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Multielement Determination of Trace Elements in Coastal Seawater by Inductively Coupled Plasma Mass Spectrometry with Aid of Chelating Resin Preconcentration

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The multielement determination of trace elements in coastal seawater by inductively coupled plasma mass spectrometry has been investigated with the aid of chelating resin preconcentration. First, each coastal seawater sample (250 ml) was treated with a chelating resin (Chelex 100) at pH 6 for preconcentration of trace elements. After filtration with a glass filter, the resin on the filter was carefully rinsed with 8 ml of 1 M ammonium acetate solution. Then, trace elements adsorbed on the resin were eluted with 6 ml of 2 M HNO_3. As a result, the preconcentration factor of 41.7 fold was obtained, with the total concentration of matrix elements (Na, K, Mg, and Ca) less than 200 mg dm^{-3}. The recovery values were larger than 80% for 22 elements among 29 elements determined. The present method was applied to the determination of trace elements in the coastal seawater certified reference material CASS-3, issued from National Research Council of Canada (NRC), as well as to the coastal seawater sample collected from Tokoname off-shore.

Nowadays, it is known that almost all stable-isotope elements in the major-to-ultratrace concentration range exist in seawater.[1] Although trace elements in seawater are extremely low, the concentration variations of such elements often reflect the physicochemical or biochemical changes in the sea. Thus, the accurate determination of trace elements in seawater is still important to elucidate the kinetic behaviors of the elements or to evaluate environmental pollution in the sea. It is, therefore, desirable to determine the major-to-ultratrace elements as many as possible for comprehensive appreciation of the distributions of trace elements and their multielement correlation in the marine environment.

Inductively coupled plasma mass spectrometry (ICP-MS) has analytical features such as simultaneous multielement detection capability with high sensitivity and wide linear dynamic ranges of the calibration curves, 5—6 orders of magnitude for most metallic elements. Consequently, ICP-MS has been extensively applied to the determination of trace elements in seawater. Since concentrations of trace elements in seawater are very low, compared to those of major (matrix) elements such as Na, K, Mg, and Ca, separation of matrix elements and preconcentration of trace elements should be performed prior to the determination of trace elements in seawater. As the separation and/or preconcentration methods, coprecipitation,[2—6] chelating resin adsorption,[7—17] and solvent extraction[18,19] have been widely employed in seawater analysis. In general, the elements such as Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb[3—5,8,9,16,19] and rare earth elements (REEs)[10,11,13,14,18] were separately determined by the analytical methods so far developed. However, there have been a few reports in which both of the transition elements and rare earth elements were determined at the same time.[2,15]

Several works using the Chelex 100 resin for preconcentration of trace elements in coastal seawater have been reported in terms of REEs[10,11] and other metallic elements (Al, Ti, Mn, Fe, Co, Ni, Zn, Y, Mo, Cd, and Pb).[20—22] The Chelex 100 resin which is a chelating resin with the iminodiacetate groups has rather non-selective adsorption capability for a variety of elements, although most metallic elements show slightly different pH dependences of the recoveries in chelating resin preconcentration. Thus, the experimental conditions for the multielement determination of trace elements in seawater should be optimized to obtain better recoveries and larger concentration factors for most analyte elements.

In the present paper, hence, chelating resin preconcentration of trace elements has been further investigated in detail, to assist their multielement determination by ICP-MS. In addition, the present analytical method was applied to the multielement analysis of coastal seawater certified reference material CASS-3, issued from National Research Council of Canada, and of off-shore seawater collected from the Ise Bay.

Experimental

Instruments. An ICP-MS instrument of model SPQ 8000A (Seiko Instruments Inc., Chiba) was used for the determination of trace elements; it consisted of a quadrudpole-type mass spectrom-

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eter. An ICP-AES of model Plasma AtomComp MKII (Jarrell-Ash, Franklin, MA, USA) with a polychromator was also used for the simultaneous multielement determination of major and minor elements. The instrumental components and operating conditions are shown in Table 1. These operating conditions were chosen after optimization of each instrumental parameter in the ICP-MS and ICP-AES instruments. A pH meter of model twin pH meter from Horiba (Kyoto) was used for pH adjustment.

Chemicals. Nitric acid, acetic acid, and aqueous ammonia solution used were of electronic industrial grade (Kanto Chemicals Co., Tokyo). The multielement standard solutions were prepared by mixing the single-element standard stock solutions (1000 mg dm^{-3}) of analyte elements for atomic absorption spectrometry, purchased from Wako Chemicals Co. (Osaka). The multielement standard solutions used for the ICP-MS measurement are listed in Table 2. The compositions of the elements in the standard solution were chosen, taking into consideration the stabilities of the elements dissolved in the 2 M HNO_3 solution (1 M = 1 mol dm^{-3}) as well as correction of polyatomic ion interferences. Since Ti and W were unstable in the HNO_3 solution, the standard solutions of these elements were prepared as the 1 M HCl solution for the former and the pure water solution for the latter.

The Chelex 100 resin in 100—200 mesh was purchased from Bio-Rad Laboratories (USA). The resin was soaked in 5 M HCl which was changed 5-times every 12 h, and washed with water before use. Purified water used throughout the present experiment was prepared by a Milli-Q purification system.

Seawater Samples. Coastal seawater reference material CASS-3 obtained from National Research Council of Canada was analysed for evaluation of the present analytical method. The coastal seawater samples collected at about 1 km off-shore from Tokoname (Aichi Prefecture) in the Ise Bay were also subjected to the present experiment. The seawater samples were filtrated with a membrane filter (pore size; 0.45 μm) immediately after sampling, and then acidified to pH 1 with nitric acid. A polyethylene bottle used for collection and preservation of the seawater samples were soaked in 6 M HNO_3 for more than 1 week and rinsed with pure water before use.

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

ICP-MS	Seiko SPQ 8000A
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 16 dm^3 min^{-1}
Auxiliary gas flow rate	Ar 1.0 dm^3 min^{-1}
Carrier gas flow rate	Ar 1.0 dm^3 min^{-1}
Sampling depth	12 mm
Nebulizer:	Concentric type
Sample uptake rate	1.0 ml min^{-1}
Data acquisition:	
Dwell time	10 ms/channel
Data points	3 points/peak
Number of scans	100
ICP-AES	Jarrell-Ash Plasma AtomComp MK II
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 17 dm^3 min^{-1}
Auxiliary gas flow rate	Ar 1.0 dm^3 min^{-1}
Carrier gas flow rate	Ar 0.48 dm^3 min^{-1}
Observation height	18 mm
Nebulizer:	Cross-flow type
Sample uptake rate	1.2 ml min^{-1}
Polychromator:	Paschen–Runge mounting
Focal length	75 cm
Grating	2400 grooves/mm
Entrance slitwidth	25 μm
Exit slitwidth	50 μm

Table 2. The Compositions of the Standard Solutions for ICP-MS Measurement[a)]

No.	Element	Concentration
1	Al, V, Co, Ga, Zr, Pb	50 μg dm^{-3}
	Dy, Ho, Er, Tm, Lu, Bi	5 μg dm^{-3}
2	Mn, Mo, Sn, U, Th	50 μg dm^{-3}
	Sm, Eu, Gd, Tb	5 μg dm^{-3}
3	Cr, Fe, Ni, Cu, Zn, Y, La, Ce, Pr, Nd	50 μg dm^{-3}
	Cd, Yb	5 μg dm^{-3}
4	Ti	50 μg dm^{-3}
5	W	50 μg dm^{-3}
6	Ca[b)]	50 μg dm^{-3}

a) The all standard solutions except for Ti and W were of 2 M HNO_3. The standard solutions of Ti and W were of 1 M HCl (Ti) and pure water (W), respectively. b) This standard solution was used for correction of isobaric ion interferences with ^{57}Fe and ^{59}Co due to $^{40}Ca^{16}O^{1}H$ and $^{43}Ca^{16}O$, respectively.

Preconcentration Procedure. The following preconcentration procedure for the coastal seawater samples was established as a recommended method after optimization, as will be described later. First, 250 ml of the seawater sample was taken in a beaker, and then the pH of the sample solution was adjusted to 6.0 with acetic acid and aqueous ammonia solution. Next, 0.2 g (dry weight) of the chelating resin was added into it, and then the solution was stirred with a magnetic stirrer for 2 h. The resin was collected on a glass filter (1.4 cm, i.d.), and washed with 10 ml of water and 8 ml of 1 M ammonium acetate (pH 6.0) to reduce major elements adsorbed on the resin. After washing with 10 ml of water, trace elements were eluted with 6 ml of 2 M HNO_3, into which 0.5 ml of a mixed solution of Ge, In, Re, and Tl (100 μg dm^{-3} each) was added as the internal standard elements for correction of matrix effects due to major elements.[3,25]

In the recovery test, 5 ml of the mixed standard solution containing the analyte elements (5 mg dm^{-3}—2 μg dm^{-3}) were added into 250 ml of the seawater sample solution, and the experimental procedure described above was carried out to estimate the recovery values.

Results and Discussion

In order to perform the accurate and precise determination of trace elements in seawater, less contamination, efficient removal of matrix salts, large concentration factor, and good recoveries of analyte elements should be taken into consideration in the chelating resin preconcentration. Therefore, in the case of chelating resin preconcentration using the Chelex 100 resin, the following conditions are usually investigated: (i) resin amounts, (ii) pH dependence, (iii) stirring time, (iv) volume of ammonium acetate solution needed to eliminate matrices (Ca, Mg) adsorbed on the resin, and (v) volume of the eluent solution. In the present experiment, the experimental conditions of (ii), (iv), and (v) were investigated by using 250 ml of the seawater sample. The other conditions such as (i) amount of resin (0.2 g) and (iii) stirring time (2 h) were chosen after the reference.[10]

pH Dependence of Recoveries of Trace Elements in Seawater. The recoveries of various analyte elements were examined in the pH range of 2—8, where the preconcentration procedure described in the experimental section was carried out. The results are illustrated in Figs. 1a—1d. Four types of characteristic behaviors of analyte elements were observed when the pH was varied. As can be seen in Fig. 1a, the recoveries of Ti, V, Fe, Mo, Sn, and W were maximum near pH 4. The recovery curves in Fig. 1b show that the recoveries of Al, Y, and REEs increased in the pH range of 2—5, and they were the largest near pH 5—6. On the other hand, Fig. 1c shows that the recoveries of Cu, Ni, Zn, and Co increased with the pH increase from 2 to 4, and they were almost constant at larger than 80% values in the pH range of 4—8. As is shown in Fig. 1d, the recoveries of Mn and Cd were constant at ca. 60% and ca. 100%, respectively, above pH 6, while that of Cr was very poor in the pH range of 2—8.

It is further seen in Fig. 1 that the recoveries for most elements were generally very low in the pH range of 2—3. Since the iminodiacetate functional groups of the resin rarely dissociate proton at the lower pH, trace elements are prevented from adsorbing on the chelating resin through the complex formation,[23] which results in the poor recoveries of most heavy metals. It should be noted here that the recoveries of V, Mo, and W which form oxoanions decreased in the higher pH region. The following elements provided the largest recoveries at pH 3 for Sn, 4 for Ti, 4 for Fe, 6 for Al, and 5—6 for REEs. These pHs are close to the pH value at which hydroxides of these elements begin to precipitate.[24] Accordingly, these results indicate that the coordinations of the hydroxy groups with these elements increase at the higher pH, and thus the complex formations of these elements with the chelating resin are prohibited.

Next, the recoveries of Mn and Cd in seawater and in the aqueous solution were investigated at pH 4. As is seen in Fig. 1d, the recoveries of these elements were 4.0% for Mn and 19.8% for Cd in seawater. On the other hand, they were 38.7% for Mn and 78.7% for Cd in water. The results that the recoveries of Mn and Cd in the aqueous solution is larger at pH 4 than those in seawater may be explained by the formation of chloro-complexes of these elements in seawater.

As is seen in Fig. 1, the larger recoveries of almost all elements were obtained in the pH range of 4—6. Thus, the recoveries of analyte elements at pH 4 and 6 were further examined in detail to decide the optimum pH value for simultaneous multielement preconcentration. The recoveries for 33 elements at pH 4 and 6 are summarized in Table 3. It is seen from Table 3 that the recoveries were more than 80% for 19 elements at pH 4 and for 22 elements at pH 6, respectively. The recoveries for Al, Mn, Co, Ni, Zn, Cd, Y, REEs, Pb, and U are larger at pH 6 than at pH 4. The relative standard deviations (RSDs) of almost all elements, except for Ti, Fe, and Ga, were also better at pH 6 than at pH 4. Accordingly, pH 6 was employed for simultaneous

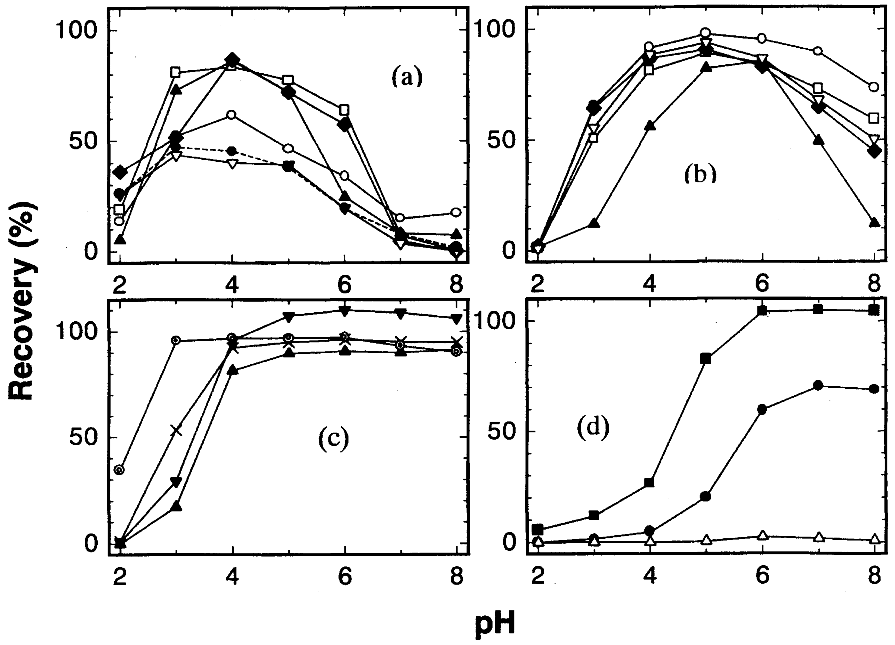

Fig. 1. pH dependence of the recoveries of trace elements in chelating resin preconcentration.
(a)▲ : Ti, □ : V, ○ : Fe, ◆ : Mo, ● : Sn, ▽ : W,
(b)▲ : Al, ○ : Y, □ : La, ◆ : Tb, ▽ : Lu,
(c)▲ : Co, × : Ni, ◎ : Cu, ▼ Zn,
(d)△ : Cr(VI), ● : Mn, ■ : Cd.

Table 3. Recoveries of Trace Elements in Chelating Resin Preconcentration at pH 4 and pH 6

Element	pH 4		pH 6	
	Recovery/%	RSD[a]/%	Recovery/%	RSD[a]/%
Al	48.7	14.7	72.6	0.6
Ti	86.0	5.7	27.8	21.2
V	87.6	10.8	63.9	6.8
Cr	0.6	13.1	8.0	12.0
Mn	4.0	8.0	53.9	3.0
Fe	91.8	7.9	55.9	17.4
Co	83.1	6.1	97.1	0.8
Ni	87.0	9.5	91.0	3.8
Cu	97.0	6.3	96.0	1.5
Zn	90.9	5.1	93.9	3.5
Ga	73.1	6.8	67.6	14.5
Y	80.9	5.4	91.3	1.9
Zr	38.5	5.7	14.3	2.2
Mo	86.1	10.7	57.8	9.1
Cd	19.8	13.0	85.5	4.4
Sn	52.9	7.9	33.0	2.7
La	80.4	5.3	89.3	1.3
Ce	82.0	5.2	87.9	1.6
Pr	84.8	5.2	89.5	1.4
Nd	82.3	5.0	88.8	1.1
Sm	85.5	5.4	90.8	1.7
Eu	86.6	4.9	91.4	2.0
Gd	79.6	4.7	89.4	1.7
Tb	87.0	4.7	92.8	1.7
Dy	80.6	4.9	90.0	2.2
Ho	81.0	4.6	90.3	2.0
Er	80.4	4.8	91.7	1.1
Tm	79.9	4.4	91.2	2.3
Yb	75.6	4.5	89.1	2.3
Lu	79.8	4.6	93.4	1.6
W	69.5	3.7	43.2	4.9
Pb	74.5	6.0	94.1	3.2
U	74.4	4.4	81.1	4.1

a) The RSDs were calculated from three replicate preconcentration procedures.

preconcentration of trace elements in seawater.

Removal of Matrix Elements Adsorbed on the Chelating Resin. It is known that alkaline earth elements are significantly adsorbed on the resin[10,20,21] when seawater is treated with the Chelex 100 resin. It has been, thus, proposed that alkaline earth elements retained on the resin should be removed by washing the resin with ammonium acetate aqueous solution so as to minimize matrix effect to analyte elements in the ICP-MS measurement.[10,20,21] However, when an excess amount of the buffer solution is used for washing the resin, significant amounts of analyte elements might be lost in this washing process.

Thus, removal of matrix elements was examined by using various volumes of ammonium acetate solution. The results are summarized in Table 4. Without washing, the concentrations of Na, Ca, and Mg were 50, 259, and 465 mg $\mathrm{dm^{-3}}$, respectively. In this case, the total concentration of matrix elements was about 800 mg $\mathrm{dm^{-3}}$. Table 4 shows that the concentrations of matrix elements decreased with increasing volume of ammonium acetate solution. The total concentration of Mg and Ca was below 200 mg $\mathrm{dm^{-3}}$, when the washing volume was more than 8 ml. When the total concentration of matrix elements was 200 mg $\mathrm{dm^{-3}}$, the signal intensities of most analyte elements in the ICP-MS measurement were suppressed by about 20%, compared to those for the matrix-free solution. However, the signal suppression at this level could be corrected by the internal standard method employed in the present experiment.

The recoveries for Al, Mn, Co, Ni, Zn, Cd, and U were almost constant with and without washing. However, the recoveries for REEs decreased by about 10%, when the resin was rinsed with 15 ml of ammonium acetate solution. As a result, taking into consideration both removal of major elements and the recoveries of trace elements, the compromised washing volume of ammonium acetate solution was chosen to be 8 ml.

The elution of trace elements from the resin was investigated by eluting each 2-ml fraction of 2 M $\mathrm{HNO_3}$. Almost all elements were completely removed with 4 ml of 2 M $\mathrm{HNO_3}$. Since at least 5 ml of the sample solution was necessary for the ICP-MS measurement, analyte elements on the resin were eluted with 6 ml of 2 M $\mathrm{HNO_3}$.

Correction of Polyatomic and Divalent Ion Interferences. In the ICP-MS measurement, major elements in the sample solution often cause spectral interferences with analyte elements due to polyatomic and divalent ions.[26] Thus, polyatomic and divalent ion interferences to all analyte elements were examined. The ions subjected to correction in the present experiment are listed in Table 5, together with their interference correlation coefficients. The interference correction coefficients (ng $\mathrm{dm^{-3}}$/μg $\mathrm{dm^{-3}}$) in Table 5 are expressed as the apparent analyte concentration (ng $\mathrm{dm^{-3}}$) which is provided by 1 μg $\mathrm{dm^{-3}}$ of each interferent element at the mass number of analyte element. As is shown in Table 5, $^{57}\mathrm{Fe}$ and $^{59}\mathrm{Co}$ overlap with $^{40}\mathrm{Ca}^{16}\mathrm{O}^{1}\mathrm{H}$ and $^{43}\mathrm{Ca}^{16}\mathrm{O}$, respectively.[27] The interference of $^{95}\mathrm{Mo}^{16}\mathrm{O}$ with $^{111}\mathrm{Cd}$ is not negligible because the ratio of Mo to Cd in seawater is usually ca. 300. Although monoxide ions of light REEs often interfere with heavy REEs, the interference of $^{141}\mathrm{Pr}^{16}\mathrm{O}$ with $^{157}\mathrm{Gd}$ was particularly severe in the present experiment.[28]

The following simple formula was used for correction of polyatomic ion interference, where the correction coefficient is assumed to be a linear function of the concentration of analyte element examined:[27,29]

$$C_{\mathrm{cor}} = C_{\mathrm{obs}} - F \times C_{\mathrm{int}}, \tag{1}$$

where C_{cor}, C_{obs}, F, and C_{int} are the corrected concentration of analyte element (ng $\mathrm{dm^{-3}}$), the observed concentration of analyte element (ng $\mathrm{dm^{-3}}$), interference correction coefficient (ng $\mathrm{dm^{-3}}$/μg $\mathrm{dm^{-3}}$), and the concentration of the inteferent element (μg $\mathrm{dm^{-3}}$), respectively.

When $F \times C_{\mathrm{int}}$ is comparable to or larger than C_{obs}, a large error may be caused in estimation of the corrected concentration of analyte element. In Table 5, the ratio of $(F \times C_{\mathrm{int}})$ to the observed concentration (C_{obs}) was larger than 1 in the

Table 4. Concentrations of Major Elements and the Recoveries of Trace Elements in the Analysis Solution after Chalating Resin Preconcentration[a)]

Element	Volume of ammonium acetate soln/ml		
	0	8	15
(A) Concentration of major element			
Na[b)]	50.8 mg dm^{-3}	—[c)] mg dm^{-3}	—[c)] mg dm^{-3}
Ca[b)]	259	85.0	65.3
Mg[b)]	465	95.2	84.0
K[b)]	—[c)]	—[c)]	—[c)]
Sr[b)]	3.11	0.59	0.57
Ba	0.0035	0.0005	0.0004
(B) Recovery of trace element			
Al	87.8%	86.2%	83.5%
Mn	58.0	55.8	59.9
Co	99.6	98.1	100.4
Ni	97.0	96.5	99.2
Zn	100.2	96.7	98.7
Cd	92.9	96.0	95.6
La	96.1	95.3	92.5
Eu	93.1	94.4	86.0
Lu	94.9	92.6	82.3
U	87.6	86.5	84.8

a) The analysis solution was obtained by the recommended preconcentraion procedure described in the experimental section.
b) Measured by ICP-AES. c) Not detected.

Table 5. Polyatomic and Divalent Ions and Their Interference Correction Coefficients for Each Analyte Element in the ICP-MS Measurement after Chelating Resin Preconcentration

Element	Polyatomic and divalent ion	Interference correction coefficient[a)] ng dm^{-3}/μg dm^{-3}
^{57}Fe	^{40}Ca^{16}O^{1}H, ^{40}Ca^{17}O	3.02
^{59}Co	^{43}Ca^{16}O	5.4×10^{-4}
^{111}Cd	^{95}Mo^{16}O	1.75
^{157}Gd	^{141}Pr^{16}O	123
^{159}Tb	^{143}Nd^{16}O	2.01

a) The coefficient is defined as the ratio of the apparent concentration (ng dm^{-3}) of the interfered element provided by 1 μg dm^{-3} of the interferent element which produces polyatomic or divalent ions shown in the table.

cases of Fe, while those of other elements were much smaller than 1. Thus, the concentration of Fe in Table 7 was shown in the parentheses just for reference.

Analytical Figures of Merit. In order to evaluate the lower limit of determination by the present method, the analytical detection limits were estimated from the instrumental detection limits, taking into account the concentration factor and the recovery values. The instrumental detection limits were obtained as the concentration of analyte element corresponding to 3-fold the standard deviation (3σ) of background signal intensities for the blank solution (2 M HNO_3), where the standard deviation was calculated from the 10-times repeated measurements at each mass number. The analytical detection limits estimated are shown in Table 6. As can be seen in Table 6, the analytical detection limits for 33 elements were in the range from 0.1 μg dm^{-3} of Fe to 0.000007 μg dm^{-3} of Ho. The poor detection limits of ^{52}Cr and ^{57}Fe may be ascribed to large background intensities due to isobaric molecular ions such as ^{40}Ar^{12}C and ^{40}Ar^{16}O^{1}H,[30] respectively, together with their low recovery values (Cr: 8.0%, Fe: 55.9%).

The blank values in the present method are also summarized in Table 6. The blank values were almost negligible because they were much lower than the abundances of analyte elements in seawater.

Determination of Trace Elements in Coastal Seawater Reference Material (CASS-3). Trace elements in coastal seawater reference material CASS-3 were determined by the present analytical method. The results are summarized in Table 7, along with the certified and reference values.[12,15,31,32] As is seen in Table 7, the concentrations of 29 elements (Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Y, all-REEs, W, Pb, and U) in CASS-3 were obtained in the present study. In addition, since Ti and W provided the recovery values below 50% and the correction percentage of isobaric ion interference for Fe was larger than 50%, the concentrations of these elements were seemingly less reliable, and then they are shown in the parentheses for reference in Table 7. Although we also tried to determine Cr, Ga, Zr, and Sn, their concentrations were below the analytical detection limit. It is seen in Table 7 that the relative standard deviations (RSDs) for 27 elements in CASS-3 were less than 10%.

The analytical results for Mn, Co, Ni, Cu, Zn, Mo, Cd, and Pb were in rather good agreement with the certified values issued from NRC. As for the elements whose certified values have been not issued from NRC, their concentrations were compared with the literature values for CASS-3[12,32] or CASS-

Table 6. Analytical Detection Limits and Blank Values Obtained by ICP-MS with Chelating Resin Preconcentration

Element	*m*/*z*	Analytical detection limit[a)] $\mu g\ dm^{-3}$	Blank value $\mu g\ dm^{-3}$	Element	*m*/*z*	Analytical detection limit[a)] $\mu g\ dm^{-3}$	Blank value $\mu g\ dm^{-3}$
Al	27	0.005	0.070	La	139	0.00002	0.00029
Ti	47	0.04	0.05	Ce	140	0.00002	0.00018
V	51	0.0003	0.0007	Pr	141	0.000008	0.000044
Cr	52	0.02	—[b)]	Nd	146	0.00002	0.00008
Mn	55	0.0004	0.0058	Sm	147	0.00003	0.00004
Fe	57	0.1	—[b)]	Eu	151	0.00001	0.00002
Co	59	0.0001	0.001	Gd	157	0.00007	0.00003
Ni	62	0.0009	0.0086	Tb	159	0.00001	0.00002
Cu	63	0.0002	0.0036	Dy	163	0.00002	0.00004
Zn	68	0.002	0.039	Ho	165	0.000007	0.000015
Ga	69	0.00005	0.00020	Er	166	0.00002	0.00003
Y	89	0.00001	0.00017	Tm	169	0.000008	0.000015
Zr	90	0.008	—[b)]	Yb	174	0.00003	—[b)]
Mo	95	0.004	—[b)]	Lu	175	0.000009	0.000014
Cd	111	0.0001	0.0007	W	184	0.0003	—[b)]
Sn	118	0.0008	0.016	Pb	208	0.0001	0.011
				U	238	0.04	0.05

a) Analytical detection limits were calculated from instrumental detection limits, taking into account the concentrated factor (41.7) and recovery values. b) Not detected.

2.[15,31] It is seen in Table 7 that the analytical results for Al and V were also in good agreement with the literature values. Since the concentrations of REEs for CASS-3 have been not reported so far, the literature values for REEs in CASS-2 are listed in Table 7. As is seen in Table 7, the concentrations of REEs in CASS-3 were much higher than those in CASS-2.

Determination of Trace Elements in the Coastal Seawater Collected from the Ise Bay. The analytical method explored in the present experiment was also applied to the determination of trace elements in the coastal seawater sample collected at off-shore of the Ise Bay near Tokoname. The results are summarized in Table 7. The analytical values for 29 elements were also obtained in the concentration range over 5 orders of magnitude from 9.20 $\mu g\ dm^{-3}$ of Mo to 0.00032 $\mu g\ dm^{-3}$ of Tm. The RSDs for the analytical values were below 10% except for Ti, V, Mn, Fe, Mo, W, and Pb. The concentrations of V, Mo, and U in coastal seawater from the Ise Bay were almost at the same levels as those in CASS-3. These results indicate that V, Mo, and U exist as the stable oxo-ions, and thus it can be considered that they are well mixed and keep their concentrations almost constant over all the sea areas of the world. The concentrations of Al, Mn, and Pb are relatively higher in the Ise Bay, compared to those in CASS-3, while those of Cd and REEs are lower. Aluminum, Mn, and Pb are known as the anthropogenic elements: thus the higher concentrations of these elements in the coastal area of the Ise Bay may be caused by the terrestrial supply or artificial pollution.

REE Patterns of Coastal Seawater. There are no saline water reference materials for which the concentrations of REEs are certified. Thus, the REE distribution patterns which are shown as the relative concentrations of REEs normalized to their concentrations in chondrite or shale[10,33] are often examined in order to evaluate internal consistency of the REEs data. Such REE patterns for CASS-3, CASS-2, and Ise Bay seawater are shown in Fig. 2, where the concentrations of REEs were normalized to those in Post Australian Average Shale.[34] As is seen in Fig. 2, the REE patterns show the quite smooth curves. It is noted here that the concentrations of heavy REEs are relatively higher than those of light REEs, and the negative anomalies of Ce are clearly observed for all seawater samples, in similarity to the previous reports.[10,33] A high concentration of Sm was observed for CASS-3 in the present work. Such high concentration of Sm was also reported for CASS-2 in the previous work.[15] Jarvis et al.[15] suggested that the high concentration of Sm in CASS-2 might be due to contamination occurred at some stage in preparation procedure of the reference material. Since the

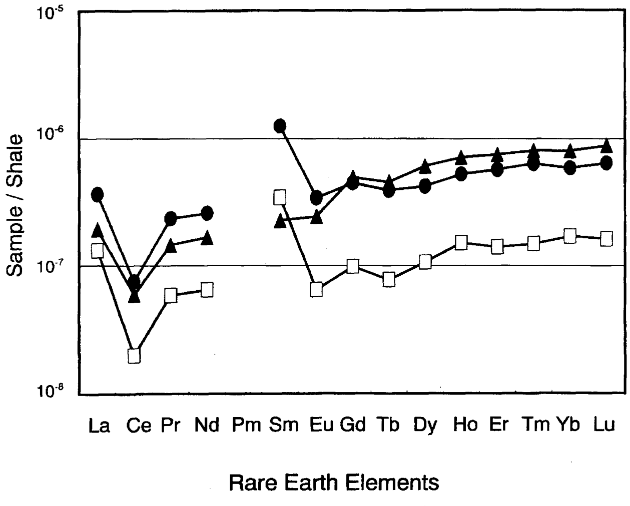

Fig. 2. Shale-normalized REE patterns of coastal seawaters. ▲: Ise Bay seawater, ●: CASS-3, □: CASS-2 (cited from Ref. 15).

Table 7. Analytical Results for Trace Elements in Coastal Seawater Reference Material CASS-3 and Ise Bay Seawater Sample Determined by ICP-MS after Chelating Resin Preconcentraion

Element	CASS-3		Ise Bay seawater
	Concentration[a]	Certified or literature value	Concentration[a]
	μg dm^{-3}	μg dm^{-3}	μg dm^{-3}
Al	0.32 ± 0.03	0.389[b]	2.11 ± 0.11
Ti	(0.10 ± 0.03)		(0.15 ± 0.03)
V	1.43 ± 0.04	1.50,[c] 2.49[d]	1.39 ± 0.20
Mn	2.71 ± 0.17	2.51±0.36	4.35 ± 1.09
Fe	(2.3 ± 0.4)	1.26±0.17	(0.8 ± 0.1)
Co	0.038 ± 0.003	0.041±0.009	0.056 ± 0.004
Ni	0.39 ± 0.01	0.386±0.062	1.32 ± 0.11
Cu	0.48 ± 0.01	0.517±0.062	0.62 ± 0.01
Zn	1.38 ± 0.03	1.24±0.25	1.68 ± 0.11
Y	0.024 ± 0.0004		0.034 ± 0.002
Mo	9.98 ± 0.71	8.95±0.26	9.20 ± 1.75
Cd	0.032 ± 0.002	0.030±0.005	0.012 ± 0.0009
La	0.014 ± 0.0004	0.00510[e]	0.0075 ± 0.0004
Ce	0.0061 ± 0.0003	0.00159[e]	0.0048 ± 0.0003
Pr	0.0021 ± 0.00004	0.00052[e]	0.0013 ± 0.00009
Nd	0.0089 ± 0.0001	0.00222[e]	0.0057 ± 0.0003
Sm	0.0069 ± 0.0003	0.00191[e]	0.0013 ± 0.00005
Eu	0.00037 ± 0.00002	0.00007[e]	0.00027 ± 0.00003
Gd	0.0021 ± 0.0001	0.00046[e]	0.0023 ± 0.0002
Tb	0.00030 ± 0.00002	0.00006[e]	0.00035 ± 0.00003
Dy	0.0020 ± 0.00008	0.00050[e]	0.0028 ± 0.0001
Ho	0.00051 ± 0.00003	0.00015[e]	0.00070 ± 0.00006
Er	0.0016 ± 0.00002	0.00040[e]	0.0021 ± 0.00012
Tm	0.00025 ± 0.00002	0.00006[e]	0.00032 ± 0.00002
Yb	0.0016 ± 0.00009	0.00048[e]	0.0022 ± 0.00008
Lu	0.00027 ± 0.00001	0.00007[e]	0.00037 ± 0.00001
W	(0.012 ± 0.001)		(0.037 ± 0.007)
Pb	0.0095 ± 0.0007	0.012±0.004	0.032 ± 0.006
U	3.35 ± 0.09	2.84	3.54 ± 0.19

a) The mean value and standard deviation obtained by 3-times measurements. Data in the parentheses are the results for the elements with the recovery values lower 50% or polyatomic ion interference correction larger than 50%. b) Literature value for CASS-2, cited from Ref. 31. c) Cited from Ref. 32. d) Cited from Ref. 12. e) Literature values for CASS-2, cited from Ref. 15.

concentration of Sm in the off-shore seawater from the Ise Bay was not relatively high, it may be reasonable to consider that Sm in CASS-3 and CASS-2 was contaminated during preparation of these reference materials.

Conclusion

The concentrations of 29 elements in the coastal seawater samples could be determined by ICP-MS after chelating resin preconcentration. The analytical values for most elements in coastal seawater reference material (CASS-3) were in rather good agreement with the certified values (Mn, Co, Ni, Cu, Zn, Mo, Cd, and Pb). These results indicate that the present method is reliable enough to apply to the multielement determination of trace elements in seawater. The concentrations of V, Mo, and U are at almost the same level in the coastal seawater samples from both CASS-3 and the Ise Bay. In terms of REEs, their concentrations obtained in the present experiment were almost the same in both CASS-3 and the coastal seawater from the Ise Bay, although they were quite different from the literature values of CASS-2. In addition, it was found from the comparison of the REE patterns that the concentration of Sm in CASS-3 and CASS-2 was remarkably high, perhaps due to contamination.

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