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Multielement Determination of Trace Metals in Seawater by ICP-MS Using a Chelating Resin-Packed Minicolumn for Preconcentration

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A chelating resin-packed minicolumn was developed to pretreat seawater samples for the determination of trace metals by inductively coupled plasma mass spectrometry (ICP-MS). The preconcentration conditions, such as the flow rate of sample loading, pH for adsorption, amount of ammonium acetate for eliminating matrix elements, and the amount of nitric acid for eluting trace metals from the resin, were investigated and optimized. Firstly, 50 mL of seawater samples was adjusted to pH 6.0 and loaded into the column at the flow rate of 3 $\mathrm{mL\,min^{-1}}$. Secondly, 8 mL of 1 M ammonium acetate and 5 mL of pure water were passed through the column for eliminating matrix elements, such as Mg and Ca. Finally, trace metals were eluted with 2.25 mL of 2 M nitric acid, and then 0.25 mL of internal standard elements (Ge, In, Re, Tl, 100 $\mu\mathrm{g\,L^{-1}}$ each) was added to the eluted solution in order to correct matrix effects in the ICP-MS measurements. The recoveries for 23 elements (Mn, Co, Ni, Cu, Zn, Y, Cd, all-REEs, Pb, and U) were more than 80%. The analytical results for the concentrations of trace metals in seawater reference material (NASS-5) agreed well with certified or reference values. The present method was also applied to the multielement analysis of the coastal seawater samples from the Take Island (Gamagoori, Aichi prefecture, Japan) and the Ise Bay (Nagoya, Aichi prefecture, Japan).

Inductively coupled plasma mass spectrometry (ICP-MS) provides some excellent analytical features of multielement detection capability with high sensitivity and wide linear dynamic range, its use allows direct determination of trace metals at sub-ppb ($\mu\mathrm{g\,L^{-1}}$) levels.[1] However, seawater analysis is still a challenging research target, because the high contents of dissolved salt in seawater cause instrumental drift, isobaric polyatomic interferences, signal suppression and cloggings of the sample introduction system in ICP-MS. Therefore, various pretreatment techniques have been developed for the determination of trace metals in seawater by ICP-MS, such as co-precipitation[2–6] and chelating resin adsorption.[7–19] In the chelating resin adsorption techniques, the column[10–16] and disk/cartridge[17–19] preconcentration systems are recently preferred over the batch method, because these systems require only a small amount of sample and can minimize contamination from various vessels and airborne particles, although the number of elements determined were limited to at most 10 by using such preconcentration systems.

There were two kinds of resins mainly used in the chelating resin methods: iminodiacetic acid (IDA) and 8-hydroxyquinoline (8-HQ)-based resins. A Chelex 100 resin (Bio-Rad Laboratories), with IDA as a functional group, has been proved to be very effective and convenient for batch preconcentration of trace metals in seawater.[7–9] Although the Chelex 100 resin has a problem of volume change at different pH values, some researchers utilized it successfully in the column method.[13,20–22] In the present research, the Chelex 100 rein was also used to construct the chelating resin-packed minicolumn. Since the optimum pH for seawater preconcentration was pH 6.0 in the present research, the Chelex 100 resin was soaked in 1 M ammonium acetate buffer (pH 6.0) overnight and then packed in the column. As a result, the resin did not cause any volume change during sample loading.

A typical column usually consists of a PTFE tube, a certain amount of resin, two parts of glass wool and two caps or tubing connectors.[16] In general, the use of a small number of parts in constructing the column is preferable to avoid opportunities for contamination. Then, a column which consisted of only three parts, i.e., two syringe filters and 0.40 g of Chelex 100 resin in wet weight, was prepared in the present experiment. The present authors named it a chelating resin-packed minicolumn; this minicolumn was applied to preconcentration of trace metals in seawater for their determination by ICP-MS.

The flow rate of sample loading, pH for adsorption, amount of ammonium acetate buffer for proper matrix removal, elution volume, and sample volume were investigated to obtain the optimum experimental conditions. The present method was applied to analysis of seawater reference material (NASS-5) from the National Research Council (NRC) of Canada as well as to analysis of coastal seawater samples.

Experimental

Instruments. An ICP-MS instrument, model Agilent HP4500 (Yokogawa, Tokyo, Japan), was used for the determination of trace metals. This instrument consisted of a quadrupole mass spectrometer. An ICP-AES instrument with a polychromator, model Plasma AtomComp MkII (Jarrell-Ash, Franklin, MA, USA), was also used for simultaneous multielement determinations of matrix elements such as Na, K, Mg, and Ca. The operating conditions for the ICP-MS and ICP-AES instruments are shown in Table 1.

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Table 1. Operating Conditions for ICP-MS and ICP-AES Instruments

ICP-MS Agilent HP4500	
Plasma conditions:	
incident power	1.3 kW
coolant gas flow rate	Ar 15.0 $\mathrm{L\,min^{-1}}$
auxiliary gas flow rate	Ar 1.0 $\mathrm{L\,min^{-1}}$
carrier gas flow rate	Ar 1.1 $\mathrm{L\,min^{-1}}$
sampling depth	9 mm from load coil
Nebulizer:	Concentric-type
sample uptake rate	0.7 $\mathrm{mL\,min^{-1}}$
Data acquisition:	
measurement mode	Peak hopping
dwell time	50 ms/point
data point	3 points/peak
number of scans	100
ICP-AES Jarrell Ash Plasma AtomComp Mk II	
Plasma conditions:	
RF power	1.0 kW
coolant gas flow rate	Ar 20 $\mathrm{L\,min^{-1}}$
auxiliary gas flow rate	Ar 1.0 $\mathrm{L\,min^{-1}}$
carrier gas flow rate	Ar 0.48 $\mathrm{L\,min^{-1}}$
sample uptake rate	1.2 $\mathrm{L\,min^{-1}}$
Nebulizer:	Cross-flow type
observation height	18 mm
Data acquisition:	
integration time	10 s
accumulation	3 times
repetition	3 times

These operating conditions were chosen after optimization of each instrumental parameter in the ICP-MS and ICP-AES instruments. A TWIN pH meter, model B-212 from HORIBA (Kyoto, Japan), was used for pH adjustment. A magnetic stirrer, model SR100 (ADVANTEC, Tokyo, Japan), was used for stirring of the solutions. A laboratory-made 7-port syringe pump was used to load the seawater samples into the column with a syringe. A syringe pump, model KDS200 (KD Scientific, MA, USA), was used for passing the rinsing solutions through the column as well as for on-line monitoring of the signal profiles for trace metals and matrix elements with ICP-MS. The prefilters for HPLC (model DISMIC-25HP from ADVANTEC, Tokyo, Japan, and model Millex-LH from Nihon Millipore Kogyo, Tokyo, Japan) were used to construct the minicolumns. The pore sizes of built-in membrane filters of both syringe filters were 0.45 µm. A syringe of Terumo series (Terumo Corporation, Tokyo, Japan) was used for loading the samples, rinsing the column, and eluting the analytes with nitric acid solution.

Chemicals. Nitric acid, acetic acid, and aqueous ammonia solution of electronics industry grade were purchased from Kanto Chemicals (Tokyo, Japan). The multielement standard solutions for making the working calibration curves were prepared from the single-element standard stock solutions (1000 $\mathrm{\mu g\,L^{-1}}$) for atomic absorption spectrometry (Wako Pure Chemicals, Osaka, Japan). The Chelex 100 resin in 100–200 mesh was purchased from Bio-Rad Laboratories (Richmond, CA, USA). The resin was purified according to the previously reported method.[8] The pure water used throughout the present experiment was prepared by a Milli-Q purification system, model Element A-10 (Nihon Millipore Kogyo).

Seawater Samples. Coastal seawater samples from the Take Island (Gamagoori, Aichi prefecture, Japan) were collected near the shore of the island, and those from the Ise Bay were collected at about 1 km off-shore near the Nagoya Port (Nagoya, Aichi prefecture, Japan). The samples were filtered with a membrane filter (pore size 0.45 µm) immediately after sampling, and then acidified to pH 1 with conc. nitric acid. The coastal seawater samples were preserved in polypropylene tanks, which were soaked in 6 M nitric acid for more than a week and rinsed with pure water just before use. The coastal seawater samples from the Take Island were used for optimizing the experimental conditions for the present preconcentration method. Seawater reference material (NASS-5) from NRC (Canada) was used for evaluating the analytical results obtained by the present method.

All bottles, beakers, stirring bars, test tubes, and pipettes used in the present experiment were soaked in 6 M nitric acid for more than a week and then rinsed with pure water.

Structure of the Chelating Resin-Packed Minicolumn. The structure of the chelating resin-packed minicolumn is shown in Fig. 1. It consists of only 3 parts, i.e., two syringe filters (a, b) and the Chelex 100 resin (c). The Chelex 100 resin was soaked in 1 M of ammonium acetate buffer (pH 6.0) overnight before packing in the column. The slurry of Chelex 100 resin was packed in the space from the outlet of HPLC prefilter tube (a) with a bed volume of *ca.* 0.08 mL, and then a smaller HPLC prefilter tube (b) was capped to construct the minicolumn. The amount of Chelex 100 resin in the column was 0.40 ± 0.01 g in wet weight ($n = 10$). One min is enough for packing the resin in the minicolumn. As is shown in Fig. 1, the size of the minicolumn was 39 mm × 29 mm, so that it was portable and then easily applicable to the field experiment on board. All the solutions could be loaded with the syringes.

Procedure for Preconcentration. The procedure for preconcentration of trace metals in seawater was as follows. Firstly, 5 mL of 1 M ammonium acetate buffer (pH 6.0) was passed through the chelating resin-packed minicolumn for conditioning, and then 50 mL of seawater sample (adjusted to pH 6.0) was loaded into the chelating resin-packed minicolumn at the flow rate of 3 $\mathrm{mL\,min^{-1}}$ by using a 50 mL volume syringe. Since alkali and alkaline earth elements ($\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Mg^{2+}}$, and $\mathrm{Ca^{2+}}$), which were matrix elements in seawater, were partly adsorbed on the resin, 8 mL of 1 M ammonium acetate buffer (pH 6.0) and 5 mL of pure water were successively injected at the flow rate of 2 $\mathrm{mL\,min^{-1}}$

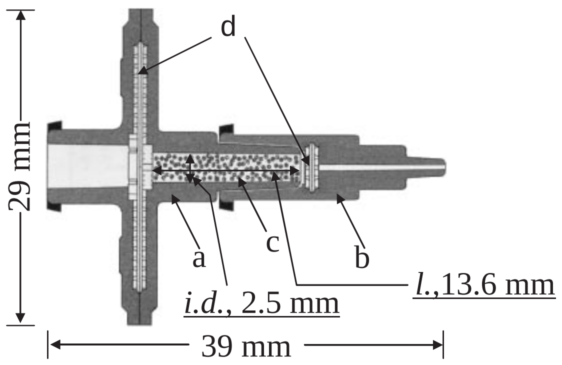

Fig. 1. A schematic diagram of the chelating resin-packed minicolumn. a) prefilter tube (DISMIC-25HP, ADVANTEC); b) prefilter tube (Millex-LH, Nihon Millipore Kogyo); c) Chelex 100 resin, 100–200 mesh (Bio-Rad Laboratories); d) membrane filter (pore size 0.45 µm).

for rinsing to minimize the amounts of matrix elements adsorbed on the resin. Then, trace metals adsorbed on the chelating resin were eluted with 2.25 mL of 2 M HNO_3 to a 5 mL test tube. After 0.25 mL of internal standard solution (Ge, In, Re, Tl 100 ppb each) was added in the eluted solution to correct matrix effects, and the final analysis solution was subjected to the determination of trace metals by ICP-MS.

In the recovery test, trace metals (from 0.1 $\mu g\,L^{-1}$ of rare earth elements to 100 $\mu g\,L^{-1}$ of Mn and Mo) were spiked in the coastal seawater, taking into consideration their concentrations in coastal seawater. The same preconcentration procedure as described above was carried out to estimate the recoveries for trace metals. The concentrated samples were diluted properly in the determination of Mn and Mo by ICP-MS, since their concentrations were out of the linear dynamic range of the instrument if the samples were not diluted.

Results and Discussion

Flow Rate of Sample Loading. The coastal seawater samples collected from the Take Island were adjusted to pH 6.0 and then used for optimization of the sample-loading flow rate. The optimization was performed by observing the relative signal intensities for trace metals in preconcentrated samples. The sample-loading flow rates of 0.5, 2, 3, and 4 $mL\,min^{-1}$ were investigated with the aid of the syringe pump. The results are shown in Fig. 2. It was found that the relative signal intensities for Cu, Zn, and Co in preconcentrated samples did not vary apparently throughout the flow rates investigated. However, those for W, V, and Mo, which exist mostly as oxoanions in seawater,[22] decreased rapidly when the flow rate was larger than 3 $mL\,min^{-1}$. In order to obtain the better recoveries for the elements as many as possible in relatively short times, 3 $mL\,min^{-1}$ was chosen as the optimum flow rate of sample loading.

pH Dependences of Analyte Signal Intensities in Chelating Resin Preconcentration. In chelating resin preconcentration, the pH of the samples significantly influences the recoveries of trace metals.[7–9] In the present research, the recoveries, which were estimated from the relative signal intensities for trace metals in the preconcentrated samples, were investigated for values of the sample pH from 1 to 9, where the preconcentration procedure described in the experimental section was carried out. Since Mg^{2+} in seawater precipitated at pH over 9, the pH range beyond 9 was not examined. The results are shown in Figs. 3(a)–(d). There were four types of characteristic behaviors of analyte elements in the pH range examined. As is shown in Fig. 3(a), the recoveries for Co, Cu, Ga, Ni, U, and Zn were almost constant between pH 4.5–8.0, which provided the wide optimum pH range for chelating resin preconcentration. The recoveries for Mo, Sn, Ti, V, and W provided the maximum near pH 4, as is seen in Fig. 3(b). On the other hand, as is shown in Fig. 3(c) and Fig. 3(d), the largest recoveries for rare earth elements (REEs), including Y, were obtained at pH 5.5–6, while Cd and Mn provided the larger recoveries in the higher pH of 7–9. Therefore, in order to obtain the better recoveries for the elements as many as possible, pH 6.0 was chosen as the compromise optimum condition in the present experiment.

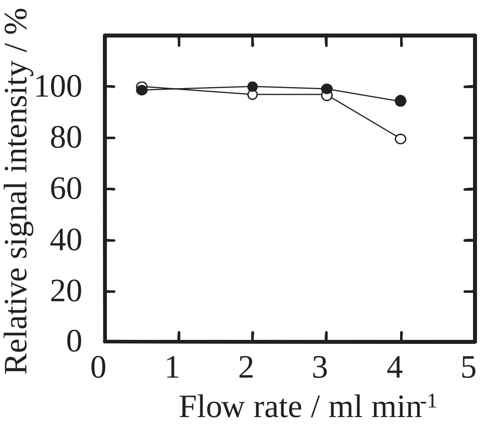

Fig. 2. Effects of the flow rates of sample loading on the relative signal intensities of Cu and W in preconcentrated sample. ●: Cu, ○: W.

Elution of Matrix Elements in Seawater. Matrix elements usually cause instrumental drift, isobaric polyatomic interferences, and signal suppression in the determination of trace metals by ICP-MS. Ammonium acetate buffer was often used for elimination of matrix elements adsorbed on the chelating resin.[7–9] However, an excessive amount of the buffer used resulted in loss of trace analyte metals.[7–9] The optimization for amount of ammonium acetate buffer (1 M, pH 6.0) was then investigated after the sample loading procedure in the present experiment. The ammonium acetate buffer was injected into the minicolumn at the flow rate of 1.0 $mL\,min^{-1}$ with the syringe pump, with monitoring the signal profile observed by ICP-MS. The elution signal profiles of Ca^{2+} are shown in Fig. 4. This figure shows that 95% and 98% of the Ca^{2+} adsorbed were eluted from the chelating resin, when 8 mL (480 s) and 10 mL (600 s) of the buffer were injected, respectively. The optimum amount of the buffer for matrix elution was estimated from the following concentrations of matrix elements in the preconcentrated samples. The results are shown in Table 2. As is seen in Table 2, when 8 mL of ammonium acetate buffer was used, the total concentration of matrix elements (Na, Mg, K, and Ca) was 77 ± 16 $mg\,L^{-1}$. It was considered that 8 mL of ammonium acetate was enough for eliminating matrix elements, because the effects of matrix elements less than 200 $mg\,L^{-1}$ could be corrected by the internal standard correction method.[9] Although 10 mL of ammonium acetate buffer resulted in the lower total concentration of matrix elements in the preconcentrated solution, it caused loss of trace metals. As the compromise condition, 8 mL of ammonium acetate buffer was chosen for elimination of matrix elements in the following experiments.

Elution Profiles of Trace Metals in Seawater. As stated in the experimental section, trace metals adsorbed on the chelating resin were eluted with 2 M nitric acid. When the excessive amount of nitric acid was used, it caused a lower concentration factor, which resulted in the poorer determination limits for trace metals. On the other hand, if the amount of nitric acid was insufficient, trace metals adsorbed on the resin could not be recovered well. Therefore, the optimum volume of nitric acid for elution of trace metals was investigated in the present experiment. After 50 mL of seawater sample was loaded in the minicolumn, 8 mL of 1 M ammonium acetate buffer (pH 6.0)

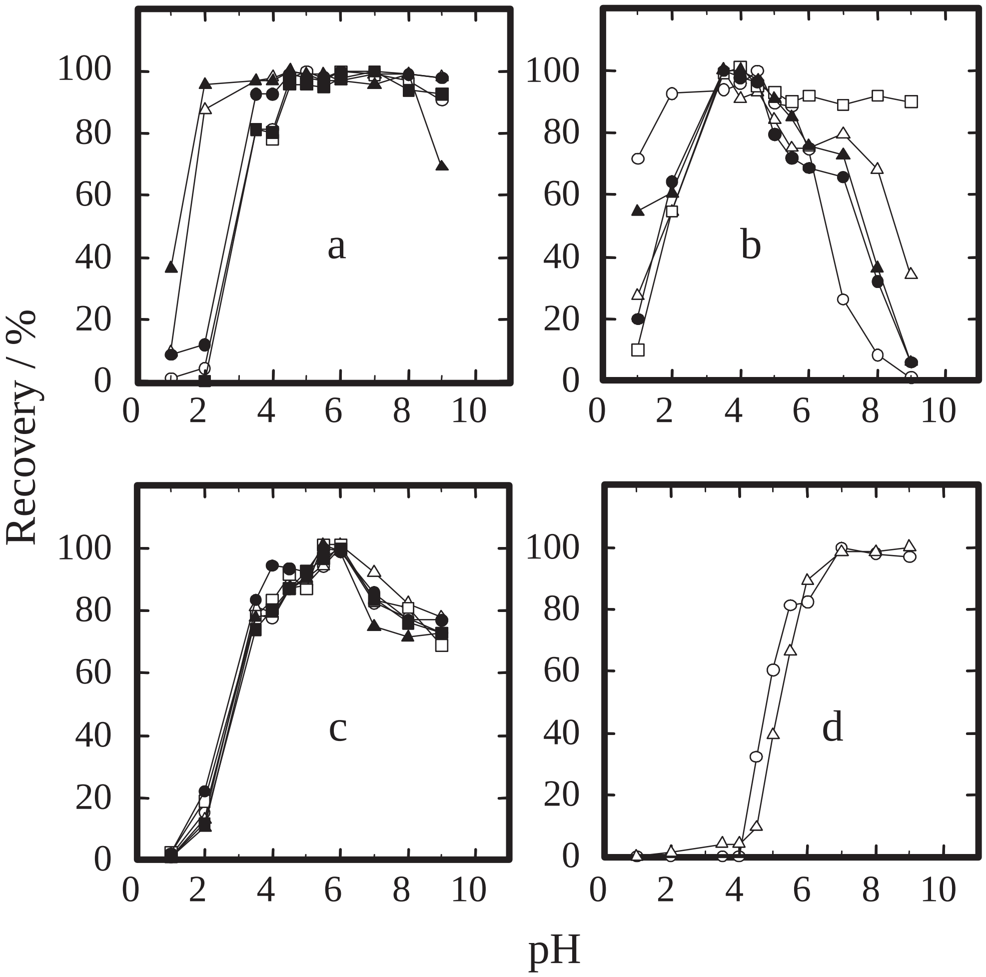

Fig. 3. pH dependence of the recoveries for trace metals in preconcentrated sample. (a) ○: Co, △: Cu, □: Ga, ●: Ni, ▲: U, ■: Zn. (b) ○: Mo, △: Sn, □: Ti, ●: V, ▲: W. (c) ○: Ce, △: La, □: Nd, ●: Sm, ▲: Tb, ■: Yb. (d) ○: Cd, △: Mn.

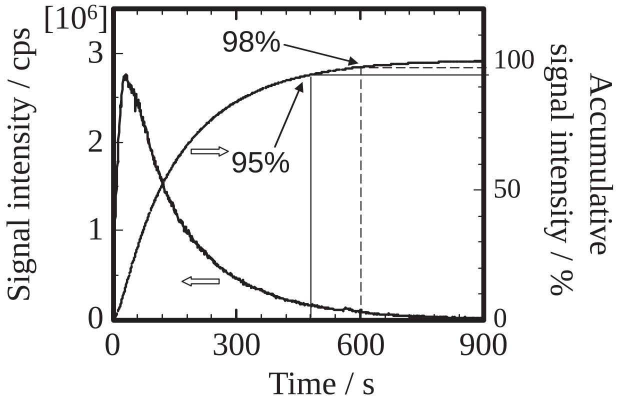

Fig. 4. Elution signal profile for Ca^{2+} from the minicolumn with 1 M ammonium acetate (pH 6.0).

and 5 mL of pure water were successively passed through the minicolumn for elimination of matrix elements. Thereafter, nitric acid solution (2 M) was injected to the minicolumn at the flow rate of 0.9 $mL\,min^{-1}$, and then the elution signal profiles of trace metals were on-line monitored by ICP-MS. The result is shown in Fig. 5. Since all the elution signal profiles for trace metals provided similar patterns to each other, the signal profile is shown as the total counts of 36 trace metals. It was found that 98% of analyte could be eluted with 2.25 mL (150 s) of nitric acid. Even if another 2.25 mL of nitric acid was used for elution, only 2% of analyte was additionally eluted, but the preconcentration factor decreased to half. Therefore, only 2.25 mL of nitric acid was chosen as the optimum volume of nitric acid for elution of trace metals.

Exchange Capacity of the Minicolumn. It was stated in the experimental section that 0.40 g of Chelex 100 resin in wet weight was packed in the minicolumn. In the present research, the exchange capacity of the minicolumn was investigated by preconcentrating 50, 100, 150, 200, and 250 mL of seawater sample to 2.5 mL. The concentrations of trace metals in the preconcentrated samples were determined by ICP-MS. It was found that the concentrations of ^{65}Cu in the preconcentrated samples were in proportion to the volume of pretreated samples up to 250 mL, with $R^2 = 0.9989$ (R, the correlation coefficient). Other trace metals showed the similar correlations to ^{65}Cu. However, the correlation coefficients were lower for oxoanion- or hydroxide-forming elements such as Mo, V, and W in seawater; for example, $R^2 = 0.9204$ for W. These results could be attributed to the fact that the pH condition in the present research was not optimum for these elements. No sample volume over 250 mL was investigated in the present research,

Table 2. Concentrations of Matrix Elements in Preconcentrated Samples

	Concentration$^{a)}$/mg L^{-1}				
	Na	Mg	K	Ca	Total
A$^{b)}$	4 ± 1	31 ± 8	n.d.$^{d)}$	42 ± 7	77 ± 16
B$^{c)}$	3 ± 1	11 ± 2	n.d.$^{d)}$	8 ± 2	22 ± 5
Detection limit	0.04	0.02	3	0.01	

a) Mean value ± standard deviation, $n = 3$. b) Eight milliliter of 1 M ammonium acetate buffer (pH 6.0) was used to eliminate matrix elements. c) Ten milliliter of 1 M ammonium acetate buffer (pH 6.0) was used to eliminate matrix elements. d) Not detected.

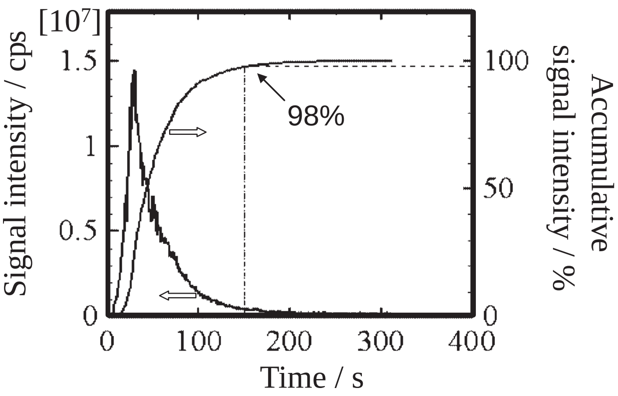

Fig. 5. Elution signal profile for total counts of 36 trace metals from the minicolumn with 2 M nitric acid.

because the throughput of pretreatment was in proportion to the volume of sample. It was, thus, concluded that the exchange capacity of the present chelating resin-packed minicolumn was large enough to pretreat 250 mL of seawater sample, although only 50 mL of seawater sample was used for analysis in the present experiment.

Correction of Polyatomic Interferences. In the ICP-MS measurements, major and trace elements in the sample solution often cause spectral interferences.[23] In the present research, the interferences of ^{44}Ca^{1}H, ^{43}Ca^{16}O, ^{48}Ca^{16}O^{1}H, ^{95}Mo^{16}O, ^{137}Ba^{16}O, ^{141}Pr^{16}O, ^{143}Nd^{16}O, ^{147}Sm^{16}O, ^{149}Sm^{16}O, ^{153}Eu^{16}O, ^{156}Gd^{16}O with ^{45}Sc, ^{59}Co, ^{65}Cu, ^{111}Cd, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{169}Tm, and ^{172}Yb, respectively, were corrected according to the interference correction coefficient method reported by Yabutani et al.[9] The interference ratios (the ratios of the apparent interference concentrations to the concentrations of analyte elements) for all of elements examined were less than 10%.

Analytical Figures of Merit. The recoveries, blank values and analytical detection limits for trace metals are summarized in Table 3, as the analytical figures of merit of the present method. The recovery values in Table 3 are the mean values and the standard deviation (σ) estimated from 3-times duplicated experiments. The recoveries for 23 elements were more than 80%, while those for 7 elements were between 80% and 50%, and those for 6 elements were less than 50%. However, the standard deviations of the recoveries for all elements were less than 5%.

The blank values in the present method are also shown in Table 3. In the estimation of the blank values, 50 mL of 0.1 M nitric acid was used as a test solution, and the same preconcentration and measurement procedures as used for seawater samples were performed. The blank values for most of trace metals were almost negligible, because they were much lower than the abundances of analyte elements in seawater. However, the blank values for Zn and Pb were at almost the same level as their concentrations in seawater. The concentrations of Zn and Pb in 1 M ammonium acetate buffer were found to be 0.01 and 0.03 μg L^{-1}, respectively; these values were estimated after a batch preconcentration method. Thus, the relatively large blank values for Zn and Pb were attributed to the impurities in ammonium acetate. Hence, the use of ultra pure grade acetic acid and aqueous ammonia for preparation of ammonium acetate buffer and pH adjustment may reduce the blank values for Zn and Pb. The present authors are now attempting to lower the blank values of trace metals by purifying ammonium acetate.

The analytical detection limits of the present method are also shown in Table 3. They were calculated from the instrumental detection limits, taking into account the concentration factor (20) and the recovery values for trace metals examined. The instrumental detection limits were defined as the concentrations corresponding to 3 times the standard deviation of the background signal intensity, which were estimated from the 10-times duplicated measurements of the background solution, i.e., mixed solution of internal standard elements (Ge, In, Re, Tl 10 μg L^{-1} each) in 2 M nitric acid. The analytical detection limits for 36 elements were in the range from 0.07 μg L^{-1} of Ti to 0.00006 μg L^{-1} of Lu.

Analytical Results for Trace Metals in Seawater Reference Material (NASS-5). Trace metals in seawater reference material (NASS-5) were determined by the present analytical method. The results are summarized in Table 4, along with the certified or reference values. The concentrations of trace metals were corrected with the recovery values listed in Table 3. As is shown in Table 4, the concentrations of 27 elements (Al, Ti, V, Mn, Co, Ni, Cu, Ga, Y, Zr, Mo, Cd, Sn, all-REEs, Hf, W, Bi, Th, and U) in NASS-5 were obtained in the present study. The concentrations of trace metals ranged from 9.1 μg L^{-1} of Mo to <0.0002 μg L^{-1} of Tb and Tm. Since the concentrations of Al, Ti, V, Zr, Sn, Eu, Gd, and W were close to blank values or determination limits, their concentrations were seemingly less reliable, so their results are shown in parentheses for reference. The concentrations of Sc, Zn, Nb, and Pb could not be obtained by the present method.

The analytical results for V, Mn, Co, Ni, Cu, Mo, Cd, and U agreed well with the certified values issued by NRC; these elements are shown in bold fonts in Table 4. The concentrations of rare earth elements (REEs) were compared with reference values reported by Willie and Sturgeon.[14] Taking into account

Table 3. Analytical Figures of Merit for Trace Elements with Aid of Preconcentration Using the Chelating Resin-Packed Minicolumn

Element	m/z	Recovery[a) /%	Blank /μg L^{-1}	Analytical detection limit[c) /μg L^{-1}
Al	27	59 ± 3	0.76	0.06
Sc	45	65 ± 2	<0.002	0.0007
Ti	47	48 ± 2	<0.2	0.07
V	51	43 ± 5	<0.002	0.0007
Mn	55	84 ± 3	n.d.b)	0.02
Co	59	101 ± 2	0.0023	0.0004
Ni	60	101 ± 4	0.042	0.002
Cu	65	100 ± 1	0.025	0.001
Zn	68	103 ± 2	0.35	0.009
Ga	71	74 ± 1	n.d.b)	0.0005
Y	89	95 ± 3	<0.0004	0.0001
Zr	90	35.5 ± 0.1	<0.005	0.002
Nb	93	38 ± 2	0.001	0.0003
Mo	98	63 ± 4	<0.003	0.001
Cd	111	91 ± 3	n.d.b)	0.003
Sn	118	50 ± 1	0.007	0.001
La	139	96 ± 3	0.0004	0.0001
Ce	140	101 ± 3	<0.0004	0.0001
Pr	141	92 ± 1	n.d.b)	0.00007
Nd	143	98.2 ± 0.2	n.d.b)	0.0003
Sm	147	92 ± 2	n.d.b)	0.0005
Eu	153	92.8 ± 0.3	n.d.b)	0.0001
Gd	157	85 ± 5	n.d.b)	0.0004
Tb	159	88 ± 2	n.d.b)	0.00008
Dy	163	83 ± 3	n.d.b)	0.0003
Ho	165	94 ± 1	n.d.b)	0.00007
Er	166	98 ± 3	n.d.b)	0.0002
Tm	169	93 ± 1	n.d.b)	0.00008
Yb	172	91 ± 2	n.d.b)	0.0003
Lu	175	94 ± 3	n.d.b)	0.00006
Hf	178	44 ± 3	n.d.b)	0.003
W	184	23 ± 3	n.d.b)	0.002
Pb	207	93.7 ± 0.4	0.04	0.001
Bi	209	56 ± 4	<0.0006	0.0002
Th	232	57 ± 2	n.d.b)	0.0001
U	238	95.2 ± 0.3	n.d.b)	0.00008

a) Mean value ± standard deviation, $n = 3$. b) Not detected. c) Analytical detection limits were calculated from instrumental detection limits, taking into account the concentration factor (20) and recovery values.

the concentration levels of REEs, it can be stated here that the results agreed well with reference values, too. The analytical results of NASS-5 indicate that the present method is applicable to multielement preconcentration and determination of trace metals in the seawater samples.

Analytical Results for Trace Metals in Coastal Seawater Samples. The present analytical method was also applied to the multielement determination of trace metals in the coastal seawater samples from the Take Island and the Ise Bay. The results are summarized in Table 5, which were also corrected with the recovery values listed in Table 3. In the present analytical method, 31 and 34 trace metals could be determined in the Take Island coastal seawater and the Ise Bay coastal seawater, respectively. As is seen in Table 5, the concentrations of Sc, Nb, Hf, Bi, and Th in the Take Island coastal seawater and those of Eu and Hf in the Ise Bay coastal seawater were lower than the determination limits of the present analytical method. The concentrations of trace metals in the Take Island coastal seawater were in the range from 9.5 μg L^{-1} of Mn to 0.00025 μg L^{-1} of Tb, and the relative standard deviations (RSDs) were less than 15%, except for Sn, whose concentration was close to the blank value. On the other hand, the concentrations of trace metals in the Ise Bay coastal seawater were in the range from 36 μg L^{-1} of Mn to 0.00040 μg L^{-1} of Tb, and the RSDs were less than 15%, except for Sn and Bi. The concentrations of Ti and Sn in the Take Island coastal seawater, and those of Ti, Sn, and Bi in the Ise Bay coastal seawater are shown in parentheses for reference, because their concentrations were close to blank values or determination limits. The concentrations of trace metals in the Ise Bay coast-

Table 4. Analytical Result for Trace Elements in Seawater Reference Material (NASS-5)

Element	m/z	Concentration/μg L^{-1}	
		Observed value a)	Certified value
Al	27	(0.11 ± 0.02)	
Sc	45	n.d. b)	
Ti	47	(0.21 ± 0.03)	
V	51	**(1.3 ± 0.2)**	**1.2** c)
Mn	55	**0.87 ± 0.04**	**0.92 ± 0.06**
Co	59	**0.013 ± 0.002**	**0.011 ± 0.003**
Ni	60	**0.24 ± 0.01**	**0.25 ± 0.03**
Cu	65	**0.31 ± 0.03**	**0.30 ± 0.05**
Zn	68	n.d. b)	0.10 ± 0.04
Ga	71	<0.002	
Y	89	0.020 ± 0.001	
Zr	90	(0.025 ± 0.001)	
Nb	93	n.d. b)	
Mo	98	**9.1 ± 0.5**	**9.6 ± 1.0**
Cd	111	**0.030 ± 0.004**	**0.023 ± 0.003**
Sn	118	(0.0025 ± 0.0008)	
La	139	0.0111 ± 0.0005	0.0128 ± 0.0012 d)
Ce	140	0.0049 ± 0.0003	0.0040 ± 0.0006 d)
Pr	141	0.0019 ± 0.0001	0.0015 ± 0.0002 d)
Nd	143	0.0068 ± 0.0005	0.0099 ± 0.0018 d)
Sm	147	0.0040 ± 0.0003	0.0040 ± 0.0003 d)
Eu	153	(0.00040 ± 0.00001)	0.00026 ± 0.00005 d)
Gd	157	(0.0021 ± 0.0001)	0.00153 ± 0.00028 d)
Tb	159	<0.00024	0.00029 ± 0.00005 d)
Dy	163	0.0018 ± 0.0001	0.00165 ± 0.00028 d)
Ho	165	0.00044 ± 0.00002	0.00036 ± 0.00005 d)
Er	166	0.0013 ± 0.0001	0.0012 ± 0.0002 d)
Tm	169	<0.00024	0.00015 ± 0.00003 d)
Yb	172	0.0013 ± 0.0001	0.0011 ± 0.0002 d)
Lu	175	0.00022 ± 0.00002	0.00020 ± 0.00004 d)
Hf	178	<0.009	
W	184	(0.010 ± 0.001)	
Pb	207	n.d. b)	0.008 ± 0.005
Bi	209	<0.0006	
Th	232	<0.0003	
U	238	**2.66 ± 0.05**	**2.60** c)

a) Mean value ± standard deviation, $n = 5$. b) Not detected. c) Information value. d) Cited from Ref. 14.

al seawater are generally higher than those in the Take Island coastal seawater. In Table 5, the concentrations shown in bold fonts for the Ise Bay coastal seawater are more than 2-fold higher than those for the Take Island coastal seawater. These differences could be attributed to the river water inputs and to the artificial pollution caused by human and industrial activities in the Ise Bay, because many industrial factories are located around the Ise Bay. On the other hand, the Take Island coastal area is in front of the Pacific Ocean, and is not in an industrial area.

It was found that the concentrations of V, Mo, and U in seawater samples from the Ise Bay and the Take Island were almost the same as those in NASS-5. Since these elements exist as the stable oxoanions in the seawater, their concentrations are uniform as the conservative elements in seawater all over the sea areas in the world.[22,24–26] In addition, since their concentrations were at the $\mu\mathrm{g\,L^{-1}}$ level, the inputs from anthropogenic sources might be negligible, compared with their original concentrations. As for W, which also exists as the stable oxoanions in seawater, its concentration in open seawater is at lower $\mathrm{ng\,L^{-1}}$ or sub-$\mathrm{ng\,L^{-1}}$ level.[22,24–26] Therefore, the concentration of W in coastal seawater is significantly affected by the anthropogenic sources due to human activities.[24–26]

Shale-Normalized REE Distribution Patterns in Seawaters. Since the concentrations of REEs in open seawater are at the lower $\mathrm{ng\,L^{-1}}$ or sub-$\mathrm{ng\,L^{-1}}$ level, the certified values for REEs have not been established in seawater reference materials. As a result, the REE distribution patterns, which are shown as the relative concentrations of REEs normalized to their concentrations in shale, are often examined in order to evaluate the internal consistency of the REEs data for seawaters.[8,9] The REE distribution patterns for the Take Island coastal seawater, the Ise Bay coastal seawater, NASS-5, and CASS-3 are shown in Fig. 6, where the concentrations of REEs were normalized to those in Post-Archean Average Australian Shale (PAAS).[27] The REE patterns in Fig. 6 show

Table 5. Analytical Result for Trace Metals in Seawater Samples from Take Island and Ise Bay

		Take Island		Ise Bay	
Element	m/z	Concentration[a)] /μg L^{-1}	RSD[b)] /%	Concentration[a)] /μg L^{-1}	RSD[b)] /%
Al	27	2.3 ± 0.2	7.0	**17 ± 1**	5.9
Sc	45	<0.002		0.0034 ± 0.0005	13.3
Ti	47	(0.20 ± 0.01)	4.4	(0.047 ± 0.002)	4.3
V	51	1.40 ± 0.06	4.0	1.90 ± 0.05	2.6
Mn	55	9.5 ± 0.6	6.1	**36 ± 2**	5.6
Co	59	0.036 ± 0.002	6.7	0.12 ± 0.002	1.7
Ni	60	0.58 ± 0.03	4.8	**2.4 ± 0.1**	4.2
Cu	65	0.48 ± 0.01	2.9	**1.5 ± 0.1**	6.7
Zn	68	4.1 ± 0.1	2.8	**15 ± 0.5**	3.3
Ga	71	0.0066 ± 0.0004	6.6	0.012 ± 0.0004	3.3
Y	89	0.025 ± 0.001	3.0	0.032 ± 0.001	3.1
Zr	90	0.023 ± 0.001	3.9	0.014 ± 0.001	7.1
Nb	93	n.d.[c)]		n.d.[c)]	
Mo	98	9.2 ± 0.3	3.7	9 ± 1	11.1
Cd	111	0.019 ± 0.001	7.1	0.018 ± 0.002	11.1
Sn	118	(0.005 ± 0.001)	29.0	(0.007 ± 0.002)	28.1
La	139	0.00596 ± 0.00027	4.5	**0.0123 ± 0.0009**	7.3
Ce	140	0.0039 ± 0.0002	5.8	**0.0102 ± 0.0006**	5.9
Pr	141	0.00109 ± 0.00007	6.3	0.00205 ± 0.00005	2.4
Nd	143	0.0043 ± 0.0001	1.9	0.0064 ± 0.0006	9.4
Sm	147	0.0015 ± 0.0001	6.2	0.0009 ± 0.0001	11.1
Eu	153	0.00043 ± 0.00001	2.4	0.00046 ± 0.00006	13.0
Gd	157	0.0024 ± 0.0001	5.0	0.0035 ± 0.0004	11.4
Tb	159	0.00025 ± 0.00003	12.6	0.00040 ± 0.00005	12.4
Dy	163	0.0029 ± 0.0003	10.8	0.00297 ± 0.00009	3.0
Ho	165	0.00060 ± 0.00005	7.8	0.00073 ± 0.00002	2.7
Er	166	0.0020 ± 0.0002	9.3	0.003 ± 0.0002	6.7
Tm	169	0.00035 ± 0.00004	12.3	0.00051 ± 0.00005	9.8
Yb	172	0.0027 ± 0.0003	11.2	0.0039 ± 0.0002	5.1
Lu	175	0.00054 ± 0.00007	12.3	0.0009 ± 0.0001	11.2
Hf	178	<0.009		n.d.[c)]	
W	184	0.045 ± 0.003	7.1	**0.16 ± 0.01**	6.3
Pb	207	0.080 ± 0.006	7.7	**0.38 ± 0.02**	5.3
Bi	209	<0.0006		(0.0008 ± 0.0004)	50.0
Th	232	<0.0003		**0.00119 ± 0.00008**	6.7
U	238	2.68 ± 0.02	0.7	2.64 ± 0.09	3.4

a) Mean value ± standard deviation, $n = 5$. b) Relative standard deviation, $n = 5$. c) Not detected.

smooth curves in general, with slight enrichment of heavy REEs and clear negative anomalies of Ce in all seawater samples. These results are consistent with those previously reported for REEs in seawaters.[8,9] On the other hand, coastal seawaters, such as the Take Island coastal seawater, the Ise Bay coastal seawater, and CASS-3, showed relatively larger enrichment of heavy REEs than those in NASS-5, which is open seawater. This may be explained by the input of dissolved REEs in river water fluxes, which generally contain the higher concentrations of heavy REEs.[28,29] In both CASS-3 and NASS-5, the high concentrations of Sm were observed. As has been reported,[9] contamination of Sm was seemingly caused in preparation procedure of the reference material. The results for the Take Island and Ise Bay coastal seawaters did not show any high concentration of Sm like those in reference materials. Thus, it may be reasonable to consider that Sm in NASS-5 and CASS-3 was contaminated during preparation of these reference materials.

Conclusion

A chelating resin-packed minicolumn was prepared and evaluated as the pretreatment method for simultaneous multielement determination of trace metals in seawater by ICP-MS. Even though only 50 mL of seawater was used for analysis, the recovery values of more than 80% for 23 elements were obtained in the present experiment. The present chelating resin-packed minicolumn could be used repeatedly after rinsing with enough 2 M HNO_3 and pure water several times. However, it may be preferable to pack the new chelating resin in the minicolumn because the resin once used for preconcentration often provided appreciable blanks of some trace metals. The analytical results for trace metals in seawater reference material (NASS-5) agreed well with the certified or information values issued by NRC. These results indicate that the present method is suitable for preconcentration of trace metals in seawater for the determination by ICP-MS.

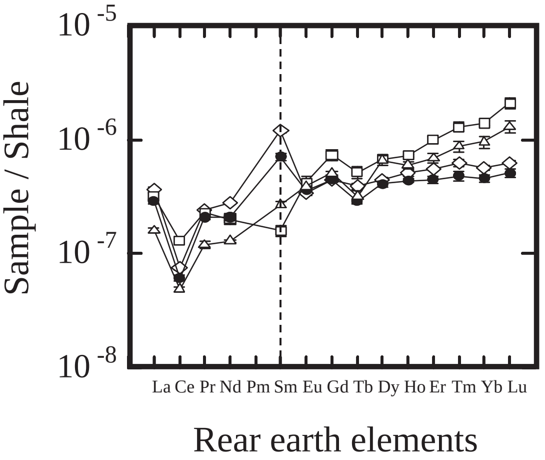

Fig. 6. Shale-normalized REE distribution patterns for seawaters. △: Take Island coastal seawater, □: Ise Bay coastal seawater, ●: NASS-5, ◇: CASS-3 (cited from Ref. 9).

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