the mixed zone, not on that in the steady-state zones. Although photometric detection may give supplementary qualitative information [7], it is not as useful for metal ions as it is for organic ions.

This is the reason why more discriminating detection methods than the conventional methods are necessary to describe the exact separation behaviour of metal ions. The use of a light-absorbing chelating agent to provide co-counter ions is a possible approach to achieving high detectability for metal ions [8], although selection of the chelating agent causes another problem for samples with complex constituents.

Our approach to the above topic is the analysis of the ITP-separated fractions by particle-induced X-ray emission (PIXE), which is a method with high detectability [9]. In the first paper in this series [10], the separation behaviour of twenty metal ions forming complexes with α -hydroxyisobutyric acid (HIB) was investigated by using ITP-PIXE, demonstrating that PIXE can be a powerful detection method for metal ions.

The aim of this paper is to clarify the separation behaviour of the same twenty metal ions forming cationic ion pairs with tartrate ions, which has been proved useful for recovering

precious metals as non-ions from a model nuclear fuel waste solution by using a free-flow ITP apparatus [11]. First, the isotachophoretic qualitative index, R_E [12], of the metal ions was measured by varying the concentration in the leading electrolyte. Next, the ITP separation behaviour of the mixture was investigated by means of ITP-PIXE. Finally, the electrolyte systems used were applied to a model waste to demonstrate the practical utility of the method.

2. Experimental

2.1. Samples

The twenty metal ions treated were Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Sr^{2+} , Cd^{2+} , $\text{Zr}^{\text{IV}}\text{O}^{2+}$, Ba^{2+} , Pb^{2+} , Y^{3+} , La^{3+} , Ce^{3+} , Gd^{3+} and Lu^{3+} . Stock standard solutions (10 mM) were prepared using the chlorides obtained from Tokyo Kasei (Tokyo, Japan). Several test mixtures containing four or five metal cations were prepared from the stock standard solutions for R_E measurement. The sample used for ITP-PIXE analysis contained all of the metal cations, each at a concentration of 0.5 mM. The pH of the sample solution was adjusted to 3 by adding a small amount of concentrated hydrochloric acid. Small amounts of cationic dyes [toluidine blue (TB) and aztrazon pink (AP)] were co-migrated in order to monitor the migration process and to determine the timing of fractionation.

2.2. Electrolytes system

The leading electrolyte was 20 mM aqueous ammonia solution containing tartaric acid (Tar) as the complexing agent at concentrations of 0, 0.5, 1, 1.5, 2, 2.5, 3, 4 and 5 mM. The pH of the leading electrolyte (pH_L) was adjusted to 4.8 by adding acetic acid. The above leading electrolytes are abbreviated as $\text{WNH}_4\text{Ac-Tar}$ (W designates aqueous solution and Ac is acetate) hereafter according to the abbreviations used by Everaerts *et al.* [5]. The leading electrolytes contained 0.05% (w/w) of hydroxypropylcellu-

lose (HPC) (Tokyo Kasei) to suppress electro-osmotic flow. The viscosity of the 2% HPC solution was 1000–4000 cP at 20°C. Although the terminating electrolyte used was 20 mM carnitine hydrochloride solution, the actual terminator was proton at the isotachophoretic steady state. Table 1 summarizes the operational electrolyte system used.

All the reagents were purchased from Tokyo Kasei. pH measurements were made using a Horiba (Tokyo, Japan) Model F-7 AD digital pH meter.

2.3. Isotachophoretic apparatus used for R_E measurement

The detector used for the measurement of R_E was a high-frequency contactless conductivity detector (HFCCD) [13,14]. The separation unit of the apparatus used was Labeco (Spišská Nová Ves, Slovak Republic) ZKI-001. The separation column consisted of a pre-separation capillary (10 cm × 0.5 mm I.D.) and a main capillary (20 cm × 0.25 mm I.D.). The migration current when detecting zones was 50 μ A, which was supplied by a high-voltage power supply for a Shimadzu IP-2A. The measurements were made at 25°C in a temperature-controlled room.

The qualitative index R_E is defined as the ratio of the potential gradient [E (V cm⁻¹)] of a sample zone (E_S) to that of the leading zone (E_L) [12]. When a conductivity detector is used, it is equal to the ratio of the specific resistances (ρ) of the respective zones. It is also equal to the ratio of the effective mobility (\bar{m}) of the leading ion to that of a sample ion in its zone from the equality of the velocities of migrating zones ($v =$

$\bar{m}E$):

$$R_E = E_S/E_L = \rho_S/\rho_L = \bar{m}_L/\bar{m}_S \quad (1)$$

As the output signal of the HFCCD shows a non-linear response to the specific resistance [13,14], the signal obtained was converted into specific resistance using a fourth-order polynomial expression of the output voltage. Na⁺ and Li⁺ were used as internal standards to correct for the slight drift of the HFCCD signals. The simulated R_E values were 1.495 and 1.963, respectively.

2.4. Preparative isotachophoretic analyser

The micro-preparative analyser used was a capillary type as reported [15]. The separation column consisted of a PTFE precolumn (37 cm × 1 mm I.D.) and a PTFE main column (37 cm × 0.5 mm I.D.). The total volume of the column was 0.32 ml. A typical single run took about 1 h. The migration current was 300 μ A for the first 57 min, then it was decreased to 150 μ A during detection and fractionation. After monitoring with a potential gradient detector, the separated zones were fractionated dropwise on to Nucleopore filter backings (thickness 5 μ m and pore size 0.1 μ m) through a platinum capillary. A 15- μ m square filter was mounted on a aluminium flame. One drop (*ca.* 5 μ l) was one fraction, which contained *ca.* 5 nmol of component. The interval of fractionation was *ca.* 10 s.

2.5. PIXE analysis

The ITP fractions were bombarded by a 2-MeV H⁺ beam after drying in a desiccator. The

Table 1
Operational electrolyte system (W_NH₄Ac–Tar) used in isotachopheresis

Leading electrolyte	20 mM ammonia solution
Complexing agent	Tartaric acid (0, 0.5, 1, 1.5, 2, 2.5, 3, 4 and 5 mM)
pH-buffering agent	Acetic acid (40.2, 34.1, 32.5, 30.9, 29.2, 27.6, 26.0, 22.8, 19.5 mM) ^a
pH of leading electrolyte	4.8
Additive	0.05% Hydroxypropylcellulose
Terminating electrolyte	20 mM Carnitine hydrochloride

^a Simulated values.

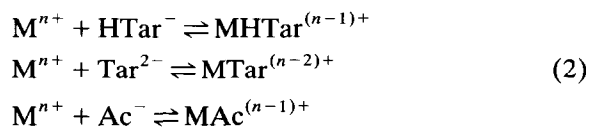
probe beam was generated by using a Van de Graaff accelerator Model AN-2500; (Nisshin High Voltage, Tokyo, Japan). The beam current was 50 nA. A typical single run to acquire an X-ray spectrum of an ITP fraction was ca. 200 s. The detector used was a Ge detector (Ortec Model GLP-10180) and the multi-channel pulse-height analyser used was a Laboratory Equipment (Tokyo, Japan) Model AMS-1000. Owing to the limitations of the X-ray detection system used, light elements below atomic number 14 (Si) could not be detected.

3. Results and discussion

3.1. Complex-forming equilibria

The pK_a values of tartaric acid are 3.036 and 4.366 [16]. At $pH_L = 4.8$, ca. 80% of tartaric acid exists as divalent ions and the rest as monovalent ions. However, the abundance of divalent tartrate ions in each sample zone decreases at the steady state, because the pH of the zone is lower than pH_L (e.g., pH 4.5) depending on the effective mobility of the sample. The pK_a value of acetic acid is 4.756, and 50% or less of acetic acid exists as acetate ions.

The ion-pair-forming equilibria among metal cations (M^{n+}), tartrate ion ($HTar^-$, Tar^{2-}) and acetate ion (Ac^-) can be written assuming 1:1 ion pairs as



The effective mobility of a metal ion M^{n+} can be expressed as in Eq. 3, where the brackets represent the concentrations of ionic species, m_1 , m_2 , m_3 and m_4 are the mobilities of M^{n+} , $MHTar^{(n-1)+}$, $MTar^{(n-2)+}$ and $MAC^{(n-1)+}$, respectively, and K_1 , K_2 and K_3 are the stability constants of $MHTar^{(n-1)+}$, $MTar^{(n-2)+}$ and $MAC^{(n-1)+}$, respectively.

$$\bar{m}_M = \frac{m_1[M^{n+}] + m_2[MHTar^{(n-1)+}] + m_3[MTar^{(n-2)+}] + m_4[MAC^{(n-1)+}]}{[M^{n+}] + [MHTar^{(n-1)+}] + [MTar^{(n-2)+}] + [MAC^{(n-1)+}]} = \frac{m_1 + m_2K_1[HTar^-] + m_3K_2[Tar^{2-}] + m_4K_3[Ac^-]}{1 + K_1[HTar^-] + K_2[Tar^{2-}] + K_3[Ac^-]} \quad (3)$$

As the mobility of the ion pairs formed is smaller than that of non-complexing metal ions, Eq. 3 indicates that the effective mobility of metal ions decreases with increase in the concentration of the complexing counter ions.

3.2. R_E values

Fig. 1 shows the R_E values of the metal ions observed for nine leading electrolytes containing 0–5 mM tartaric acid. Although the R_E values increased with increase in tartaric acid concentration (C_{Tar}), the increments were different among the metal ions, indicating that the stability constants differed. It seemed that La^{3+} , Ce^{3+} , Gd^{3+} , Y^{3+} , Lu^{3+} , Cu^{2+} and Pb^{2+} had higher stability constants than the others. When C_{Tar} was >1 mM, the above ions tended to form a mixed zone even if two components with sufficiently different R_E values were selected. Further, the reproducibility of the R_E values shown in Fig. 1 was not good for these ions. The reason is not clear.

Among the twenty metal ions, the R_E values of $Zr^{IV}O^{2+}$ could not be measured, because the ions did not form a quantitative zone. On the other hand, the R_E values of Fe^{2+} were measurable for all of the operational systems used. However, quantitative analysis was difficult with every system because the zone length corresponding to the same amount injected quickly decreased with increase in C_{Tar} . This is probably due to oxidation of Fe^{2+} to Fe^{3+} and the successive formation of hydroxyl complexes.

The R_E value of the terminating H^+ zone was 5.5 ± 0.5 on average. The reproducibility was not as good as those for the sample ions (usually the error in the observed R_E values is ± 0.1 or less). The corresponding effective mobility was $12.7 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ according to our simulation. The metal ions with smaller effective mobilities such as ZrO^{2+} did not migrate isotachophoretically, but migrated zone electrophoretically in the terminating zone.

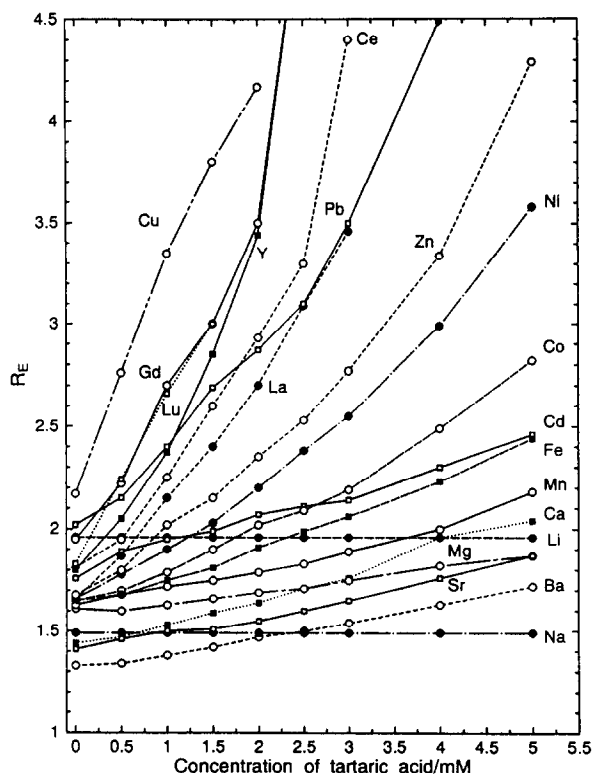


Fig. 1. R_E values of nineteen metal cations observed by using a high-frequency contactless conductivity detector. Operational electrolyte system as in Table 1. Na^+ and Li^+ were the internal standards for R_E measurement.

3.3. Separation behaviour of the twenty metal cations and migration order

Fig. 2 shows isotachopherograms of the mixture of the twenty metal cations obtained by using an HFCCD, where C_{Tar} was varied as (a) 0, (b) 1, (c) 2.5 and (d) 5 mM. A 1.2- μl volume of sample mixture containing 0.6 nmol of each metal cation (total 12 nmol) was separated. The quantity of electric charge integrated until the first sample zone was 0.282 C (125 $\mu\text{A} \cdot 36$ min + 50 $\mu\text{A} \cdot 4$ min) and the electric charge applied for a unit molar amount was 23.5 mC nmol^{-1} .

Fig. 3 shows the analytical results for ITP fractions obtained by PIXE. A 20- μl volume of the sample mixture (10 nmol of each compo-

nent) was separated and fractionated using three leading electrolytes ($C_{\text{Tar}} = 0, 1$ and 2.5 mM). The zone passing time of all the sample zones was ca. 8 min (migration current = 150 μA). The quantity of electric charge applied was 1.09 C (300 $\mu\text{A} \cdot 57$ min + 150 $\mu\text{A} \cdot 7$ min) and the electric charge applied for a unit molar amount was 5.5 mC nmol^{-1} . It should be noted that the electric charge per sample amount was different between the above two experiments, and obviously a better separation was expected with HFCCD detection (Fig. 2).

The assignments shown in Fig. 2 were made in comparison with the analytical results obtained by PIXE shown in Fig. 3. As Li, Na and Mg could not be detected with the PIXE detection system used, they were assigned by using a conventional isotachopheretic method using standard samples.

When tartaric acid was not present in the leading electrolyte, as shown in Fig. 2a, the Mn, Co, Ni and Zn zones had the same conductivity, suggesting mixed-zone formation. This conclusion was partly valid judging from the PIXE result shown in Fig. 3a. On the other hand, a similar situation was found for the zones of Ce, Cd and Y in Fig. 2a. However in these instances, they were completely separated, as shown in Fig. 3a.

When a leading electrolyte containing 1 mM tartaric acid was used, in general a good separability was obtained, as shown in Figs. 2b and 3b. Although the separations between Cd and Ni and between Ce and Pb were incomplete, a slight amount of additional charge might allow complete separation.

When the concentration of tartaric acid was increased to 2.5 mM, the quality of separation become poor again. Obviously, from Figs. 2c and 3c a major mixed zone of Pb, Y, La, Ce and Gd was formed. Mg and Ca of the same step height were separated, as were Cd and Co.

For ZrO^{2+} , no quantitative steps were observed for any of the electrolyte systems examined. It was found from PIXE analysis that the ions migrated just before the terminating zone, presumably forming colloidal particles of

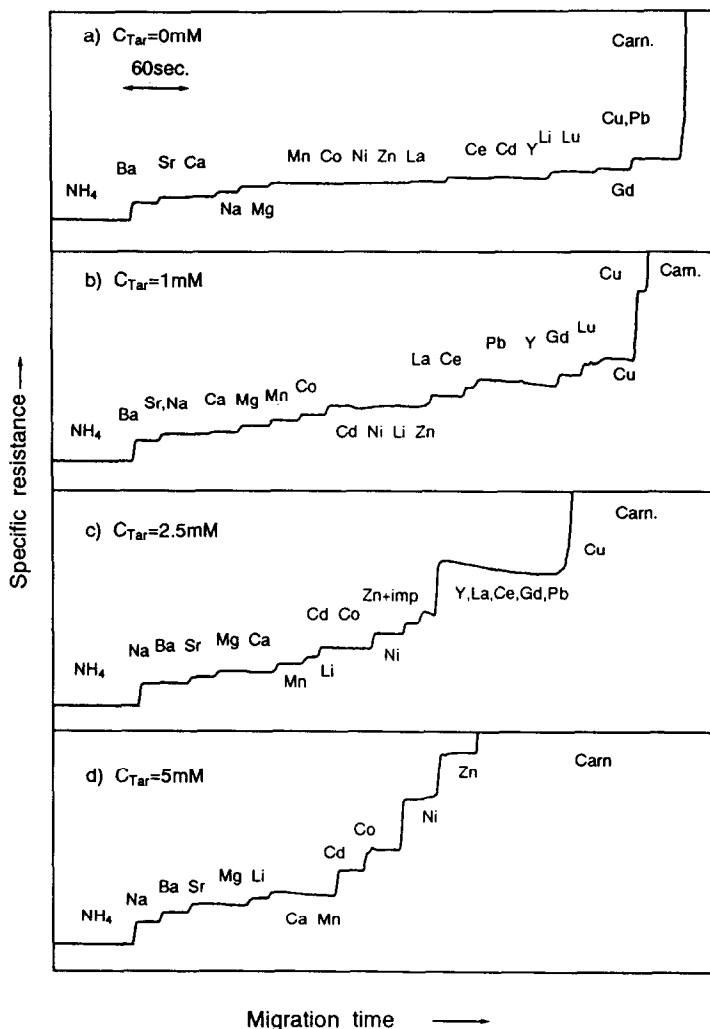


Fig. 2. Observed isotachopherograms of a test mixture containing twenty metal cations. The injected sample amount was 1.2 μl (12 nmol of metal ions). Operational electrolyte systems as in Table 1. Migration current = 150 μA . Quantity of integrated charge = 0.28 C.

the hydroxides. This observation was limited to the operational system without tartaric acid. The addition of tartaric acid so decreased the effective mobility of colloidal particles of ZrO and Fe^{III} that they were not detection as cations.

Fig. 4 summarizes the migration order with the electrolyte systems used. The effective mobilities of Na⁺ and Li⁺ can be regarded as constant with the electrolyte systems used, because the interaction with tartrate and acetate ions is negligibly small.

With increase in tartaric acid concentration, the number of analysable ionic species gradually decreased. When WNH₄Ac–Tar (5 mM) was used, it decreased to half of that with the WNH₄Ac system. However, a high separability was obtained for the detectable ionic species, as already shown in Fig. 2d. This phenomenon can be utilized for selective separation from the other metal ions. When C_{Tar} is as high as 5 mM, for example, lanthanide ions in a sample can be purged to facilitate the detection of the other

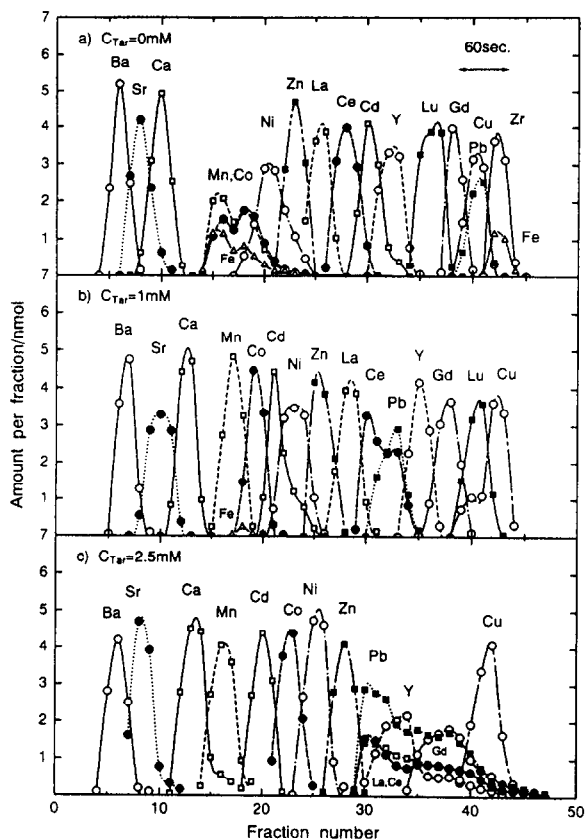


Fig. 3. Analytical results for ITP fractions of a test mixture containing twenty metal cations using PIXE. The injected sample amount was 20 μ l (200 nmol of metal ions). Operational electrolyte system as in Table 1. Quantity of integrated charge = 1.1 C.

Table 2
Recoveries (%) of fractionated metal cations evaluated by PIXE

Z	Metal ion	Electrolyte system			
		WNH ₄ Ac	WNH ₄ Ac–Tar (1 mM)	WNH ₄ Ac–Tar (2.5 mM)	WNH ₄ Ac–Tar (5 mM)
26	Fe ^{II}	100 ^a	17	n.d. ^b	n.d.
29	Cu	104	102	99	n.d.
39	Y	100	99	77	n.d.
40	Zr ^{IV} O	88	n.d.	n.d.	n.d.
57	La	101	98	97	n.d.
58	Ce	99	97	101	n.d.
64	Gd	100	96	98	n.d.
71	Lu	102	100	20	n.d.
82	Pb	100	101	100	n.d.

^a 10% was found as Fe^{III}.

^b n.d. = Not detected.

ions in the sample. Light lanthanide ions can be detected when C_{Tar} is as low as 1 mM.

3.4. Sample recovery

The isotachophoretic recovery of metal cations was evaluated on the basis of PIXE analysis as

Recovery (%)

$$= \frac{\text{measured amount of element in fractions}}{\text{measured amount of element injected}} \cdot 100 \quad (4)$$

Table 2 shows the percentage recoveries of nine ions, which were selected because no recovery was obtained at $C_{\text{Tar}} = 5 \text{ mM}$. Although 88% of $\text{Zr}^{\text{IV}}\text{O}^{2+}$ and 90% of Fe^{2+} were recovered using the WNH_4Ac system ($C_{\text{Tar}} = 0$), they were not recovered when tartaric acid was present in the leading electrolyte and the amount injected was 10 nmol.

When $C_{\text{Tar}} = 2.5 \text{ mM}$, an isotachophoretic Lu zone was not detected (Fig. 3c). The 20% recovery of Lu in Table 2 was due to the Lu zone which migrated zone electrophoretically in the terminating zone (fractions 52–60, not shown in Fig. 3c). This suggested that the effective mobility of Lu was slightly smaller than that of the terminating ion when C_{Tar} was 2.5 mM. A similar situation was observed with Y with a 77% recovery.

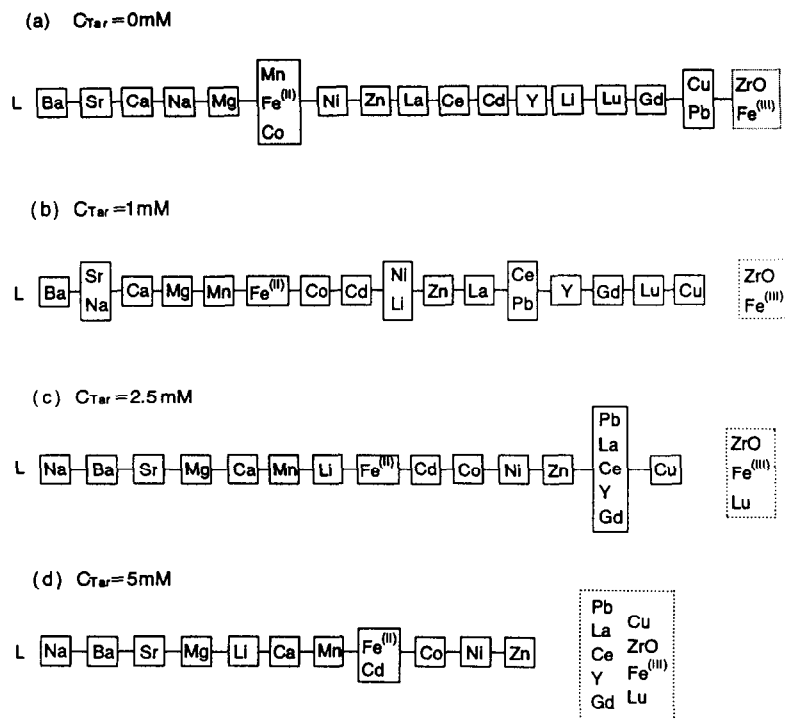


Fig. 4. Migration order of twenty metal cations observed for five operational electrolyte systems. Operational electrolyte system as in Table 1. Metal ions in a different solid box can be separated. Metal ions in a dashed box were not detected before the terminating zone of proton.

Table 3
Sample composition of model waste from nuclear fuel cycle (MW-2)

Z	Element	Concentration (mM)	Form ^a	Z	Element	Concentration (mM)	Form ^a
11	Na	19.6198	NaNO ₃	46	Pd	0.1732	Pd(NO ₃) ₂
13	Al	0.00901	Al	47	Ag	0.0068	AgNO ₃
15	P	0.2538	P	48	Cd	0.0092	Cd(NO ₃) ₂
24	Cr	0.0788	Cr(NO ₃) ₃	50	Sn	0.0066	Sn
25	Mn	0.2622	Mn(NO ₃) ₂	52	Te	0.0714	TeO ₂
26	Fe	1.5538	Fe(NO ₃) ₃	55	Cs	0.322	CsNO ₃
28	Ni	0.1874	Ni(NO ₃) ₂	56	Ba	0.1944	Ba(NO ₃) ₂
34	Se	0.0110	Na ₂ SeO ₃	57	La	0.1642	La ₂ (CO ₃) ₃
37	Rb	0.0728	RbNO ₃	58	Ce	1.1780	Ce(CO ₃) ₂
38	Sr	0.175	Sr(NO ₃) ₂	59	Pr	0.1492	Pr ₆ O ₁₁
39	Y	0.1256	Y ₂ O ₃	60	Nd	0.5000	Nd ₂ O ₃
40	Zr	0.722	ZrO(NO ₃) ₂	62	Sm	0.1020	Sm ₂ O ₃
42	Mo	0.612	Na ₂ MoO ₄	63	Eu	0.0160	Eu ₂ O ₃
44	Ru	0.338	Ru(NO ₃) ₃	64	Gd	0.0078	Gd ₂ O ₃
45	Rh	0.06789	Rh(NO ₃) ₃				

^a Chemicals used for preparation.

3.5. Separation of a nuclear fuel model waste solution

The operational electrolyte systems containing tartaric acid were applied to the analysis of a nuclear fuel model waste, the components of which are several metal cations with different abundances, as shown in Table 3.

Fig. 5 shows isotachopherograms of the model waste obtained by using the HFCCD. A 10- μ l volume of sample containing 270 nmol of the components was separated. Fig. 6 shows the analytical results for the ITP fractions obtained by using four leading electrolytes ($C_{\text{Tar}} = 0, 1, 2.5$ and 5 mM). A 60- μ l volume of sample containing 1.62 μ mol of the components was

separated. Fractionation was started at the end of the Na^+ zone, which was the matrix component of the model waste treated (Table 3). The quantity of electric charge integrated through the migration process was 1.4 C (300 $\mu\text{A} \cdot 65$ min + 150 $\mu\text{A} \cdot 25$ min).

When tartaric acid was not used as a complexing agent, a mixed zone of Ce and Nd was observed, as is obvious from Fig. 6a. Additionally, the separability of Mn, Ni and La was not high. On the other hand, a good separation was achieved on addition of 1 mM tartaric acid to the leading electrolyte (Fig. 6b). The separation behaviour of the model waste with the electrolyte systems used was very similar to that with a leading electrolyte containing α -hydroxy-

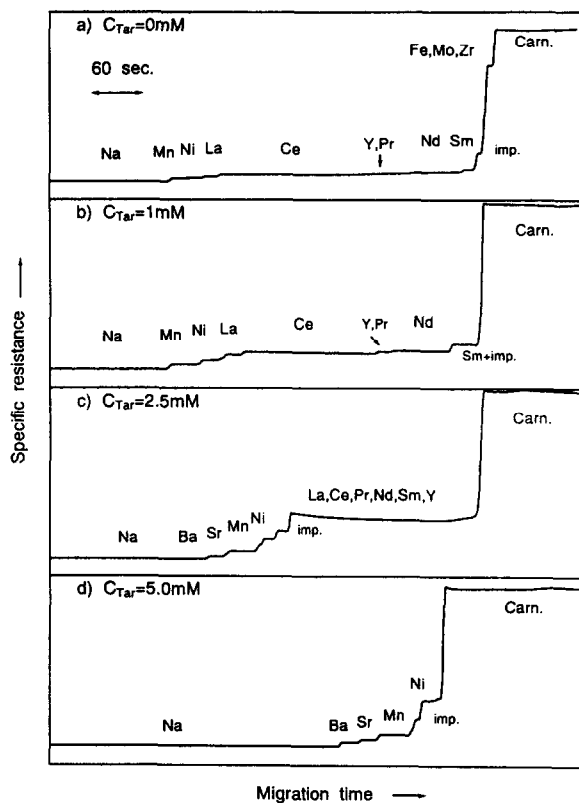


Fig. 5. Observed isotachopherogram of a model waste produced in a nuclear fuel cycle. The injected sample amount was 10- μ l (270 nmol of metal ions). Operational electrolyte system as in Table 1. Migration current = 150 μA . Quantity of integrated charge = 0.3 C.

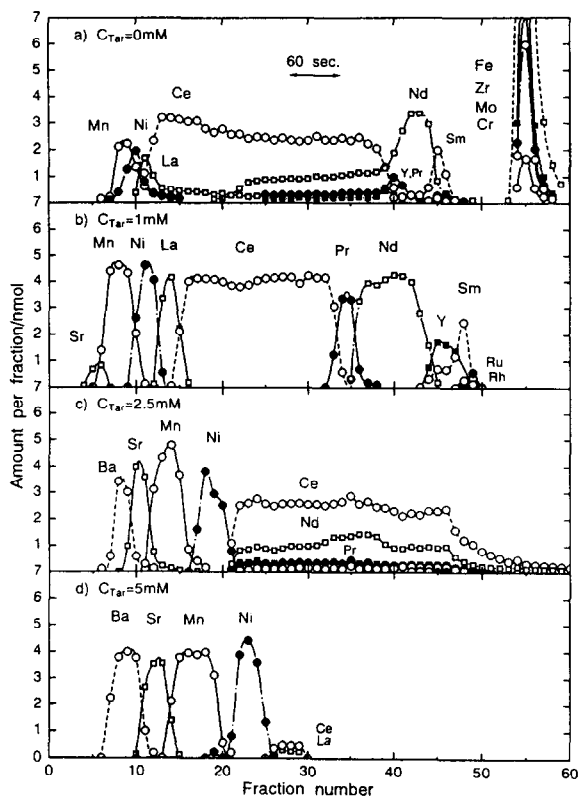


Fig. 6. Analysis results for the cationic fractions of the nuclear fuel model waste obtained by PIXE. The injected sample amount was 60 μ l (1.6 μ mol of metal ions). Operational electrolyte system as in Table 1. Quantity of integrated charge = 1.4 C.

isobutyric acid [10], except for the migration order of Sm and Y.

With increase in tartaric acid concentration, the separability of lanthanide ions became poor, as shown in Fig. 6c ($C_{\text{Tar}} = 2.5 \text{ mM}$). When C_{Tar} was increased to 5 mM, the lanthanide ions did not migrate isotachophoretically, as expected. This allowed the selective detection of Ba^{2+} , Sr^{2+} , Mn^{2+} and Ni^{2+} contained in the sample. If the number of detectable samples can be decreased in such a way, conventional detection methods using a potential gradient detector and a conductivity detector become very useful.

The other metal ions (not detected as cations) might partly migrate in the terminating zone as cations when the effective mobilities are smaller than that of the terminator. Another part of them might stop around the injection port if non-ionic ion pairs are formed, with the other part migrating as anions towards the cathode if the ion pairs are anions. Such a conversion from cations is important from the viewpoint of preparative applications [11]. It is also important for analytical purposes because cations and anions can be detected simultaneously when dual detection systems are used with a bidirectional electrolyte system [17].

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