CHROM. 24 759

Study of isotachophoretic separation behaviour of metal cations by means of particle-induced X-ray emission

IV. Separation of metal ions in a non-radioactive model solution of a high-level liquid waste

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ABSTRACT

The isotachophoretic separation behaviour of metal ions in a model solution of a high-level liquid waste (HLLW) was investigated by means of the isotachophoresis–particle-induced X-ray emission (ITP–PIXE) method for the purpose of fractionation of useful elements contained in the HLLW. The leading electrolyte used was 20 mM ammonia solution buffered by acetic acid (pH 4.8), in which a complex-forming agent (10 mM α-hydroxyisobutyric acid) was contained. The migration order of the cationic components was (Rb$^+$, Cs$^+$), NH$_4^+$, Ba^{2+}, Sr^{2+}, Na$^+$, Mn^{2+}, Fe^{2+}, (Cr^{2+}, Rh^{2+}, Cd^{2+}), Ni^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+} and Y^{3+}, where the ions in parentheses could not be separated from each other. The separation efficiency of rare earth elements was 178 nmol/C and it was decreased to 96 nmol/C when NaNO$_3$ coexisted as the matrix. Part of the Fe^{3+}, Zr^{IV}O^{2+}, Mo^{VI}O$_4^{2-}$ and platinum group elements formed a cationic colloidal zone. Although the cationic recovery was 100% for most of the components, a substantial part of Fe, Te^{VI}O$_3$, Zr^{IV}O, Ru, Rh and Pd did not migrate, suggesting the formation of non-ionic hydrolysis species. Although ITP was not suitable for their analysis, platinum group metals in the HLLW might be partitioned efficiently as non-ionic components.

INTRODUCTION

In coupled isotachophoresis–particle-induced X-ray emission (ITP–PIXE), isotachophoretically fractionated zones are analysed off-line by PIXE. As PIXE is a sensitive, non-destructive and rapid method with multi-elemental capacity, it is useful as a detection method for the components in the micro-fractions obtained using a capillary isotachophoretic apparatus.

A PIXE detector permitted a detailed investigation of the isotachophoretic separation behaviour of metal ions [1,2], such as the migration order, the separability and the recoveries. Also, its high sensitivity allowed the determination of trace metal ions in a sample solution. In a previous paper [3], we demonstrated the determination of trace heavy lanthanoids in a crude rare earth chloride: the number of cationic components was fifteen and their abundance varied over four orders of magnitude.

This paper deals with the separation behaviour of another sample of complex composition, a model solution of a high-level liquid waste (HLLW). HLLW is generated in the reprocessing of nuclear fuels after recovering Pu and U. It contains 30 or more elements of the fission products of U, cladding

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materials of the fuel and the extracting agent for Pu and U (sodium tributylphosphate). Moreover, a large amount of $NaNO_3$ may be added for solidification. The abundances of the components differ widely.

HLLW is chemically heterogeneous, as it contains almost all of the chemical groups. Representative components are light lanthanoids, Cs, Sr, Fe^{III}, $Zr^{IV}O$ and platinum group elements, such as Ru, Rh and Pd.

We have already reported low cationic recoveries of Fe^{III} and $Zr^{IV}O$, probably owing to the formation of hydrolysis species, suggesting that ITP was not useful for the measurement of these ions [1]. The leading electrolyte used contained a useful complex-forming agent for lanthanide separation, α-hydroxyisobutyric acid. As summarized in a comprehensive review on the isotachophoretic separation of inorganic compounds [4], transition metals form complicated mixtures of hydrolysis species and the reaction rate of the complex-forming equilibria is not rapid enough that the complexes formed may split into different zones (zone splitting). Although this is an unfavourable feature for analytical use, from a preparative viewpoint the formation of a non-ionic zone is not always a negative feature, that is, high efficiency can be expected for the fractionation of non-ionic substances from mobile ions.

In this work, the isotachophoretic separation of the HLLW components was investigated for the purpose of elucidating the separation behaviour of platinum group elements. Two non-radioactive model waste solutions were analysed by the ITP–PIXE method. The most significant difference between the two models was the abundance of Na^+. From our previous study on the effect of composition on separation efficiency [5], low separability was estimated for the components of the model solution containing a large amount of Na^+. Taking account of the zone splitting problem and the composition effect, the recoveries, the migration order and the separation efficiency of the HLLW components were studied in detail. In addition to the above-mentioned complex-forming electrolyte system, non-buffered electrolyte systems were also used to evaluate the effect of counter ions on the recoveries.

EXPERIMENTAL

Samples

The composition of the fission products in the following two model waste solutions was determined according to computer simulation appropriately taking into account the burn-up and cooling time of the actual fuel. One of the model waste solutions (MW-1) was of low Na^+ abundance, which was prepared in our laboratory. MW-1 contained twenty metal ions and it was prepared from stock solutions of chloride salts obtained from Katayama Kagaku (Tokyo, Japan). They were dissolved in high-purity deionized water obtained by using a Puric-R ion exchanger (Japan Organo, Tokyo, Japan). The specific resistance of the water used was $18.3 \cdot 10^6 \ \Omega$ cm. The concentrations of the sample components are summarized in Table I.

The other model waste solution (MW-2) contained 27 metal ions. The composition was simulated by Power Reactor and Nuclear Fuel Development (Tokyo, Japan). Table I also shows the constituents of MW-2. Obviously the concentration of Na^+ was very high. As the original solution was strongly acidic (a 2.5 M nitric acid solution), it was not suitable as the sample for isotachophoresis. Therefore, the solution was dried by using an evaporator to remove nitric acid, and the residue was dissolved in deionized water. This process was repeated three times. The pH of the stock solution obtained was 1.5. Just before migration experiments, it was diluted with deionized water to 2% of the concentration of the original solution and this diluted solution (pH 2.74) was used as the ITP sample.

Small amounts of cationic dyes, toluidine blue (TB) and astrazon pink (AP), were added to the above model solutions in order to monitor the migration process and determine the timing of fractionation appropriately. Extra-pure grade dyes were purchased from Tokyo Kasei (Tokyo, Japan).

Electrolyte system

Table II summarizes the operational electrolyte systems used. WNH_4Ac–HIB is the abbreviation for the leading electrolyte in which the solvent used was water (W), the leading ion was NH_4^+, the pH buffer was acetic acid (Ac) and the complex-forming agent was α-hydroxyisobutyric acid (HIB). The

TABLE I

COMPOSITIONS OF SAMPLES MW-1 AND MW-2

Element (Z)	Concentration (mM)		Form[a]	Element (Z)	Concentration (mM)		Form
	MW-1	MW-2			MW-1	MW-2	
11 Na	0.901	19.6198	$NaNO_3$	46 Pd	0.214	0.1732	$Pd(NO_3)_2$
13 Al	0.00901	0.00901	Al	47 Ag	–	0.0068	$AgNO_3$
15 P	–	0.2538	P	48 Cd	0.0102	0.0092	$Cd(NO_3)_2$
24 Cr	0.108	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	0.451	1.5538	$Fe(NO_3)_3$	55 Cs	–	0.322	$CsNO_3$
28 Ni	0.0715	0.1874	$Ni(NO_3)_2$	56 Ba	0.246	0.1944	$Ba(NO_3)_2$
34 Se	–	0.0110	Na_2SeO_3	57 La	0.174	0.1642	$La_2(CO_3)_3$
37 Rb	–	0.0728	$RbNO_3$	58 Ce	0.391	1.1780	$Ce(CO_3)_2$
38 Sr	0.196	0.175	$Sr(NO_3)_2$	59 Sr	0.163	0.1492	Pr_6O_{11}
39 Y	0.0996	0.1256	Y_2O_3	60 Nd	0.515	0.5000	Nd_2O_3
40 Zr	0.818	0.722	$ZrO(NO_3)_2$	62 Sm	0.102	0.1020	Sm_2O_3
42 Mo	–	0.612	Na_2MoO_4	63 Eu	0.0255	0.0160	Eu_2O_3
44 Ru	0.403	0.338	$Ru(NO_3)_3$	64 Gd	0.0119	0.0078	Gd_2O_3
45 Rh	0.0949	0.06789	$Rh(NO_3)_3$				

[a] Chemicals used for the preparation of MW-2. Chloride salts were used for MW-1.

pH of the leading electrolyte (pH_L) was 4.8. Hydroxypropylcellulose (HPC) was added to the leading electrolyte (0.1%, w/w) to suppress electroosmotic flow. HPC was obtained from Tokyo Kasei and the viscosity of a 2% aqueous solution was given as 1000–4000 cP at 20°C.

Ammonia solution was used because NH_4^+ was inactive in a PIXE analysis. The conventional leading ion K^+ was highly sensitive and it affected the rapid acquisition of spectral data. The electrolyte system WNH_4Ac–HIB is compatible with WKAc–HIB, as the mobilities of NH_4^+ and K^+ are almost the same. The terminating electrolyte used was a 10 mM carnitine hydrochloride solution. This operational electrolyte system permits bidirectional isotachophoresis [6,7]: both cations and anions in a sample migrate isotachophoretically in the opposite direction to each other when these operational electrolytes are used in combination. The leading anion is 10 mM Cl^- and the terminating ion is 10 mM HIB.

The other two leading electrolyte systems were

TABLE II

ELECTROLYTE SYSTEMS USED FOR ISOTACHOPHORETIC SEPARATION

HIB = α-Hydroxyisobutyric acid; HPC = hydroxypropylsellulose.

Parameter	WNH_4Ac–HIB	WHCl	$WHClO_4$
Leading electrolyte	20 mM NH_3	10 mM HCl	10 mM $HClO_4$
Complexing agent	10 mM HIB	–	–
pH buffer	Acetic acid	–	–
pH	4.80	2	2
Additive	0.1% HPC	0.1% HPC	0.1% HPC
Terminating electrolyte	10 mM carnitine hydrochloride		
pH	2.5		

non-buffered systems of WHCl and $WHClO_4$, which were simply 10 mM HCl and 10 mM $HClO_4$ solution, respectively. The terminating electrolyte was 10 mM carnitine hydrochloride solution. All the reagents used for the operational electrolytes were purchased from Tokyo Kasei. pH measurements were carried using a Horiba (Tokyo, Japan) Model F7ss expanded pH meter.

Preparative isotachophoretic analyser

The micro-preparative analyser used was of the capillary type as reported previously [8]; the separation tube used was of 0.5 mm I.D. Separated sample zones migrating towards the leading electrolyte compartment were fractionated dropwise by a counter-flow of the leading electrolyte. A syringe pump was used to make the counter-flow. One drop (*ca.* 5 μl) constituted one fraction, which contained *ca.* 5 nmol of components. The amount in the fraction can be controlled by varying the velocity of the counter-flow and the migration current. In the present experiment, the interval of fractionation was *ca.* 10 s and the migration current was 150 μA. The migration of the zones was monitored by a potential gradient detector placed before the fractionating compartment. In addition to the separation unit, a Shimadzu (Kyoto, Japan) IP-2A isotachophoretic analyser was used.

PIXE analysis

A Model AN-2500 Van der Graaff accelerator (Nisshin High Voltage, Tokyo, Japan) was used for PIXE measurements. The energy of the H^+ beam was 2.0 MeV and the beam current was 50 nA. A typical single run for an ITP fraction took 200 s. The detector used was a highly pure Ge detector (Ortec Model GLP-10180); the multi-channel analyser used was a Laboratory Equipment (Tokyo, Japan) Model AMS-1000. The elements analysable using this system were those with atomic numbers greater than 16. The detection limit of a conventional PIXE analysis was of the order of nanograms and the amount of sample necessary was as small as a few micrograms or less.

The Nuclepore filter used as the target backing was of thickness 5 μm and pore size 0.1 μm. The diameter of the fraction spot was *ca.* 3 mm on the filter. The PIXE spectrum of each fraction was measured after drying in a desiccator.

In order to calibrate the PIXE sensitivities for quantification, 5 μl of standard sample solution was spotted on the Nuclepore filter and the PIXE spectrum was measured (1000 ppm (w/w) solution for atomic absorption spectrometry, Tokyo Kasei).

As the volume of one fraction was *ca.* 5 μl, a few or more components were contained in the fraction when the abundances were small. Our data reduction software PIXS [9] was used to analyse the PIXE spectrum. A least-squares fitting was applied for spectrum deconvolution, in which an X-ray relative intensity database optimized to our measurement system was utilized. Calculations were carried out on an NEC (Tokyo, Japan) PC-9801RA microcomputer (CPU 80386, co-processor 80387, clock 20 MHz).

RESULTS AND DISCUSSION

As the present model samples contained significant amount of rare earth elements, first WNH_4Ac–HIB was used as the operational electrolyte system as it is well known that this system gives good separation for rare earth elements [1–4].

Separation behaviour of MW-1 using WNH_4Ac–HIB

The model waste solution MW-1 contained twenty metal ions. The main components were the fission products of U and cladding materials of the fuel. As shown in Table I, the composition was essentially the same as for the other model waste (MW-2) except for the number of elements contained and the abundance of Na^+. Na^+ was present to simulate the counter ion of tributylphosphate but tributylphosphate ion itself was not present.

Fig. 1 shows the isotachopherogram obtained by using a potential gradient detector. The sample volume was 60 μl, which contained 300 nmol of metal ions. The amounts of major components injected were, in decreasing order, 54 nmol Na, 49 nmol ZrO, 31 nmol Nd, 27 nmol Fe, 24 nmol Ru, 23 nmol Ce, 15 nmol Ba, 13 nmol Pd, 12 nmol Sr and 10 nmol La. The amount of total rare earth elements was 89 nmol.

Fig. 2 shows the PIXE results for the 37 fractions obtained for the same sample. The observed migration order was NH_4^+, Ba^{2+}, Sr^{2+}, Na^+, (Cd^{2+}, Cr^{2+}), Ni^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+},
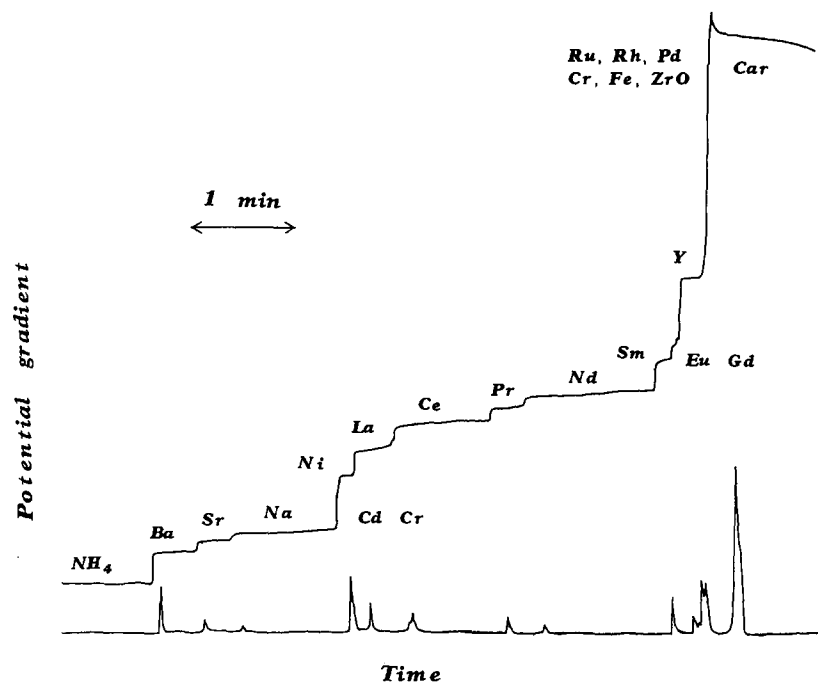
Fig. 1. Observed isotachopherogram of MW-1 model solution under the WNH$_4$Ac–HIB system. The injected sample amount was 60 μl (300 nmol of metal ions). For electrolyte conditions, see Table II. Migration current, 150 μA; amount of electricity, 0.5 C.
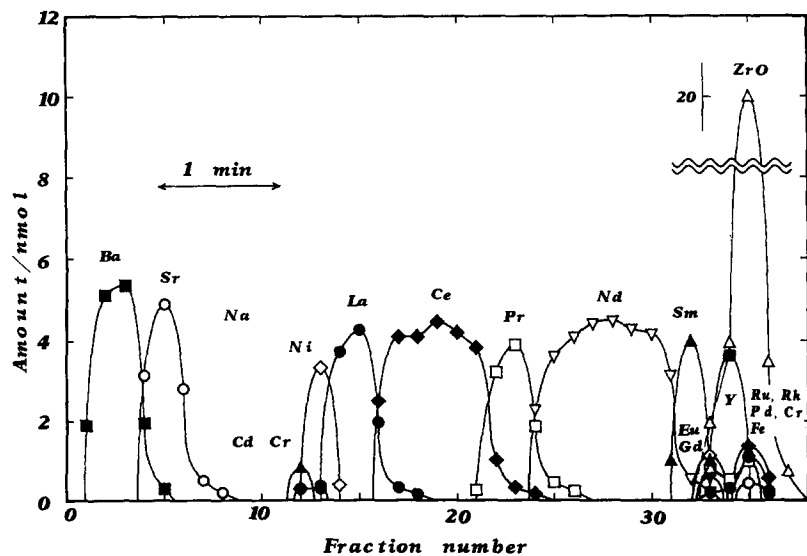
Fig. 2. Analytical results for cations for the 37 fractions of MW-1 obtained by PIXE. The corresponding isotachopherogram is shown in Fig. 1. Operational conditions as in Fig. 1.

Eu^{3+}, Gd^{3+}, Y^{3+}, ($Zr^{IV}O^{2+}$, Fe^{3+}, Ru^{3+}, Rh^{3+} and Pd^{3+}), where the ions in parentheses could not be separated from each other. Although Eu (1.5 nmol) and Gd (0.7 nmol) were found in the same fraction (No.33), they had been separated in the separation tube, as shown in Fig.1. Among the components of MW-1, Na and Al were inactive to our PIXE detection system. Fractions 7–12 were analysed by ITP and it was found that the main component was Na^+. The Al zone could not be assigned.

The amount of electricity applied was 0.5 C (300 μA for 18 min + 150 μA for 20 min). The separability was 178 nmol/C for the separation of rare earth elements and 600 nmol/C for the whole sample. When the amount of electricity was decreased, a mixed zone of Pr and Nd developed.

An interesting observation was that $Zr^{IV}O^{2+}$ formed a concentrated zone (fraction 35) with small amounts of Ru, Rh, Pd, Cr and Fe. According to Kohlrausch's regulating function, the equivalent concentration of the isotachophoretically steady-state zones should decrease from the leading towards the terminating zone with decrease in effective mobility. The concentration irregularity of fraction 35 suggested that $Zr^{IV}O^{2+}$ formed positive-

ly charged colloidal particles of hydrolysis species including Fe, Ru and Rh. From a PIXE analysis, it was found that ca. 60% of the $Zr^{IV}O^{2+}$ injected contributed to forming the cationic colloid (zone splitting).

This anomalous migration of the colloidal zone might affect the recoveries of the other components. The recoveries of the other components were evaluated using the following equation:

Recovery (%) =

$$\frac{\text{amount of element in fractions}}{\text{amount of element injected}} \cdot 100 \qquad (1)$$

where the amount in fractions denotes the amount determined by the PIXE method and the amount injected was calculated from the composition shown in Table I. The recoveries of cations are summarized in Table III. The error of the evaluated recoveries was less than 5%, which was mainly due to the error in the PIXE analysis. Obviously from Table III the recoveries can be regarded as 100% for Ba^{2+}, Sr^{2+}, Cd^{2+}, Cr^{2+}, Ni^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+} and Y^{3+}. The recovery of Na^+ might be also 100% although it was not measured. Although we have already confirmed

TABLE III

RECOVERIES OF CATIONS (%) FOR MW-1 AND MW-2 USING WNH$_4$Ac–HIB, WHCl AND WHClO$_4$ SYSTEMS

Element (Z)	MW-1: HIB[a]	MW-2			Element (Z)	MW-1: HIB[a]	MW-2		
		HIB[a]	HCl[b]	HClO$_4$[c]			HIB[a]	HCl[b]	HClO$_4$[c]
24 Cr	93	50	29	23	47 Ag	nc	—	—	—
25 Mn	nc[d]	100	22	23	48 Cd	100	99	—	—
26 Fe	6	22	49	33	50 Sn	nc	—	—	—
28 Ni	98	101	25	24	52 Te	nc	45	36	15
34 Se	nc	42	29	0	55 Cs	nc	nf	103	98
37 Rb	nc	nf[e]	104	75	56 Ba	97	nf	100	98
38 Sr	101	nf	99	100	57 La	100	99	102	100
39 Y	100	100	102	100	58 Ce	102	101	102	102
40 Zr	64	56	48	17	59 Pr	101	100	99	97
42 Mo	nc	33	32	10	60 Nd	98	98	102	99
44 Ru	12	61	40	13	62 Sm	99	100	—	—
45 Rh	54	51	0	0	63 Eu	101	97	—	—
46 Pd	1	17	3	0	64 Gd	98	97	—	—

[a] WNH$_4$Ac–HIB.
[b] WHCl.
[c] WHClO$_4$.
[d] Not contained in MW-1.
[e] Not fractionated.

the 100% recovery of these metal ions [1], an important conclusion was that the recoveries of these ions were not affected by the coexistence of excess of Fe^{III} and $Zr^{IV}O$, the recoveries of which were low: most of the Fe^{3+}, Ru^{3+}, Rh^{3+} and Pd^{3+} and half of the $Zr^{IV}O^{2+}$ and Rh^{2+} did not migrate as cations. These elements with unrecovered chemical forms migrated as anions or did not migrate, forming non-ionic substances of hydrolysis species.

Separation behaviour of MW-2 using WNH_4Ac–HIB

The model waste solution MW-2 was similarly separated and the fractions were analysed. A remarkable difference between MW-1 and MW-2 was that the Na^+ concentration in MW-2 added as $NaNO_3$ was twenty times as large as that of MW-1. The separability of rare earth elements might be smaller than for MW-1 because of the coexistence of a large amount of Na^+ (effect of composition on separability [5]).

The sample was 60 μl of the preprocessed MW-2, which contained 1619 nmol of metal ions. The amount of Na^+ was 1177 nmol and those of the other major components were 93 nmol Fe, 71 nmol

Ce, 43 nmol ZrO, 37 nmol MoO_4, 30 nmol Nd, 20 nmol Ru, 16 nmol Mn, 12 nmol Ba, 11 nmol Ni, 11 nmol Sr, 10 nmol Pd and 10 nmol La. After a steady state had been reached, most of the Na^+ zone was discarded and the zones behind the Na^+ zone were fractionated; the fractions were analysed by PIXE. Among the components of MW-2, Na, Al and P were inactive to PIXE.

Fig. 3 shows the isotachopherogram for rare earth zones and Fig. 4 shows the analytical results for the 46 fractions. The amount of electricity necessary for complete separation of the rare earth elements was 1.4 C (300 μA for 68 min + 150 μA for 20 min). The separability of the rare earth elements was calculated as 96 nmol/C, *i.e.*, about half that for MW-1. This decrease was due to the composition effect[5] caused by a large amount of coexisting Na^+. The separability for the whole sample was 1156 nmol/C. The observed migration order was essentially the same as that for MW-1.

A concentrated colloidal zone containing Fe^{3+}, $Zr^{IV}O^{2+}$, $Mo^{VI}O_4^{2-}$ and platinum group elements was also observed at fraction 40 just before the terminating zone. It seems that $Mo^{VI}O_4^{2-}$ formed ion pairs with Fe^{3+} and/or $Zr^{IV}O^{2+}$. Although Fe
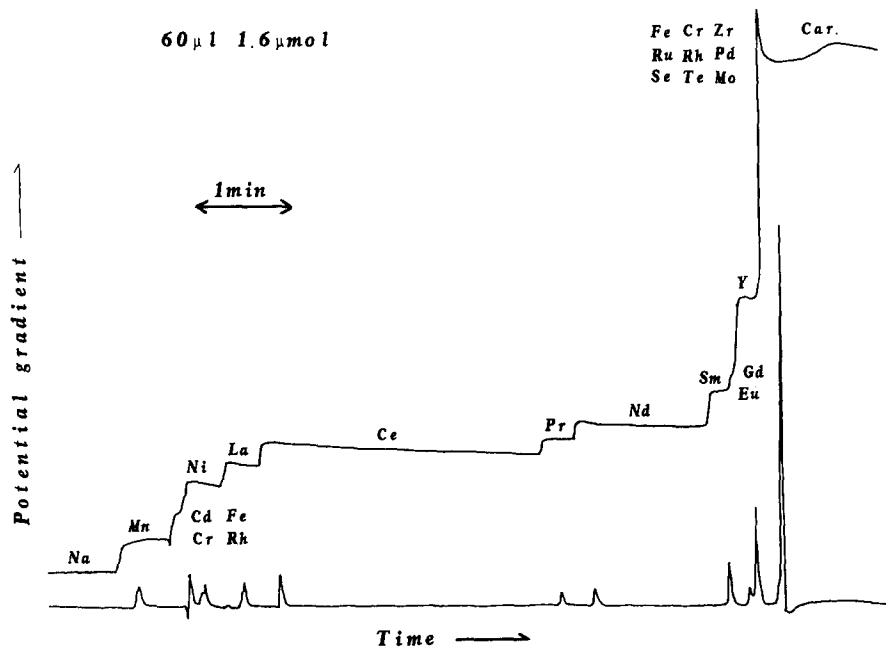

Fig. 3. Observed isotachopherogram of MW-2 using the WNH_4Ac–HIB system. The injected sample amount was 60 μl (1619 nmol of metal ions). Amount of electricity, 1.4 C. Other operational conditions as in Fig. 1.
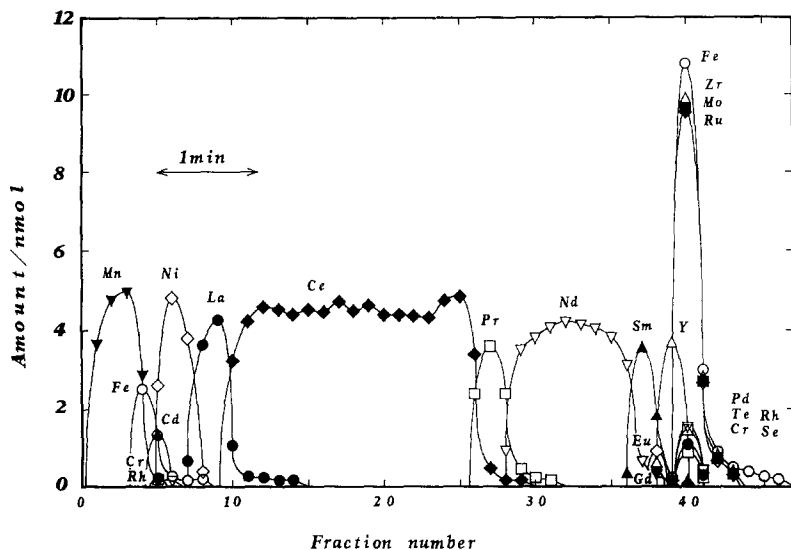
Fig. 4. Analytical results for cations for the 46 fractions of MW-2 obtained by PIXE. The corresponding isotachopherogram is shown in Fig. 3. Operational conditions as in Fig. 1.

$(NO_3)_3$ was used in the sample preparation, a considerable amount of Fe^{2+} was found in fraction 4. Rh and Cr split into two zones (5 and 40). Although Ag was analysable, it was not found in the cationic fractions. Fraction 40 also contained small amounts of Pd and Sn. Table III also summarizes the recoveries of the cationic components of MW-2: obviously, Mn, Ni, Y, La, Ce, Pr and Nd were recovered completely as cations. However, about 50% recoveries were obtained for Cr, Se, Zr, Ru, Rh and Te and very low recoveries of *ca.* 20% were obtained for Fe and Pd; most of them did not migrate as cations.

In order to clarify whether the unrecovered components in the cationic fractionation had anionic or non-ionic forms, the anionic zones of MW-2 were fractionated in the same manner using the same electrolyte system. The electrolyte system used in this work was bidirectional [6,7]: the leading electrolyte was carnitine hydrochloride and the terminating electrolyte was the WNH_4Ac–HIB system. The leading anion was Cl^- and the terminating ion was HIB^-, which migrated faster than acetate ion. Fig. 5 shows the analytical results for the anionic fractions. The components migrating as anions were $Mo^{VI}O_4^{2-}$, $Se^{IV}O_3^{2-}$ and a Zr anion. The chemical species of the Zr anion was not identified. The

concentration profile in Fig. 5 suggests that these components migrated isotachophoretically. A small amount of Fe was observed, which had a triangle zone profile: the migration of Fe was not isotachophoretic but zone electrophoretic [10]. Although migration of $Mo^{VI}O_4^{2-}$ as an anion was natural, an interesting observation was that small amounts of Zr and Fe were detected as anions. It seemed that these ions formed ion pairs with abundant counter ions.
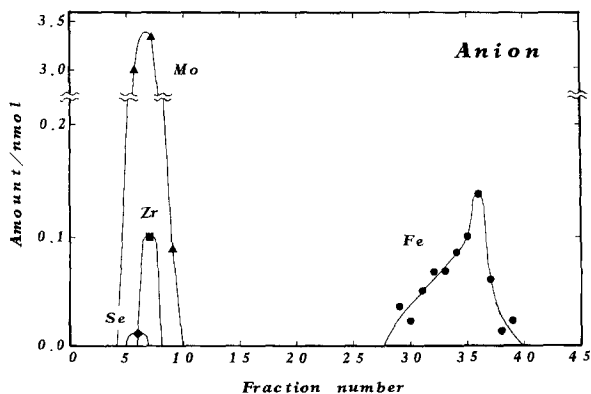

Fig. 5. Analytical results for anions for the 31 fractions of MW-2 obtained by PIXE. Amount of electricity, 1.4 C. Other operational conditions as in Fig. 1.

TABLE IV

RECOVERIES OF CATIONS, ANIONS AND NON-IONIC COMPONENTS (%) FOR MW-2 USING THE WNH$_4$Ac–HIB SYSTEM

Element (Z)	Cation	Anion	Non-ionic[a]	Element	Cation	Anion	Non-ionic[a]
24 Cr	50	0	50	47 Ag	–	–	–
25 Mn	100	0	0	48 Cd	100	–	–
26 Fe	22	1	77	50 Sn	–	–	–
28 Ni	101	0	0	52 Te	45	0	55
34 Se	42	3	55	55 Cs	100	0	0
37 Rb	100	0	0	56 Ba	100	0	0
38 Sr	100	0	0	57 La	99	0	0
39 Y	100	0	0	58 Ce	108	0	0
40 Zr	56	4	44	59 Pr	110	0	0
42 Mo	33	16	51	60 Nd	98	0	0
44 Ru	61	0	39	62 Sm	97	0	0
45 Rh	51	0	49	63 Eu	112	0	0
46 Pd	17	0	83	64 Gd	100	0	0

[a] Calculated values: 100 − (cation recovery + anion recovery). These values contain errors from the two observed values.

The recoveries of anions are summarized in Table IV together with the recoveries of cations and the calculated recoveries of non-ionic substances. Obviously Fe, Se, Zr, Mo, Ru, Rh, Pd and Te split into two or three zones. Most of the Fe and Pd formed non-mobile species, but the chemical species are unknown. The other possibility was that their mobilities were very small and they migrated zone electrophoretically in the terminating zone like the Fe zone in Fig. 5.

Fig. 6 summarizes the migration order of the MW-2 components using the WNH$_4$Ac–HIB system; the components in a particular box could not be separated.

Separation behaviour of MW-2 using WHCl and WHClO$_4$ systems

The low cationic recoveries of platinum group metals and Fe^{III} ions is due to the formation of hydrolysis species. The formation might be suppressed
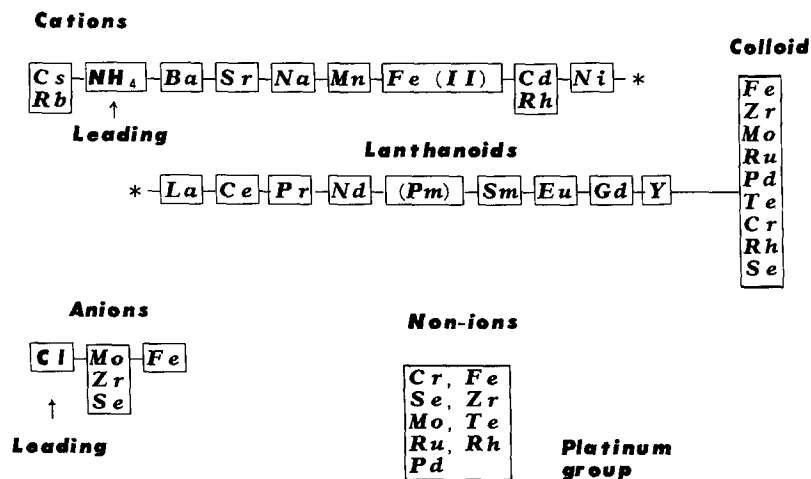

Fig. 6. Migration order of MW-2 using the WNH$_4$Ac–HIB system. The sample components in a particular box could not be separated.
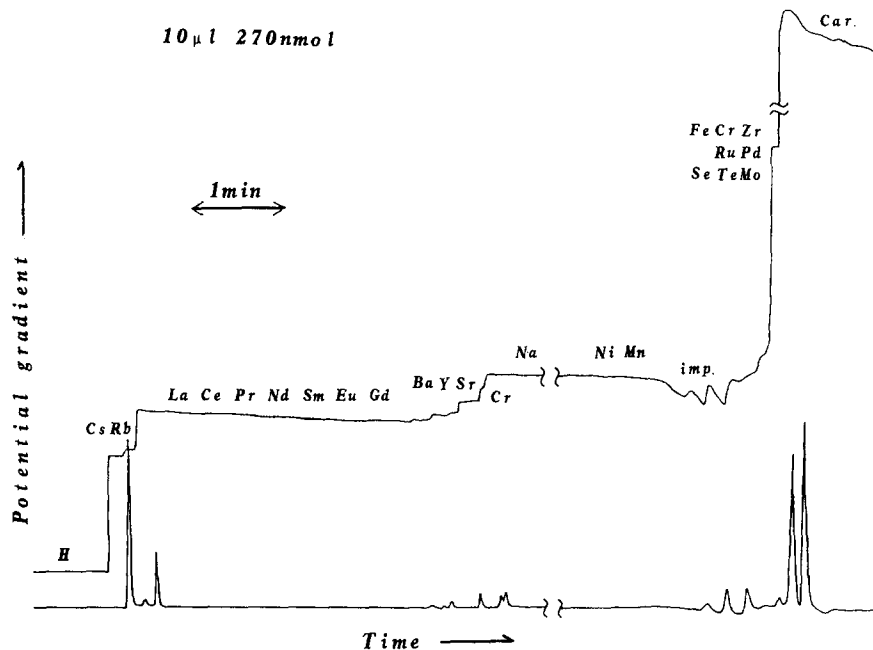
Fig. 7. Observed isotachopherogram of MW-2 using the WHCl system. The injected sample amount was 10 μl (270 nmol of metal ions). Amount of electricity, 1.1 C.
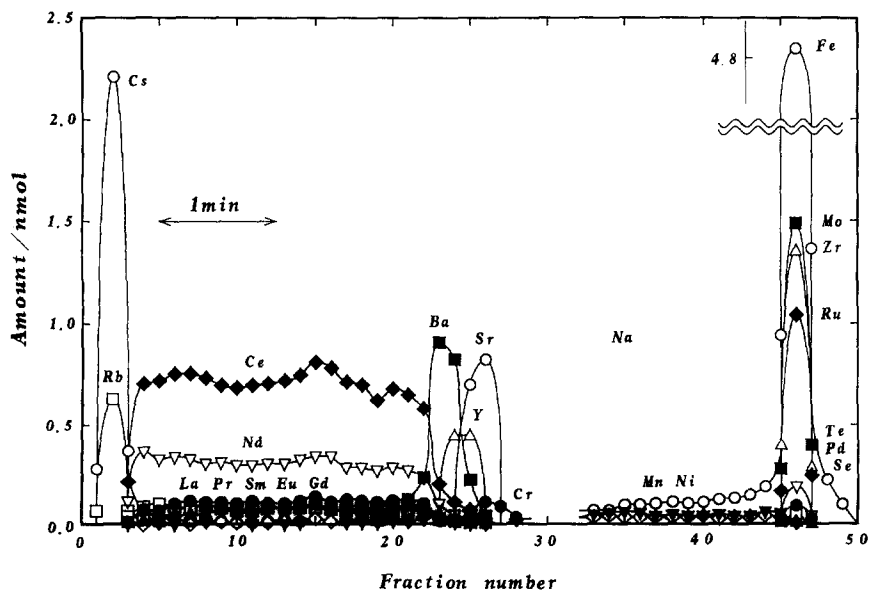

Fig. 8. Analytical results for cations for the 50 fractions of MW-2 using the WHCl system. The corresponding isotachopherogram is shown in Fig. 7.

to some extent by using a leading electrolyte of a low pH and consequently the cationic recoveries might be improved. MW-2 was analysed by using the non-buffered leading electrolytes WHCl and $WHClO_4$ where the leading ion was 10 mM H$^+$ (pH 2). The terminating electrolyte used was 10 mM carnitine hydrochloride solution.

Fig. 7 shows the isotachopherogram with the WHCl system obtained by using a potential gradient detector. The sample volume was 10 μl, which contained 270 nmol of metal ions. The amount of electricity applied was 1.1 C (300 μA for 28 min + 150 μA for 51 min). Fig. 8 shows the analytical results for 50 fractions evaluated by PIXE. Most of Na$^+$ zone was not fractionated. Obviously from Fig. 8, the separability was poor and the observed migration order was (Cs$^+$,Rb$^+$),(La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}), Ba^{2+}, Y^{3+}, Sr^{3+}, Cr^{2+}, (Na$^+$, Mn^{2+}, Ni$^+$), (Fe^{3+}, MoO$_4^-$, Ru^{3+}, Rh^{3+}, Zr^{IV}O^{2+}, Pd^{3+}, Sn^{2+}), where the ions in parentheses were not separated from each other. The separability with the $WHClO_4$ system was almost the same as that with the WHCl system.

Table III shows the recoveries of cations for MW-2 using the WHCl and $WHClO_4$ systems. The recoveries of Mn^{2+} and Ni^{2+} were estimated as 100% but they could not be evaluated because they formed a mixed zone with Na$^+$ as shown in Fig. 7 and the mixed zone was not fractionated.

Among the transition elements in MW-2, only the recovery of Fe^{3+} was improved slightly by using non-buffered systems (pH 2). The recovery of Zr^{IV}O^{2+} using WHCl was almost the same as that with the WNH$_4$Ac–HIB system (pH 4.8), but it became worse when $WHClO_4$ was used. Similarly, the recoveries of Ru, Rh and Pd could not be improved by using non-buffered electrolyte systems. These observations suggested that the recoveries of Fe, Zr and platinum group elements were affected by both the formation of hydrolysis species and the ion pairing with the other counter ions, in this instance Cl$^-$ and ClO$_4^-$. As the rate of complex-forming equilibrium is small, the pH of the sample solution and the reaction time before measurement are presumably important factors affecting the recoveries of cations, as exemplified in the isotachophoretic separation of Al^{3+} [11]. However, this problem was not investigated in further detail.

As far as the present electrolyte systems are concerned, the isotachophoretic analysis of Fe^{3+}, Zr^{IV}O^{2+} and platinum group elements cannot be recommended owing to the formation of a colloidal zone and the low recoveries of cations. However, from a preparative viewpoint platinum group elements will be fractionated as non-mobile substances very efficiently by using continuous free-flow equipment. For example, 80% of Pd in MW-2 might be recovered as non-ionic substances with the WNH$_4$Ac–HIB (pH$_L$ 4.8) system. Among the actual HLLW components of unfavourably long-lived and highly radioactive nuclides, the activity of the platinum group metals is very low and if they could be separated from the others they might be useful as industrial catalysts, for example.

The present model wastes did not contain transuranium elements, which are inevitable in real HLLW samples. However, the successful separation of transuranium elements and rare earth elements has already been reported by Bilal et al. [12] using a counter-flow technique. The separation behaviour of a model HLLW using continuous free-flow equipment is now under investigation and will be reported in due course.

ACKNOWLEDGEMENTS

REFERENCES

1 T. Hirokawa, J. Hu, S. Eguchi, F. Nishiyama and Y. Kiso, J. Chromatogr., 538 (1991) 413.
2 J. Hu, T. Hirokawa, F. Nishiyama and Y. Kiso, J. Chromatogr., 589 (1992) 339.
3 J. Hu, T. Hirokawa, F. Nishiyama, Y. Kiso, K. Ito and E. Shoto, J. Chromatogr., 594 (1992) 371.
4 P. Boček and F. Foret, J. Chromatogr., 313 (1984) 189.
5 T. Hirokawa, A. Omori, Y. Yokota, J. Hu, and Y. Kiso, J. Chromatogr., 585 (1991) 297.
6 W. Thormann, D. Arn and E. Schumacher, Electrophoresis, 6 (1985) 10.
7 T. Hirokawa, K. Watanabe, Y. Yokota and Y. Kiso, J. Chromatogr., 633 (1993) 251.
8 T. Hirokawa, J. Hu, K. Umeda, G. Kimura, H. Ikeda, F. Nishiyama and Y. Kiso, J. Chromatogr., 513 (1990) 297.
9 T. Hirokawa, F. Nishiyama and Y. Kiso, Nucl. Instrum. Methods, B31 (1988) 525.
10 F. E. P. Mikkers, F. M. Everaerts and Th. P. E. M. Verheggen, J. Chromatogr., 169 (1979) 11.

11 S. Schmid, W. Kordel, H. Kloppel and W. Klein, *J. Chromatogr.*, 470 (1989) 289.

12 B. A. Bilal, F. Herrmann, K. Metscher, B. Muhig, C. Reuchmuth and B. Schwartz, in J. D. Narvatil and W. Schulz (Editors), *Actinide Separations* (*ACS Symposium Series*, No. 117), American Chemical Society, Washington, DC, 1980, p. 561.