Multielement Determination of Trace Metals in Seawater by Inductively Coupled Plasma Mass Spectrometry after Tandem Preconcentration Using a Chelating Resin

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A tandem preconcentration method using a chelating resin was exploited for simultaneous multielement determination of trace metals in seawater by inductively coupled plasma mass spectrometry (ICP-MS). In the first preconcentration step, 500 mL of seawater sample was adjusted to pH 6.0, and the adsorption of trace metals on 0.4 g of Chelex-100 resin in dry weight was carried out at 55 °C. After equilibrium, the resin was collected on a glass filter and rinsed with 30 mL of ammonium acetate solution (pH 6.0) to reduce major elements such as Na, K, Mg, and Ca that had been partly adsorbed on the resin. Then, trace metals on the resin were eluted with 7.5 mL of 2 M nitric acid and collected in a 30 mL polypropylene bottle. In the second preconcentration step, the mixture of the filtrate and the rinsing solution obtained in the first step was adjusted to pH 4.0, and metal adsorption on another 0.4 g of Chelex-100 resin was carried out at 20 °C. In a similar manner to the first step, the resin collected on a glass filter was rinsed with 10 mL of ammonium acetate solution (pH 4.0), and trace metals adsorbed on the resin were eluted with 6 mL of 2 M nitric acid. This eluate was taken into the same polypropylene bottle as used in the first step. The final sample volume thus obtained was 15 mL including 1.5 mL of internal standard solution. Then a 33-fold preconcentration factor was achieved, where the recoveries for 33 elements were larger than 80%. The analytical results for trace metals in coastal seawater reference material (CASS-4) were in fairly good agreement with the certified or information values after correction with the recovery values. The coastal seawater samples from the Ise Bay and the Take Island were also analyzed by the present method. The concentrations for 20 trace metals in the Ise Bay coastal seawater were found to be more than 2-fold larger than those in the Take Island coastal seawater, indicating considerable anthropogenic pollution in the Ise Bay area.

The determination of trace metals in seawater is of great importance in environmental sciences and geochemical researches, because trace heavy metals often cause environmental pollution in the coastal areas.[1,2] Inductively coupled plasma mass spectrometry (ICP-MS) provides excellent analytical features including high sensitivity and a wide linear dynamic range, which allow direct determination of trace metals at sub-ppb ($\mu g\,L^{-1}$) levels.[3] However, direct analysis of seawater is still very difficult, because the high contents of salts dissolved in seawater cause instrumental drift, spectral interferences, signal suppression, and cloggings of the sample introduction system of ICP-MS. Furthermore, most trace metals in seawater exist at the ppt ($ng\,L^{-1}$) or sub-ppt level,[1,4] so appropriate preconcentration of them is really required prior to their determination by ICP-MS.

So far, various preconcentration techniques have been developed,[5–11] and in these the chelating resins have been most often employed. The present authors have also explored the preconcentration method using a Chelex-100 resin, and then determined about 30 trace metals in seawater by ICP-MS.[12–14] Generally, the recoveries for trace metals show different pH dependences in the chelating resin preconcentration[5,7,8,11–14] Thus, a compromise pH condition was often chosen in chelating resin adsorption techniques, though low recoveries were obtained for some metals.[14] For example, when the pH value was set at 6.0, the recoveries for Mn, Co, Ni, Cu, Zn, Cd, and rare earth elements (REEs) were more than 80%, while those for trace metals such as V, Mo, and W that existed mainly as oxo-anions were less than 60%.[11–14] In order to overcome this problem, Yabutani et al. developed a tandem preconcentration method employing chelating resin adsorption and La coprecipitation.[15]

In the present research, a two-step chelating resin preconcentration technique was explored as another tandem preconcentration method using only the chelating resin to determine as many as possible trace metals in seawater with a limited volume of sample. The method was evaluated by analysis of coastal seawater reference material (CASS-4) from the National Research Council (NRC) of Canada. Furthermore, the present tandem preconcentration method was applied to analyses of coastal seawater samples from the Ise Bay and the Take Island.

Experimental

Instruments. An Agilent HP4500 ICP-MS (Yokogawa, Tokyo, Japan) with a quadrupole-type mass spectrometer was used for the determination of trace metals. An ICP-AES instrument, Plasma AtomComp MkII (Jarrell-Ash, Franklin, MA, USA) with a polychromator, was also used for the determination of matrix el-

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

ICP-MS Agilent HP4500 (Yokogawa, Tokyo, Japan)	
Plasma conditions:	
incident power	1.3 kW
coolant gas flow rate	Ar 15.0 L min^{-1}
auxiliary gas flow rate	Ar 1.0 L min^{-1}
carrier gas flow rate	Ar 1.1 L min^{-1}
sampling depth	9 mm from load coil
Nebulizer:	Concentric-type
sample uptake rate	0.7 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 Plasma AtomComp Mk II (Jarrell Ash, USA)	
Plasma conditions:	
RF power	1.0 kW
coolant gas flow rate	Ar 20 L min^{-1}
auxiliary gas flow rate	Ar 1.0 L min^{-1}
carrier gas flow rate	Ar 0.48 L min^{-1}
sample uptake rate	1.2 L min^{-1}
Nebulizer:	Cross-flow type
observation height	18 mm
Data acquisition:	
integration time	10 s
accumulation	3 times
repetition	3 times

ements such as Na, K, Mg, and Ca. The operating conditions for the ICP-MS and ICP-AES instruments are shown in Table 1. These operating conditions were obtained by optimizing each instrumental parameter of the ICP-MS and ICP-AES instruments. A Twin pH meter, model B-212 from HORIBA (Kyoto, Japan), was used for pH adjustment. Magnetic stirrers SR100 (ADVANTEC, Tokyo, Japan) were used for stirring the sample solutions. A model T-450 temperature controller, an L-type heater with a temperature sensor, and a polypropylene pack (475 × 328 × 131 mm^3), all of which were purchased from AS ONE (Osaka, Japan), were used to compose a water bath for heating the sample and keeping the constant temperature.

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 calibration curves were prepared from the single-element standard stock solutions (1000 μg 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.[14] Pure water used throughout the present experiment was prepared by a purification system (model Element A-10 Milli-Q; Nihon Millipore Kogyo, Tokyo, Japan).

Seawater Samples. The coastal seawater sample from the Ise Bay was collected at about 1 km off-shore near Nagoya Port (Nagoya, Aichi prefecture, Japan), while that from the Take Island (Gamagoori, Aichi prefecture, Japan) was collected near the shore of the island. These 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 the polypropylene tanks. All bottles, beakers, stirring bars, glass, filters, and pipettes used in the present experiment were soaked in 6 M nitric acid for more than a week and rinsed with pure water just before use.

The coastal seawater sample from the Ise Bay was used for optimization of the experimental conditions in preconcentration procedure. Seawater reference material (CASS-4) from NRC was used for evaluating the validities of the analytical results obtained by the present method.

Procedure for Tandem Chelating Resin Preconcentration. The flow chart for the present tandem preconcentration method is shown in Fig. 1. In the first preconcentration step, 0.4 g of chelating resin in dry weight and 0.5 mL of methyl red as a pH indicator were added to 500 mL of seawater sample in a beaker, where methyl red was used as the pH indicator to avoid contamination from the pH electrode, and then the sample solution was visually adjusted to pH 6.0 with aqueous ammonia solution and acetic acid. Subsequently, the sample beaker was put in a water bath at 55 °C, and a magnetic stirrer bar was placed in the sample beaker for stirring. After the sample solution was stirred for 2 h, the resin was collected on a glass filter (14 mm i.d., pore size 40 μm), while the filtrate was collected in a 500 mL beaker to be used for the second step preconcentration. The resin was rinsed with 30 mL of 1 M ammonium acetate (pH 6.0) and 10 mL of pure water for reducing the matrix elements such as Na, K, Mg, and Ca. These rinsing solutions were also collected in the beaker for the filtrate. Trace metals adsorbed on the Chelex-100 resin were eluted with 7.5 mL of 2 M nitric acid, and the eluate was collected in a 30 mL polypropylene bottle.

In the second preconcentration step, some metals remaining in the filtrate and the rinsing solution after the first preconcentration step were adsorbed on another 0.4 g of chelating resin under the conditions of pH 4.0 and 20 °C. After stirring for 2 h, the resin was collected on a glass filter and rinsed with 10 mL of 1.0 M ammonium acetate (pH 4.0) and 10 mL of pure water in a similar manner to the first preconcentration step. Finally, trace metals adsorbed on the Chelex-100 resin were eluted with 6.0 mL of 2 M nitric acid, and collected in the polypropylene bottle used in the first step. Thus, 13.5 mL of preconcentrated sample solution was obtained, and then 1.5 mL of internal standard solution containing 100 μg L^{-1} each of Ge, In, Re, and Tl was added to the above concentrated sample solution. This mixture was subjected as the analysis solution to the ICP-MS measurement. Accordingly, the concentration factor for the final analysis solution was 33.3 (500 mL/15 mL).

In the recovery test, trace metals (from 0.01 μg L^{-1} of Hg to 100 μg L^{-1} of Mn and Mo) were spiked into the coastal seawater, taking into consideration their concentrations in coastal seawater, and the same preconcentration procedure as described above was carried out. The concentrated analysis solution was appropriately diluted for the determination of Mn and Mo, because their concentrations after preconcentration were too high.

In the determination of trace metals in coastal seawater reference material (CASS-4), the experiment was performed in a half scale for all experimental parameters, where 250 mL of reference seawater was used.

Results and Discussion

Temperature Dependence of the Recoveries for Trace Metals. Inagaki and Haraguchi suggested that the recoveries of rare earth elements in the acid-digested serum sample in-

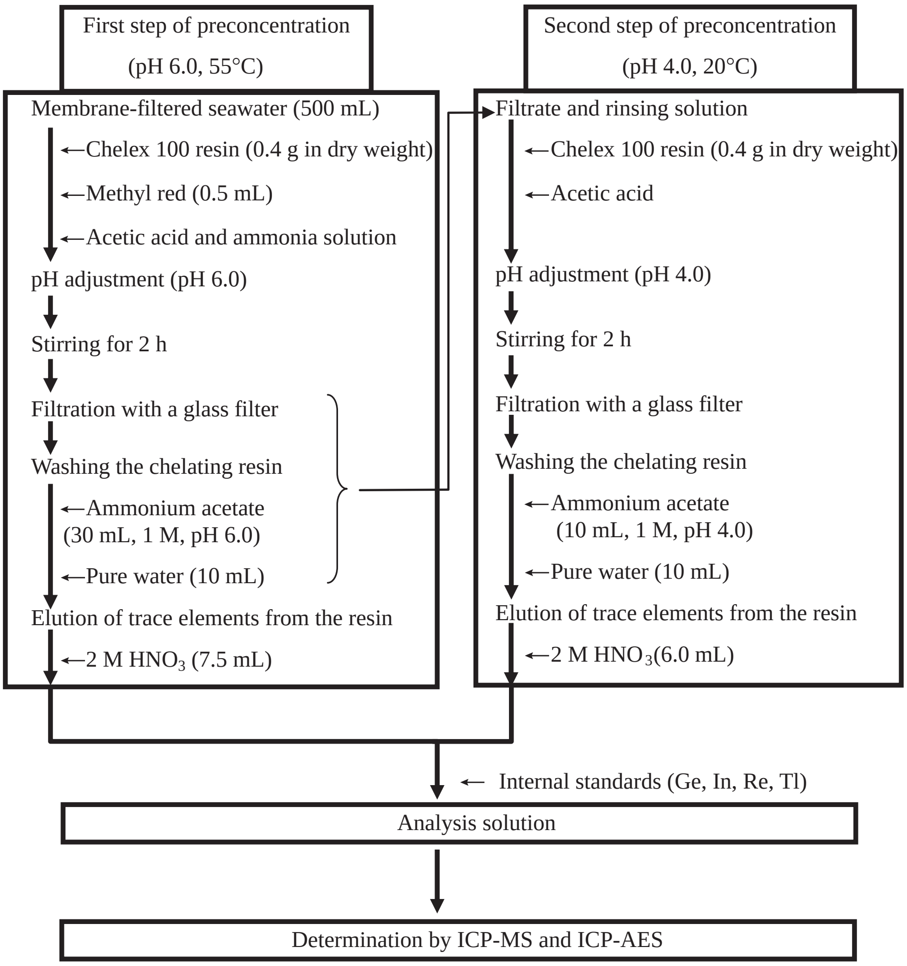


Fig. 1. Flow chart of the tandem preconcentration method using the chelating resin for the determination of trace metals by ICP-MS and ICP-AES.

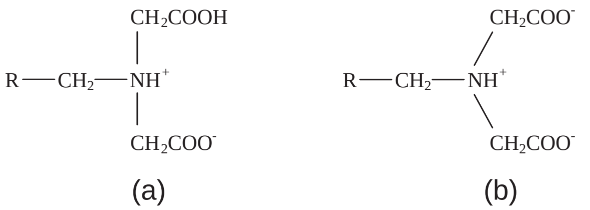
creased at higher temperatures, when the chelating resin preconcentration was employed.[16] Thus, in the present experiment, the temperature dependence of the recoveries for trace metals was examined in the range from 20 °C to 85 °C at steps of 5 °C or 10 °C. Some trace metals showed obvious changes of the recoveries from 20 °C to 60 °C, while they did not show any notable changes from 60 °C to 85 °C. On the other hand, the concentrations of matrix elements in the concentrated sample solution increased with increasing temperature from 20 °C to 85 °C. Thus, further investigation was carried out at 20 °C and 55 °C.

Table 2. Temperature Dependence of the Recoveries for Some Trace Metals

Element	m/z	Recovery[a)]/%	
		pH 6.0, 55 °C	pH 6.0, 20 °C
Bi	209	82 ± 3	66 ± 3
Th	232	63 ± 5	50 ± 3
Ti	47	68 ± 6	56 ± 2
Zr	90	46 ± 2	34 ± 2
Sc	45	106 ± 3	95 ± 3
Sn	118	51 ± 1	44 ± 1
Hf	178	39 ± 1	33 ± 3
W	184	16.4 ± 0.9	33 ± 4
Mo	98	22.2 ± 0.9	45 ± 8
V	51	18.4 ± 0.5	44 ± 7

a) Mean value ± standard deviation, $n = 3$.

Table 2 shows the recoveries for some trace metals at 20 °C and 55 °C in the first preconcentration step. As can be seen from Table 2, the recoveries for Bi, Ti, Th, Sn, Zr, and Hf, which are hydroxide-forming metals in seawater,[4] increased by more than 5% at 55 °C, compared to the recoveries at 20 °C. On the other hand, the recoveries for trace metals such as V, Mo, and W, which mainly existed as oxo-anions in seawater, decreased by more than 5% when the temperature increased from 20 °C to 55 °C. These differences may be explained by the thermodynamic properties in the complex formation between iminodiacetate and metal ions. According to Schmuckler's research, the dissociation states of a iminodiacetate-type chelating resin at pH 3.99 and pH 7.41 can be represented as shown in Figs. 2(a) and 2(b), respectively.[17] It is seen from Fig. 2 that dissociated carboxyl groups are dominant at pH 6.0. On the other hand, increasing the temperature leads to the decrease of dissociation constants (pK_a) of carboxyl group,[18] which accelerates the dissociation of carboxyl groups in the Chelex-100 resin as well as the dissolution of hydroxides of hydroxide-forming metals (for example, $Bi(OH)_3$) to free



(a) (b)

Fig. 2. The schematic of the dissociation states of the functional groups in Chelex-100 resin at (a) pH 3.99 and (b) pH 7.41.[17]

metals (for example, Bi^{3+}) so as to be easily adsorbed on the chelating resin. As a result, we concluded that the recoveries for hydroxide-forming metals increased at the higher temperature. Concurrently, the dissolution of hydroxides to free metal ions produced OH^- ions, which competed with the oxo-anions in adsorption to the chelating resin, which might result in the lower recoveries for oxo-anions. Based on these considerations, the temperature in the first preconcentration step was kept at 55 °C.

Second-Step Preconcentration of Trace Metals in the Filtrate after the First Step Preconcentration. In case of only one-step preconcentration under the conditions of pH 6.0 and 55 °C, the recoveries for oxo-anions such as V, W, and Mo were very low, and those for most hydroxide-forming metals did not exceed 80%, too. The investigations on the pH dependence of their recoveries[12,13] show that such metals are generally more retained on the chelating resin at pH 4.0. In addition, as stated above, the increase of temperature did not improve the recoveries for trace metals which existed as oxo-anions. Thus, the pH value and temperature were set at 4.0 and 20 °C at the second preconcentration step, respectively.

The recoveries for some trace metals obtained by the single (first step only) and tandem preconcentration procedures are summarized in Table 3, where oxo-anions and hydroxide-forming elements in seawater were examined. It was found that the recoveries for Th, V, Mo, W, and Hg increased by more than 10% in the tandem preconcentration. These results indicate that a large portion of these metals remained in the filtrate after the first preconcentration step.

Table 3. The Recoveries for Some Trace Metals in Single and Tandem Preconcentration Procedures

Element	m/z	Recovery[a)]/%	
		Single[b)]	Tandem[c)]
Mo	98	22.2 ± 0.9	90 ± 1
W	184	16.4 ± 0.9	82.6 ± 0.3
V	51	18.4 ± 0.5	66 ± 1
Hg	202	7 ± 2	33 ± 5
Th	232	63 ± 5	81 ± 6
Nb	93	57 ± 2	67 ± 2
Sn	118	51 ± 1	60 ± 3

a) Mean value ± standard deviation, $n = 3$. b) The first preconcentration step only was performed. c) After the first preconcentration step, trace metals in the filtrate was re-preconcentrated.

Recoveries of Trace Metals from Rinsing Solution. In the first preconcentration step, ammonium acetate was used for rinsing the chelating resin to reduce major elements. In this procedure, trace metals weakly adsorbed on the chelating resin may also be eluted partly, which would cause losses of such metals. Thus, in order to estimate the loss of trace metals in the rinsing procedure, the tandem preconcentration was performed in two cases; (i) the filtrate only and (ii) the filtrate and rinsing solution together. Thus, the amounts of trace metals eluted with the rinsing solution can be estimated as the differences of the recovery values between cases (i) and (ii). The results are shown in Table 4. As is seen in Table 4, the recoveries for Ti, Nb, Zr, Hf, and V increased by more than 10%,

Table 4. The Total Recoveries for Trace Metals after Two-Step Preconcentration Obtained Using (i) Filtrate and (ii) Filtrate and Rinsing Solution for the Second Step of Preconcentration

Element	m/z	Recovery[a)]/%		
		(i) Filtrate only	(ii) Filtrate and rinsing solution	[(ii) − (i)][b)]
Hf	178	42 ± 2	61 ± 1	19
Ti	47	74 ± 6	92 ± 3	18
Zr	90	50 ± 2	68 ± 3	18
V	51	66 ± 1	84 ± 1	18
Nb	93	67 ± 2	83 ± 1	16
Sm	147	94.9 ± 0.9	104 ± 2	9.1
Co	59	97.3 ± 0.9	105 ± 1	7.7
La	139	98.7 ± 0.4	106 ± 1	7.3
Mn	55	82.1 ± 3	89.2 ± 0.5	7.1
Ho	165	93 ± 2	99.3 ± 0.3	6.3
Dy	163	95 ± 2	101 ± 1	6
Bi	209	83 ± 3	89 ± 3	6
Er	166	97 ± 2	103 ± 1	6
Eu	153	90 ± 1	95.5 ± 0.5	5.5
Tm	169	97.5 ± 0.5	103 ± 1	5.5
Tb	159	95.5 ± 0.5	101 ± 1	5.5
Zn	66	96 ± 6	101 ± 3	5

a) Mean value ± standard deviation, $n = 3$. b) The recovery values from the rinsing solution.

Table 5. Analytical Figures of Merit for Trace Elements in the Tandem Chelating Resin Preconcentration Method

Element	m/z	Recovery[a] /%	Blank $/\mu g\,L^{-1}$	Analytical detection limit[b] $/\mu g\,L^{-1}$
Al	27	95 ± 2	0.2	0.004
Sc	45	100 ± 2	<0.002	0.0007
Ti	47	92 ± 2	0.03	0.02
V	51	84 ± 4	n.d.[c]	0.001
Mn	55	89.2 ± 0.5	0.004	0.001
Co	59	105 ± 1	n.d.[c]	0.001
Ni	62	99 ± 1	0.021	0.005
Cu	65	97.9 ± 0.3	0.027	0.001
Zn	66	101 ± 3	0.109	0.003
Ga	71	82 ± 2	n.d.[c]	0.0002
Y	89	105 ± 1	n.d.[c]	0.001
Zr	90	68 ± 1	0.033	0.001
Nb	93	83 ± 2	0.0036	0.0001
Mo	98	86.5 ± 0.6	0.003	0.001
Cd	111	98 ± 2	<0.006	0.002
Sn	118	56.8 ± 0.8	0.009	0.001
La	139	106 ± 1	0.00053	0.00004
Ce	140	104 ± 1	n.d.[c]	0.0007
Pr	141	105 ± 1	<0.0001	0.00004
Nd	143	102 ± 1	n.d.[c]	0.0003
Sm	147	104 ± 2	n.d.[c]	0.0002
Eu	153	95.5 ± 0.5	n.d.[c]	0.0001
Gd	157	101 ± 1	n.d.[c]	0.0003
Tb	159	101 ± 1	n.d.[c]	0.00004
Dy	163	101 ± 1	n.d.[c]	0.0002
Ho	165	99.3 ± 0.3	n.d.[c]	0.00003
Er	166	103 ± 1	n.d.[c]	0.0001
Tm	169	103 ± 1	n.d.[c]	0.00003
Yb	172	97.7 ± 0.7	n.d.[c]	0.0003
Lu	175	101 ± 1	n.d.[c]	0.00005
Hf	178	61 ± 2	<0.0009	0.0003
W	184	80 ± 1	0.0029	0.0003
Hg	202	23.0 ± 0.8	n.d.[c]	0.002
Pb	207	102 ± 1	0.028	0.001
Bi	209	89 ± 3	<0.0002	0.00005
Th	232	83 ± 3	<0.0002	0.00005
U	238	101 ± 1	0.00013	0.00004

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

when the tandem preconcentration was performed for the filtrate including the rinsing solution. These results indicate that the fairly amount of trace metals were adsorbed weakly on the chelating resin and they were eluted with ammonium acetate.

Concentrations of Matrix Elements in the Concentrated Analysis Solution. Matrix elements in the analysis solution usually cause instrumental drift, spectral interferences, and signal suppression in the ICP-MS measurement. In the present experiment, 30 mL of 1 M ammonium acetate of pH 6.0 and 10 mL of ammonium acetate of pH 4.0 were used in the first and second steps of preconcentration, respectively, for eliminating matrix elements, such as Na, Mg, K, and Ca, in seawater. As a result, it was found that the total concentrations of matrix elements were less than 200 $mg\,L^{-1}$ (generally, 75 $mg\,L^{-1}$ of Ca, 60 $mg\,L^{-1}$ of Mg, less than 3 $mg\,L^{-1}$ of K, less than 0.04 $mg\,L^{-1}$ of Na) in the concentrated analysis solution. As reported in the previous paper,[14] the signal suppression at these concentration levels of matrix elements could be corrected by the internal standard method. Thus, the internal standard method was also employed in the present work.

Correction of Polyatomic Interferences. In the ICP-MS measurement, matrix and trace elements in the sample solution often cause spectral interference.[19] In the present experiment, we corrected the interferences of $^{44}Ca^{1}H$, $^{43}Ca^{16}O$, $^{48}Ca^{16}O^{1}H$, $^{95}Mo^{16}O$, $^{137}Ba^{16}O$, $^{141}Pr^{16}O$, $^{143}Nd^{16}O$, $^{147}Sm^{16}O$, $^{149}Sm^{16}O$, $^{153}Eu^{16}O$, and $^{156}Gd^{16}O$ 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, according to the interference correction coefficient method reported by Yabutani et al.[14] The interference ratios (the ratios of the apparent concentration of interferents to the concentra-

Table 6. Analytical Results for Trace Metals in Coastal Seawater Reference Material (CASS-4)

Element	m/z	Concentration/$\mu g\,L^{-1}$		
		Observed value[a]	RSD[b]/%	Certified value
Al	27	(1.2 ± 0.6)	46.7	
Sc	45	n.d.[c]		
Ti	47	(0.05 ± 0.01)	20.4	
V	**51**	**1.01 ± 0.09**	7.7	**1.18 ± 0.16**
Mn	**55**	**2.72 ± 0.04**	1.5	**2.78 ± 0.19**
Co	**59**	**0.027 ± 0.001**	4.1	**0.026 ± 0.003**
Ni	**60**	**0.30 ± 0.03**	10.0	**0.314 ± 0.030**
Cu	**63**	**0.59 ± 0.01**	2.0	**0.592 ± 0.055**
Zn	**66**	**0.43 ± 0.04**	9.0	**0.381 ± 0.057**
Ga	71	0.0027 ± 0.0004	13.0	
Y	89	0.021 ± 0.001	5.4	
Zr	90	(0.036 ± 0.003)	8.9	
Nb	93	(0.0007 ± 0.0005)	77.4	
Mo	**98**	**9.1 ± 0.5**	5.4	**8.78 ± 0.86**
Cd	**111**	**0.030 ± 0.001**	3.3	**0.026 ± 0.003**
Sn	118	(0.0041 ± 0.0006)	14.6	
La	139	0.0087 ± 0.0005	6.0	
Ce	140	0.0042 ± 0.0003	7.0	
Pr	141	0.00134 ± 0.00007	5.2	
Nd	143	0.0058 ± 0.0006	10.4	
Sm	147	0.0054 ± 0.0003	6.0	
Eu	153	0.00025 ± 0.00003	12.1	
Gd	157	0.0015 ± 0.0001	4.7	
Tb	159	0.00019 ± 0.00001	5.2	
Dy	163	0.0012 ± 0.0001	9.1	
Ho	165	0.00038 ± 0.00004	9.5	
Er	166	0.00112 ± 0.0001	6.3	
Tm	169	0.00017 ± 0.00001	5.8	
Yb	172	0.0013 ± 0.0001	9.0	
Lu	175	0.00020 ± 0.00003	15.0	
Hf	178	(0.0009 ± 0.0002)	22.2	
W	184	0.042 ± 0.004	10.3	
Hg	202	n.d.[c]		
Pb	**207**	(**0.012 ± 0.006**)	51.3	**0.0098 ± 0.0036**
Bi	209	n.d.[c]		
Th	232	0.00046 ± 0.00002	4.3	
U	**238**	**3.00 ± 0.06**	2.0	**3.0**[d]

a) Mean value ± standard deviation, $n = 3$. Data in the parentheses are the results for the elements with the recovery values less than 80% or concentrations close to blank values or determination limits. Data in bold fonts are the results for the elements with certified values or information value. b) Relative standard deviation. c) Not detected. d) Information value.

tions of analyte elements) for trace metals listed above were less than 20%, except that for Sc (ca. 40%) and Cd (ca. 30%).

Analytical Figures of Merit. The recoveries, blank values, and analytical detection limits for trace metals in the tandem chelating resin preconcentration are shown in Table 5, as the analytical figures of merit of the present method. The recovery values in Table 5 are the mean values estimated from 3-times repeated experiments. The recoveries for 24 elements were more than 95%, while those for 9 elements were between 95% and 80%, and those for 4 elements were less than 80%. The standard deviations of recovery values were less than 4%.

The blank values in the present method are also shown in Table 5. In the estimation of the blank values, 500 mL of 0.1 M nitric acid was used as the test solution, and the same preconcentration and measurement procedures as those for seawater samples were performed for the test solution. 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 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 $\mu g\,L^{-1}$, respectively, these values were estimated after a batch preconcentration method by ICP-MS measurement. Thus, the relatively large blank values for Zn and Pb were attributed to the impurities in ammonium acetate. Hence, the use of more purified acetic acid and aqueous ammonia would be necessary to reduce the blank values for Zn and Pb.

Table 7. Analytical Results for Trace Metals in Coastal Seawater Samples from the Coastal Areas of Ise Bay and Take Island

Element	m/z	Concentration[a)] / $\mu g\, L^{-1}$			
		Ise Bay	RSD[b)]/%	Take Island	RSD[b)]/%
Al	27	**8.1 ± 0.2**	2.5	2.4 ± 0.4	14.9
Sc	45	**0.0027 ± 0.0001**	3.7	(0.0012 ± 0.0007)	59.1
Ti	47	(0.07 ± 0.02)	22.5	(0.036 ± 0.005)	13.2
V	51	1.50 ± 0.02	1.3	1.29 ± 0.01	1.1
Mn	55	**32.1 ± 0.1**	0.3	11.6 ± 0.1	0.7
Co	59	**0.126 ± 0.002**	1.6	0.034 ± 0.002	4.4
Ni	62	**2.71 ± 0.04**	1.5	0.642 ± 0.007	1.1
Cu	65	**2.05 ± 0.01**	0.5	0.693 ± 0.009	1.3
Zn	66	**16.3 ± 0.1**	0.6	4.46 ± 0.02	0.5
Ga	71	**0.0167 ± 0.0009**	5.4	0.0081 ± 0.0005	6.3
Y	89	0.031 ± 0.0001	0.3	0.020 ± 0.001	6.1
Zr	90	**(0.049 ± 0.004)**	8.2	(0.004 ± 0.002)	56.6
Nb	93	**(0.0070 ± 0.0005)**	7.1	(0.0014 ± 0.0001)	9.1
Mo	98	8.74 ± 0.04	0.5	8.9 ± 0.1	1.2
Cd	111	0.019 ± 0.002	10.8	0.013 ± 0.002	15.2
Sn	118	0.021 ± 0.002	9.5	0.0027 ± 0.0004	13.1
La	139	**0.012 ± 0.0005**	4.2	0.00590 ± 0.00007	1.2
Ce	140	**0.0097 ± 0.0001**	1	0.00367 ± 0.00009	2.5
Pr	141	0.00194 ± 0.00009	4.6	0.00100 ± 0.00005	4.8
Nd	143	0.0069 ± 0.0008	11.6	0.0048 ± 0.0005	10.0
Sm	147	0.0014 ± 0.0001	7.1	0.0010 ± 0.0002	19.9
Eu	153	<0.0003		0.00032 ± 0.00005	15.7
Gd	157	**0.0030 ± 0.0003**	10	0.0014 ± 0.0001	8.5
Tb	159	0.00031 ± 0.00001	3.2	0.00017 ± 0.00006	37.8
Dy	163	0.0025 ± 0.0001	4	0.0014 ± 0.0005	37.7
Ho	165	0.00076 ± 0.00001	1.3	0.00041 ± 0.00005	11.7
Er	166	0.0029 ± 0.0001	3.4	0.0015 ± 0.0001	7.5
Tm	169	0.00045 ± 0.00005	11.1	0.00024 ± 0.00004	16.1
Yb	172	**0.0039 ± 0.0001**	2.6	0.0018 ± 0.0001	6.2
Lu	175	**0.00081 ± 0.00003**	3.7	0.00032 ± 0.00004	12.0
Hf	178	(**0.0009 ± 0.0003**)	33.3	(0.0002 ± 0.0002)	100
W	184	**0.126 ± 0.002**	1.6	0.047 ± 0.001	2.7
Hg	202	<0.007		<0.007	
Pb	207	**0.42 ± 0.01**	2.4	0.080 ± 0.006	7.3
Bi	209	**0.00038 ± 0.00002**	5.3	(0.00010 ± 0.00004)	42.8
Th	232	**0.00081 ± 0.00001**	1.2	(0.00021 ± 0.00006)	26.8
U	238	2.61 ± 0.03	1.1	2.89 ± 0.03	1.0

a) Mean value ± standard deviation, $n = 3$. Data in the parentheses are the results for the elements with the recovery values less than 80% or concentrations near to blank values or determination limits. Data in bold fonts are the results for the elements with certified values or information value. b) Relative standard deviation.

The analytical detection limits of the elements examined in the present experiment are also shown in Table 5. They were calculated from the instrumental detection limits, taking into account the concentration factor (33.3) and the recovery values for trace metals examined. The instrumental detection limits were defined as the concentration corresponding to 3 times the standard deviation of the background signal intensity, which were estimated from the 10-times repeated measurements of the blank solution, i.e., 2 M nitric acid with internal standard elements (Ge, In, Re, Tl 10 $\mu g\, L^{-1}$ each). The analytical detection limits for 37 elements were in the range from 0.02 $\mu g\, L^{-1}$ of Ti to 0.00003 $\mu g\, L^{-1}$ of Ho.

Analytical Results for Trace Metals in Coastal Seawater Reference Material (CASS-4). Trace metals in seawater reference material CASS-4 were determined by the present tandem preconcentration method. The results are summarized in Table 6, along with the certified or information values. The concentrations of trace metals were corrected with the recovery values listed in Table 5. As is seen in Table 6, the concentrations of 34 elements (Al, Ti, V, Mn, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Cd, Sn, all-REEs, Hf, W, Pb, Th, and U) in CASS-4 were in the range from 9.1 $\mu g\, L^{-1}$ of Mo to 0.00017 $\mu g\, L^{-1}$ of Tm. Since the recoveries for Zr, Sn, and Hf were less than 80%, their concentrations were seemingly less reliable, so their results are shown in parentheses in Table 6 for reference. The concentrations of Al, Ti, Zn, Nb, and Pb were close to the blank values or determination limits, and thus their relative standard deviations (RSDs) were more than 15%. Therefore, their analytical results are also shown in parentheses for reference. The concentrations of Sc, Hg, and Bi were below the determination limits. It is also seen in Table 6 that the RSDs for 29 elements in CASS-4 were less than 15%.

The analytical results for V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, and U agreed well with the certified values issued by NRC, which are shown in bold fonts in Table 6. Although there have been some researches concerning CASS-4,[9,20] the analytical values for trace metals were limited to those listed above. As for the concentrations of Al, Ti, Ga, Y, Zr, Nb, Sn, all-REEs, Hf, and Th, there were no reference values available for comparison with the present analytical results.

Analytical Results for Trace Metals in Coastal Seawater Samples from the Ise Bay and the Take Island. The present analytical method was also applied to the determination of trace metals in the coastal seawater samples from the Ise Bay and the Take Island. The results are summarized in Table 7. In the present experiment, 35 and 33 trace metals could be determined in the Ise Bay coastal seawater and the Take Island coastal seawater, respectively. As is seen in Table 7, the concentrations of Eu and Hg in the Ise Bay coastal seawater and those of Sc, Hf, Hg, and Bi in the Take Island coastal seawater could not be determined by the present analytical method. The concentrations of trace metals in the Ise Bay coastal seawater were in the range from 32.1 $\mu g\,L^{-1}$ of Mn to 0.00031 $\mu g\,L^{-1}$ of Tb, and the RSDs for them were less than 15%, except for Ti and Hf. On the other hand, the concentrations of trace metals in the Take Island coastal seawater were in the range from 11.6 $\mu g\,L^{-1}$ of Mn to 0.00017 $\mu g\,L^{-1}$ of Tb, and their RSDs were less than 15%, except for Zr, Cd, Eu, Tb, Dy, Tm, and Th, whose concentrations were close to the blank values or determination limits. It is seen in Table 7 that the concentrations of trace metals in the Ise Bay coastal seawater were generally higher than those in the Take Island coastal seawater. In Table 7, the concentrations shown in bold fonts for trace metals in the Ise Bay coastal seawater are more than 2-fold higher than those in the Take Island coastal seawater.

Furthermore, in order to evaluate trace metal pollutions in the coastal sea areas, the concentrations of trace metals in the Take Island and Ise Bay coastal seawaters were compared by normalizing their concentrations to those in open seawater.[14] The results are shown in Fig. 3, in which the normalized concentrations are represented as the ratio of ($[M]_{coastal}/[M]_{open}$); the data for trace metals in open seawater were cited from Refs. 1 and 4. It is seen in Fig. 3 that the concentrations of Al, Mn, Ni, Zn, Ga, Y, Pb, and most REEs in Ise Bay coastal seawater and those of Mn and some REEs in the Take Island coastal seawater were 10-fold higher than those in open seawater, which could be attributed to the inputs from river water as well as from some anthropogenic pollution sources. Figure 3 also shows that the concentrations of Al, Mn, Co, Ni, Cu, Zn, Ga, REEs, and Pb in the Ise Bay coastal seawater are much higher than those in the Take Island coastal seawater. It should be noted that most of elements listed here are extensively used in industrial production. These results may reflect the facts that the coastal area around the Ise Bay is more industrialized with various kinds of factories, compared to the Take Island area, which is in front of the Pacific Ocean.

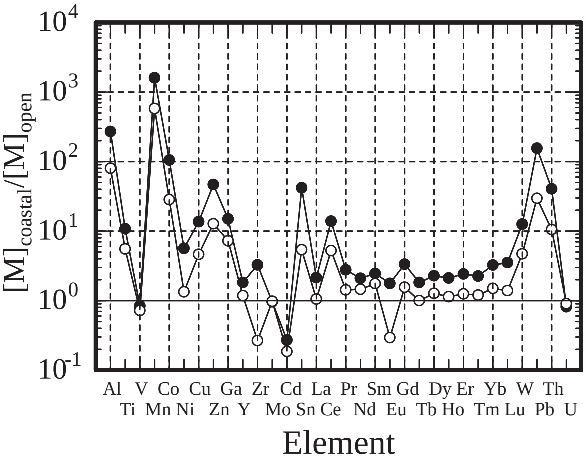


Fig. 3. Comparison of the concentrations of trace metals in coastal seawaters normalized to those in open seawater. The normalized concentrations are represented as the ratio of ($[M]_{coastal}/[M]_{open}$), where $[M]_{coastal}$ and $[M]_{open}$ indicate the concentrations of trace metals in coastal seawaters and open seawater, respectively; the concentrations of trace metals in open seawater were cited from Refs. 1 and 4. ●: Ise Bay, ○: Take Island.

It was also 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 CASS-4 as well as those in open sea. These situations can be also seen in Fig. 3, where their normalized concentrations are close to 1. Since these elements generally exist as the stable oxo-anions in seawater, their concentrations are uniform as the conservative elements in seawater in sea areas all over the world.[2,4,21] In addition, since their original concentrations are rather high, at $\mu g\,L^{-1}$ level, their inputs from artificial activities may be negligible.[2] On the other hand, the concentrations of W, which exists at the lower $ng\,L^{-1}$ level as stable oxo-anion in seawater,[1,2,4,21] were higher in the Osaka Bay and near the canal of Bungo-Suido than in open sea,[2] which indicated apparent influences due to the human activities in the inland areas.

Conclusion

A tandem chelating resin preconcentration method was developed for simultaneous multielement determination of trace metals in seawater by ICP-MS. The recovery values for 33 elements were more than 80%. The analytical results for seawater reference material (CASS-4) agreed well with the certified or information values issued by NRC. The results indicate that the present tandem preconcentration method is very useful for multielement determination of a variety of trace metals in seawater by ICP-MS.

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