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Headline Articles

Multielement Determination of Trace Elements in Seawater by Inductively Coupled Plasma Mass Spectrometry after Tandem Preconcentration with Cooperation of Chelating Resin Adsorption and Lanthanum Coprecipitation

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A tandem preconcentration method, in which chelating resin adsorption and La coprecipitation were cooperatively employed for preconcentration, was developed as a pretreatment method for simultaneous multielement determination of trace elements in seawater by ICP-MS. First, the seawater sample (250 ml) was treated with a chelating resin for preconcentration of trace elements, and then trace elements with good recoveries were determined by ICP-MS. Trace elements with the chemical properties of oxoanion- and hydride-formation, which were poorly recovered in the chelating resin preconcentration, were further subjected to preconcentration by La coprecipitation. As a result, more than 30 elements could be determined in the concentration range from 9.6 μg L^{-1} for Mo to 0.00018 μg L^{-1} for Tm, when the present tandem method was applied to the analysis of open seawater standard reference material (NASS-4). Furthermore, the analytical results for open seawater reference materials were compared with those for coastal seawater reference material as well as for coastal seawater collected in the Ise Bay. It was found that the multielement data for trace elements in these seawater samples clearly showed different elemental distributions, reflecting the different marine environments.

These days, the concentration levels of almost all the elements in seawater have been elucidated by the persistent efforts of a large number of scientists, using various kinds of analytical techniques.[1] Consequently, it has been found that trace and ultratrace elements in seawater show some characteristic vertical concentration distributions in the ocean, reflecting the physicochemical conditions and biological activities in marine environments, while major and minor elements are kept at almost uniform concentration level horizontally and vertically in the ocean.[1] Then, the kinetic behaviors of various trace elements can be well understood from such elemental distributions in the ocean. For example, Fe, Mn, and Al are interacting with settling particulates and play an important role in the transport of trace elements in the ocean.[2] It is also known that Fe, Cu, Zn, Ni, and Cd show strong relationships with bio-activities in the ocean.[3] In addition, As, Se, and Sb exist in various oxidation states, reflecting the redox conditions in seawater.[4,5] Thus, the variety of trace elements in seawater can provide some good indicators to monitor the changes of the marine ecosystems. Therefore, it is considered that the knowledge of the concentrations and distributions for as many trace elements as possible is helpful to elucidate not only the physicochemical and bio-geochemical phenomena but also environmental pollution in the open and coastal sea areas.[6]

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most powerful analytical methods for the determination of trace elements. It has a wide linear dynamic range of 5–6 orders of magnitude, extremely high sensitivity, and multielement detection capability.[7] However, the determination of trace elements in seawater is quite difficult without any preconcentration even by ICP-MS, because their concentrations are generally below the μg L^{-1} level. In addition, the high salt contents of seawater make it difficult to nebulize the seawater sample directly into the plasma in the ICP-MS measurement. Therefore, a pretreatment method for preconcentration of trace elements together with removal of matrix elements is inevitably required to determine a variety of trace and ultratrace elements in seawater.[7]

The present authors have tried to establish the analytical methods for the multielement determination of major-to-trace elements by plasma spectrometry.[7–9] The chelating resin preconcentration method has excellent analytical features of nonselective multielement preconcentration for many trace elements in seawater, along with efficient removal of matrix elements such as Na, K, Ca, and Mg.[10–12] Then, the chelating resin preconcentration/ICP-MS method was applied to the analysis of coastal seawater reference material (CASS-3), about 30 elements such as Al, V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Y, rare earth elements (REEs), Pb, and U, which were in the concentration range from 10 μg L^{-1} to 0.1 ng L^{-1}, could be determined.[10–12] However, it was found that the chelating resin provided poor recoveries for oxoanion- and hydride-forming elements. The present authors also investigated the coprecipitation methods using Ga, Al and La.[13–16] Then, it was found that La coprecipitation was useful for preconcentration of oxoanion- and hydride-forming elements such as As, Se, Mo, Sb, W, V, and U,[16] which could be determined simultaneously by ICP-MS. Accordingly, complementary use of the chelating resin preconcentration and La coprecipitation came up when we planned idea about exploration of more efficient multielement preconcentrations for trace elements in seawater.

In the present research, hence, we developed a tandem method for multielement preconcentration of trace elements in seawater, where chelating resin preconcentration was first applied to the original seawater, and then the filtrate after the chelating resin preconcentration was subjected to La coprecipitation. In order to evaluate the analytical validation of the present tandem preconcentration/ICP-MS method, it was applied to the analysis of open seawater reference material (NASS-4) issued from National Research Council of Canada (NRC).

Experimental

Instruments. An ICP-MS instrument of model SPQ-8000A (Seiko Instruments, Chiba), which consisted of a quadrupole-type mass spectrometer, was used for the determination of trace elements. The ICP-MS instrument equipped with a concentric nebulizer allowed us to determine 30 elements (or *m*/*z*) simultaneously. The operating conditions of the ICP-MS instruments are shown in Table 1. The mass numbers (*m*/*z*) for analyte elements in the ICP-MS measurement were the same as those in the previous papers.[12] A model twin pH meter from Horiba (Kyoto) was used for pH adjustment.

Chemicals. Nitric acid, hydrochloric acid, acetic acid, and aqueous ammonia solution used were of electronics industry grade, purchased from Kanto Chemicals (Tokyo). The multielement standard solutions for making the working calibration curves were prepared from the single-element standard stock solutions (1000 μg L^{-1}) for atomic absorption spectrometry (Wako Chemicals, Osaka) except for As(V) and Sb(V).[12] The standard stock solutions for As(V) and Sb(V) were prepared by dissolving potassium arsenate of analytical reagent grade (Wako Chemicals) in pure water and potassium hexahydroxoantimonate of guaranteed reagent grade (Nacalai Tesque, Kyoto) in 3 M HCl solution, respectively (1 M = 1 mol dm^{-3}). In the cases of Cr, As, and Sb, which have two different oxidation states, only Cr(VI), As(V), and Sb(V) were investigated in the present experiment, because they are dominant oxidation states in seawater.[17,18] In addition, in the case of Se, Se(IV) was almost completely recovered by La coprecipitation,[12] while Se(VI) was not. The La solution as a coprecipitation carrier was prepared by dissolving 3 g of $La(NO_3)_3$ (extra pure grade; Wako Chemicals) in 100 mL of 0.1 M HNO_3 so as to be 10 g L^{-1} of La solution.

Table 1. Operating Conditions for ICP-MS Instrument

ICP-MS:	Seiko SPQ 8000A
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 16 L min^{-1}
Auxiliary gas flow rate	Ar 1.0 L min^{-1}
Carrier gas flow rate	Ar 1.0 L min^{-1}
Sampling depth	12 mm from load coil
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 times

The Chelex 100 resin in 100–200 mesh was purchased from Bio-Rad Laboratories (Richmond, CA, USA). The resin was soaked in 5 M HCl, changing the HCl solution 5 times every 12 h, and washed with pure water before use.

Purified water used throughout the present experiment was prepared by a Milli-Q purification system (Nihon Millipore Kogyo, Tokyo).

Seawater Samples. Open seawater reference material NASS-4 was obtained from National Research Council of Canada (NRC) 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 used for the preliminary experiments of the present analytical method. The coastal seawater samples examined were filtrated with a membrane filter (pore size 0.45 μm) immediately after sampling, and then acidified to pH 1 with nitric acid. These seawater samples were preserved in the polyethylene bottles, which were soaked in 6 M HNO_3 for more than 1 week and rinsed with pure water before use.

Experimental Procedures of Tandem Preconcentration. The flow chart of the tandem preconcentration method is shown in Fig. 1. The procedure was established as a recommended method for preconcentration of trace elements in the seawater samples, taking into account the experimental conditions of the chelating resin preconcentration and La coprecipitation methods, reported in the previous papers.[12,16]

First, 250 mL of the seawater sample was subjected to chelating resin preconcentration where the pH of the sample solution was adjusted to 6.0 with acetic acid and aqueous ammonia solution. After adding 0.2 g of the chelating resin (dry weight) into the sample solution, the solution was stirred with a magnetic stirrer for 2 h, and filtered with a glass filter (1.4 cm i.d.). At this time, the filtrate was collected in a polypropylene bottle. Then, the resin was rinsed with 10 mL of pure water and 8 mL of 1 M ammonium acetate solution to reduce major elements such as Na, K, Ca, and Mg partly adsorbed on the resin. These rinsing solutions were also collected in the polypropylene bottle, in which the filtrate had already been stored. After washing with 10 mL pure water again, trace elements adsorbed on the resin were eluted with 6 mL of 2 M HNO_3, into which the internal standard elements (Ge, In, Re, and Tl; 100 μg L^{-1} each) in HNO_3 solution were added for correction of matrix effects due to major elements. Then, the 41.7-fold concentration factor in volume was achieved in the chelating resin preconcentration.

As the second stage of tandem preconcentration, the mixture of the residual seawater sample (ca. 280 mL) of the filtrate and rinsing solutions collected after chelating resin preconcentration was then subjected to La coprecipitation. Two mL of La solution (10

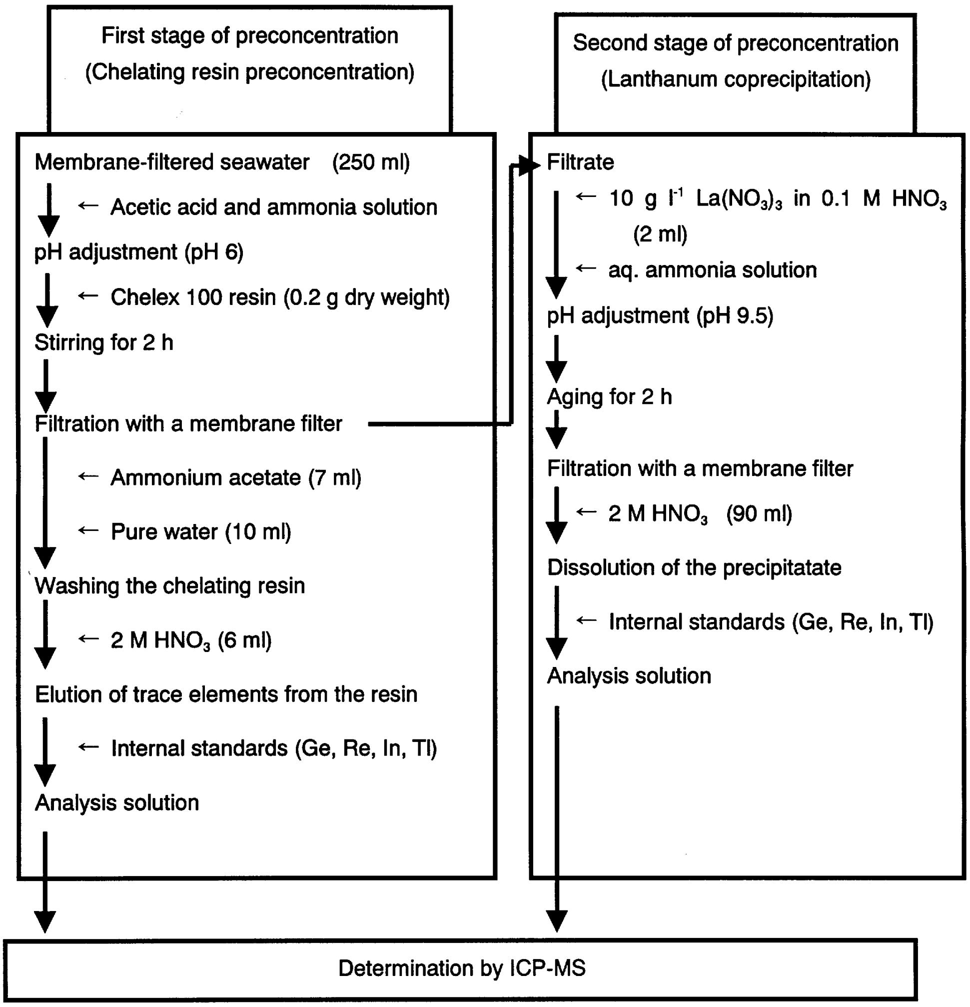

Fig. 1. Flow chart of the tandem preconcentration method, followed by ICP-MS measurement.

g L^{-1}) was added in the residual seawater sample as a coprecipitation carrier. After adjustment of pH of the sample solution to 9.5 with aqueous ammonia solution, the solution was stirred with a magnetic stirrer for ca. 5 min. The sample solution was kept standing for 2 h. Then, the precipitate which formed was collected on a PTFE membrane filter (pore size 0.45 μm), and washed with 30 mL of pure water. The precipitate was dissolved with 90 mL of 2 M HNO_3, into which 10 mL of the mixed solution of Ge, In, Re, and Tl (100 μg L^{-1} each) was added for the internal standard correction of matrix effects in the ICP-MS measurement. Consequently, 2.5-fold preconcentration was achieved in the La coprecipitation procedure.

Results and Discussion

Analytical Figures of Merit of Tandem Preconcentration/ICP-MS Method. The analytical figures of merit of the present tandem preconcentration method, in which chelating resin adsorption and La coprecipitation were cooperatively employed, were investigated by using the coastal seawater sample collected in the Ise Bay. The recoveries, analytical detection limits, and blank values obtained by the tandem preconcentration/ICP-MS method are summarized in Table 2, together with those obtained only by the chelating resin preconcentration/ICP-MS method. Although the results in Table 2 are almost the same as those reported previously,[12] they were re-examined again for comprehensive discussion of the tandem preconcentration method. In Table 2, R_{ch} indicates the recovery obtained by chelating preconcentration, and R_{total} indicates the accumulative sum of the recoveries obtained by chelating resin preconcentration and La coprecipitation, i.e., by the whole experimental procedure of tandem preconcentration. Similarly, DL_{ch} and DL_{La} are the analytical detection limits obtained by ICP-MS after chelating resin preconcentration and tandem preconcentration, respectively. It should be noted here that DL_{La} is the analytical detection limit estimated only by considering the concentration factor in La coprecipitation.

It is seen in Table 2 that the recoveries (R_{ch}) of Co, Ni, Cu, Zn, Y, Cd, REEs, Pb, and U in chelating resin preconcentration were larger than 80%, and their relative standard deviations (RSDs) were less than 5%. These recoveries and RSD values were in fairly good agreement with those reported in the previous paper.[12] Since the elements listed above were concentrated sufficiently only by chelating resin preconcentration, further

Table 2. Analytical Figures of Merit for Trace Elements in the Tandem Preconcentration Method

Element	Chelating resin preconcentration				Tandem preconcentration			
	R_{ch}[a)]/%		DL_{ch}[b)]/μg L^{-1}	Blank[c)]/μg L^{-1}	R_{total}[d)]/%		DL_{La}[e)]/μg L^{-1}	Blank[c)]/μg L^{-1}
	Mean	RSD[f)]			Mean	RSD[f)]		
Al	54.6	0.8	0.002	0.052	62.5	0.8	0.6	n.d.
Ti	27.8	21.2	0.08	n.d.	92.6	30.5	3	n.d.
V	61.3	2.1	0.001	n.d.	85.5	3.4	0.01	n.d.
Cr(VI)	3.2	23.2	0.04	n.d.	64.7	4.1	0.02	0.92
Mn	53.9	3.1	0.002	0.007	77.7	5.0	0.05	n.d.
Co	101	0.7	0.00009	0.00050				
Ni	97.2	0.9	0.0009	0.013				
Cu	97.8	0.1	0.0007	n.d.				
Zn	100	0.9	0.003	n.d.				
As(V)	2.5	16.3	0.4	n.d.	104	4.4	0.03	n.d.
Se(IV)	0.1	50.5	3	n.d.	92.0	5.0	0.06	n.d.
Y	95.8	0.6	0.00001	0.0002				
Mo	55.3	3.2	0.002	n.d.	70.2	2.7	0.01	n.d.
Cd	95.1	2.5	0.00006	0.0007				
Sn	33.0	2.7	0.0003	0.030	69.7	3.4	0.01	n.d.
Sb(V)	0.04	29.2	1	n.d.	104	4.2	0.008	n.d.
La	102	2.2	0.00002	0.00024				
Ce	97.8	1.4	0.00004	0.00036				
Pr	99.7	0.4	0.00001	0.00003				
Nd	90.5	1.2	0.00004	n.d.				
Sm	88.0	1.6	0.00004	n.d.				
Eu	87.1	0.5	0.00001	n.d.				
Gd	85.7	1.8	0.00002	n.d.				
Tb	86.6	1.6	0.000006	n.d.				
Dy	85.9	2.5	0.00001	n.d.				
Ho	86.7	1.2	0.000007	n.d.				
Er	85.0	1.1	0.00002	n.d.				
Tm	85.7	1.1	0.000006	n.d.				
Yb	84.9	0.8	0.00001	n.d.				
Lu	87.8	1.3	0.000007	n.d.				
W	43.2	4.9	0.0002	0.0010	98.0	3.8	0.002	0.004
Pb	93.1	1.1	0.0003	0.011				
Bi	30.8	14.5	0.00003	n.d.	85.0	5.5	0.002	n.d.
U	94.2	2.5	0.0008	0.0010				

a) R_{ch} is the recovery value obtained by chelating resin preconcentration.
b) DL_{ch} is the analytical detection limit obtained by the chelating resin preconcentration/ICP-MS method.
c) n.d.: Not detected.
d) R_{total} is the recovery value obtained by tandem preconcentration.
e) DL_{La} is the analytical detection limit obtained by the La coprecipitation/ICP-MS method.
f) The RSDs were calculated from three replicate preconcentration procedures.

preconcentration was not required for them. On the contrary, the recovery values (R_{ch}) of Al, Ti, V, Cr, Mn, As, Se, Mo, Sn, Sb, W and Bi were found to be below ca. 60%. In general, oxoanion- and hydride-forming elements such as Cr, V, Mo, As, Se, Sb, W, and Bi provided the poor recoveries in chelating resin preconcentration, which may be ascribed to their low adsorption abilities on the chelating resin. In the cases of Al, Ti, Mn, and Sn, their poor recoveries may be ascribed to the formation of relatively stable hydroxo- or chloro-complexes in seawater.[12,19] Then, La coprecipitation was consecutively performed to recover these elements in the residual seawater sample as the second stage of the tandem preconcentration.

The accumulative recovery values (R_{total}) of 12 elements obtained by tandem preconcentration are summarized in Table 2. As is seen in Table 2, in particular, the recoveries of Ti, V, As, Se, Sb, W, and Bi were substantially improved to be larger than 80%, although those of other elements were also larger than 60%. Under these conditions, the relative standard deviations (RSDs) of all the elements examined were within 6%, except for Ti. The RSD of R_{total} for Ti was about 30%, although its recovery was 92.6%. The poor reproducibility of Ti in tandem preconcentration might be ascribed to its adsorption on the surface of the polypropylene bottle during preservation, because hydrolysis of Ti may easily occur in weakly acidic solution.[20] The recoveries of Al, Cr(VI), Mn, Mo, and Sn were still in the range from 60 to 80% after the present tandem preconcentration. However, the RSDs for their recovery values throughout the whole tandem preconcentration procedure were kept below 5%, even though the preconcentration process became more complicated because of combination of the two different preconcentration methods.

The analytical detection limits shown in Table 2 were estimated from the instrumental detection limits obtained by ICP-MS, taking into account the concentration factors and the recovery values of each preconcentration procedure.[12] The instrumental detection limits were defined as the concentration corresponding to 3-fold standard deviation of the 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. Table 2 shows that the analytical detection limits (DL_{ch}) obtained by ICP-MS after chelating resin preconcentration were in the range from 3 μg L^{-1} for Se to 0.00006 μg L^{-1} for Tm and Tb. The poor detection limits for Se, Sb, and As were ascribed to their low recoveries (Se 0.1%, Sb 0.04%, and As 2.5%) as well as to the large background signals at m/z 82 due to $^{40}Ar_2{}^1H_2$ in the case of ^{82}Se. The blank values for analyte elements caused in chelating resin preconcentration were negligibly small, compared to the analytical detection limits except for Al, Ni, Sn, and Pb. The large blank values for Al, Ni, Sn, and Pb might be caused by contamination from the laboratory environment.

The analytical detection limits (DL_{La}) are shown in Table 2. As is seen in Table 2, DL_{La} was in the range from 3 μg L^{-1} for Ti to 0.002 μg L^{-1} for W and Bi. In general, DL_{La} was inferior to DL_{ch}, because the concentration factor of La coprecipitation was smaller by ca. 20-fold than that of chelating resin preconcentration. However, the analytical detection limits of the oxoanion- and hydride-forming elements such as Cr(VI), As(V), Sb(V), and Se(IV) obtained after La coprecipitation were better than their DL_{ch}, because their recoveries were improved up to ca. 60% for Cr(VI) and ca. 100% for As(V), Sb(V) and Se(IV) after the tandem preconcentration procedures.

The blank values caused from the tandem preconcentration procedures were also very low except for Cr(VI), although there was a possibility that the consecutive La coprecipitation method would provide the additional blanks. The large blank value of Cr(VI) was ascribed to contamination introduced during La coprecipitation procedure, as reported previously.[16]

Taking into account the analytical figures of merit in the present tandem preconcentration/ICP-MS method, analyte elements were classified into three groups. The first group consists of the elements which provided more than 80% of R_{ch} values, and they can be determined only by chelating resin preconcentration, followed with the ICP-MS determination. Although the R_{ch} values of Al, Mo and Mn were about 50%, these elements belong to the first group, because their recovery values were not improved after tandem preconcentration, and also because their detection limits (DL_{ch}) obtained by the chelating resin preconcentration/ICP-MS were one order of magnitude better than those obtained by the La coprecipitation/ICP-MS (DL_{La}).

The second group consists of Ti, V, Sn, W, and Bi, whose recoveries were in the range from 30 to 80% after chelating resin preconcentration, but they were improved to be larger than 80% after tandem preconcentration. They were determined either by the chelating resin preconcentration/ICP-MS or by the tandem preconcentration/ICP-MS. In the cases of these elements, the analytical data could thus be obtained by two different preconcentration procedures, which allowed us to complementarily evaluate the accuracies of analytical values.

The third group consists of Cr, As, Se, and Sb. Their R_{ch} values were below 10%, but their recoveries were improved to be above 60% after the tandem preconcentration. Thus, it is preferable to determine these elements by the tandem preconcentration/ICP-MS method.

Determination of Trace Elements in Open Seawater Reference Material (NASS-4). The tandem preconcentration/ICP-MS method explored in the present study was applied to the multielement determination of trace elements in open seawater reference material NASS-4. The analytical results are summarized in Table 3, along with the certified and literature values. As is seen in Table 3, the concentrations of 32 elements were obtained in the concentration range over 5 orders of magnitude from 9.6 μg L^{-1} for Mo to 0.00018 μg L^{-1} for Tm. Since the recovery values of Ti, Sn, and W were smaller than 50% in chelating resin preconcentration, the concentrations of these elements were seemingly less reliable, so that they are shown in parentheses as the reference values. Arsenic, Se, and Sb could be determined by the tandem preconcentration/ICP-MS method, in addition to the data obtained by chelating resin preconcentration. However, the analytical result of Se was still less reliable because of its poor detection limit. As for V and W, their analytical results obtained by both the chelating resin and tandem preconcentration agreed well with each other. These results would assure the validity of the present tandem preconcentration method. Chromium (VI) and Bi could not be determined even by the present tandem method, because their concentrations were below the detection limits. Table 3 shows that the relative standard deviations (RSDs) of the analytical values for analyte elements were smaller than 15% even at their extremely low concentration levels, except for Al and Pb. The poor precision for these two elements might be caused by the high blank values.

It is seen in Table 3 that the analytical values for Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, and U were in good agreement with the certified values issued from NRC, although the Zn concentration obtained here was slightly higher than the certified value. The analytical results for Al, V, and Sb, whose certified values have not been issued, were in the same concentration ranges as the literature values.[21,22] As for other elements such as Ti, Y, Sn, REEs, and W, there are no certified or literature values, and thus the analytical values obtained here are the first data reported for these elements in NASS-4. The analytical results for REEs including Y and La are considered to be quite reliable, because their concentrations are much higher than their analytical detection limits, in addition to their small RSDs below 10%.

Table 3. Analytical Results for the Concentrations of Trace Elements in Open Seawater Reference Material of (NASS-4) and Ise Bay Seawater Obtained by ICP-MS Measurement after the Tandem Preconcentration Method

Element[a)]	Concentration/μg L^{-1}		
	NASS-4		Ise Bay Seawater
	Observed values[b)]	Certified or literature values	Observed values[c)]
Al	0.15 ± 0.09	0.246[d)]	1.4
Ti	(0.16)		(0.12)
Ti†	n.d.		n.d.
V	1.8 ± 0.2	1.26[d)],1.49[e)]	1.5
V†	1.5 ± 0.1		1.5
Cr†	n.d.	0.115 ± 0.01	n.d.
Mn	0.43 ± 0.04	0.38 ± 0.023	5.2
Co	0.0089 ± 0.0014	0.009 ± 0.001	0.042
Ni	0.22 ± 0.01	0.228 ± 0.009	0.67
Cu	0.20 ± 0.01	0.228 ± 0.011	0.40
Zn	0.16 ± 0.02	0.115 ± 0.018	1.23
As†	1.26 ± 0.01	1.26 ± 0.09	1.44
Se†	0.10 ± 0.01	0.018	
Y	0.019 ± 0.001		0.026
Mo	9.6 ± 1.2	8.84 ± 0.6	9.6
Cd	0.019 ± 0.002	0.016 ± 0.003	0.01
Sn	(0.006)		(0.071)
Sn†	n.d.		n.d.
Sb†	0.14 ± 0.01	0.440[e)]	0.21
La	0.010 ± 0.001		0.0067
Ce	0.0041 ± 0.0003		0.0043
Pr	0.0016 ± 0.0001		0.0014
Nd	0.0073 ± 0.0004		0.0052
Sm	0.0032 ± 0.0002		0.0012
Eu	0.00025 ± 0.00003		0.00025
Gd	0.0015 ± 0.0001		0.0022
Tb	0.00023 ± 0.00003		0.00031
Dy	0.0016 ± 0.0001		0.0023
Ho	0.00042 ± 0.00004		0.00057
Er	0.0014 ± 0.00004		0.0019
Tm	0.00018 ± 0.00002		0.0003
Yb	0.0012 ± 0.0001		0.0020
Lu	0.0002 ± 0.00003		0.00037
W	(0.011 ± 0.002)		(0.039)
W†	0.010 ± 0.001		0.037
Pb	0.008 ± 0.003	0.013 ± 0.005	0.029
Bi	n.d.		(0.0017)
Bi†	n.d.		n.d.
U	3.0 ± 0.3	2.68 ± 0.12	3.5

a) The values with † were obtained by ICP-MS measurement after the tandem preconcentration method, and others by ICP-MS measurement after chelating resin preconcentration.

b) The observed values (means) and standard deviations were obtained from 3-times mesurements, where n.d. means "not detected". Data in the parentheses are the results for the elements of which recoveries were less than 50%.

c) The observed values are the means estimated from 2-times measurements. Data in parentheses are the results for the elements, whose recoveries were less than 50%.

d) Literature values cited from Ref. 21.

e) Literature values cited from Ref. 22.

Comparison of Elemental Concentrations in Open and Coastal Seawater Samples. The concentrations of trace elements in open seawater reference material NASS-4 obtained in the present experiment were compared with those in coastal seawater reference material CASS-3, which were reported in the previous papers.[12,16] The open seawater reference material NASS-4 was collected at about 30 km off-shore of Halifax Harbor in Canada, while coastal seawater reference material CASS-3 was collected at seashore. The elemental concentration profiles of NASS-4 and CASS-3 are shown in Fig. 2, in the order of the elements with the concentrations from the higher to the lower for open seawater. From this figure, Ti, Se, and Sn

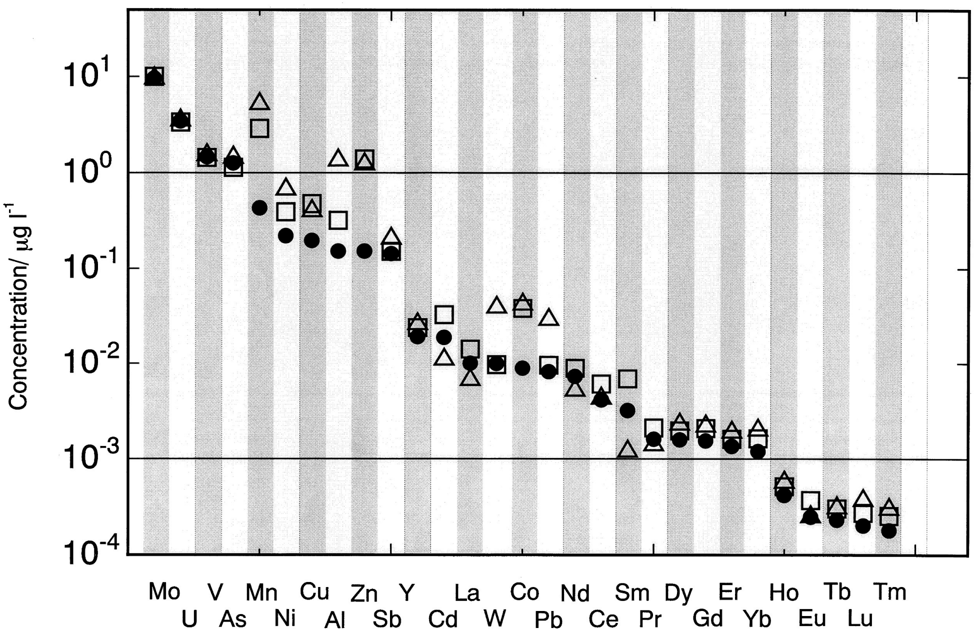

Fig. 2. Concentration distributions of trace elements in seawater reference materials (NASS-4 and CASS-3) and coastal seawater from Ise Bay. ●: NASS-4, △: CASS-3 (cited from Refs. 12 and 16), □: Ise Bay seawater.

were omitted by lack of the analytical results for Se and Sn in CASS-3 and also because of their poor reliabilities in the present experiment. In addition, the concentrations of trace elements in coastal seawater collected in the Ise Bay were also plotted in this figure as the reference data. The seawater sample from the Ise Bay used in the preliminary experiment was also analyzed by the present tandem preconcentration/ICP-MS method. The analytical results are summarized in Table 3. The analytical values for the seawater sample from the Ise Bay almost agreed with those reported in previous papers,[12,16] although they were slightly different from each other because of the different sampling seasons.

Figure 2 shows that the concentrations of Mo, U, V, As, Sb and W in NASS-4 were almost coincident with those in CASS-3 as well as with those in coastal seawater from Ise Bay, except for W. Since these elements exist as the stable oxoanions in seawater, their concentrations are uniform as the stationary elements in seawater all over the sea areas in the world.[1,6,23] In another words, the consistencies of the concentrations of these stationary elements in three different seawater samples may guarantee the accuracy and reliability of the data obtained by the tandem preconcentration/ICP-MS method for the determination of trace elements in seawater. On the other hand, the difference between the concentration values for W in the coastal seawater samples between the Halifax Harbor and Ise Bay may be caused by the different human activities in the local areas, because the concentration for W in seawater is low enough to reflect the anthropogenic pollution in the coastal sea areas.[6]

The concentrations of other elements in open seawater were generally lower than those in coastal seawater. In particular, the concentrations of Mn, Ni, Cu, Al, Zn, Cd, and Co were significantly higher in coastal seawater than in open seawater, except for Cd in the coastal seawater from the Ise Bay. The results for Mn and Al may indicate that these elements in the dissolved forms supplied from the terrestrial land would be rapidly adsorbed onto particulates and/or colloids in coastal seawater. Such characteristic behaviors of Al and Mn were also observed in the Tokyo Bay[24] and Seto Inland Sea.[25] Thus, it can be stated here that Al and Mn are easily taken into some colloids, which results in their short residence times in seawater, compared to those for other elements.[2] On the other hand, the high concentrations of Ni, Cu, Zn, Cd, and Co in coastal seawater may be caused by anthropogenic emission, because they are widely used in modern industries as alloys, catalysts, electrical materials and so on, although they are in relatively low abundances in the earth's crust. The concentrations of rare earth elements (REEs) were slightly higher in coastal seawater than in open seawater.[1,26] These results may suggest that REEs are constantly supplied into seawater from the terrestrial sources.

Conclusion

The tandem preconcentration/ICP-MS method with cooperative use of chelating resin adsorption and La coprecipitation has been explored for the determination of trace and ultratrace elements in open seawater. As a result, 32 elements could be determined in the concentration range over 5 orders of magnitude from 9.6 µg L^{-1} for Mo to 0.00018 µg L^{-1} for Tm, when the present tandem preconcentration/ ICP-MS method was applied to the analyses of open seawater reference material (NASS-4) as well as to those of coastal seawater. The analytical results for Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Cd, U and V were in fairly good agreement with the certified or literature values. These results indicate that the present method is reliable enough to apply to the multielement determination of trace elements in seawater. Since the present method requires only 250 mL for the simultaneous determination of more than

30 elements, it is very useful for multielement profiling analysis of open and deep seawater,[7] which helps to elucidate the characteristic and kinetic behaviors of trace elements in marine environments in relation to biological activities, terrestrial material supply, anthropogenic pollution and so on.

References

1 Y. Nozaki, *EOS Trans. AGU*, **78**, 221 (1997).

2 K.W. Bruland, K. J. Orians, and J. P. Cowen, *Geochim. Cosmochim. Acta*, **58**, 3171 (1994).

3 K. W. Bruland, *Earth. Planet. Sci. Lett.*, **47**, 176 (1980).

4 M. O. Andreae and P. N. Froelich, *Tellus*, **36**, 121 (1984).

5 D. R. Turner, M. W. Whitfield, and A. G. Dickson, *Geochim. Cosmochim. Acta*, **45**, 855 (1981).

6 T. Yabutani, F. Mouri, and H. Haraguchi, *Anal. Sci.*, **16**, 675 (2000).

7 H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 1163 (1999).

8 H. Haraguchi, A. Itoh, S. Ji, and T. Yabutani, *Environ. Sci.*, **13**, 313 (2000).

9 H. Haraguchi, *Chemistry Todays (Gendai Kagaku)*, **2000**, (No. 6), 16.

10 C. J. Cheng, T. Akagi, and H. Haraguchi, *Anal. Chim. Acta*, **198**, 173 (1987).

11 H. Sawatari, T. Toda, T. Saizuka, C. Kimata, A. Itoh, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **68**, 3065 (1995).

12 T. Yabutani, S. Ji , F. Mouri, H. Sawatari, A. Itoh, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 2253 (1999).

13 T. Akagi and H. Haraguchi, *Anal. Chem.*, **62**, 81 (1990).

14 H. Sawatari, E. Fujimori, and H. Haraguchi, *Anal. Sci.*, **11**, 369 (1995).

15 H. Sawatari, T. Hayashi, E. Fujimori, A. Hirose, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **69**, 1925 (1996).

16 T. Yabutani, S. Ji, F. Mouri, A. Itoh, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **73**, 895 (2000).

17 M. O. Andreae, *Deep-Sea Res.*, **25**, 391 (1975).

18 J. J. Middelbarg, D. Hoede, H. A. Van Den Sloot, C. H. Van Den Weijden, and J. Wijkstra, *Geochim. Cosmochim. Acta*, **52**, 2871 (1988).

19 G. Charlot, authorized translation by R. C. Mullay, "Qualitative Inorganic Analysis," Methuen and John Wiley Sons, London and New York (1954), pp. 153–186, pp. 221–241.

20 S. Takagi, "Qualitative Analytical Chemistry (Teisei Bunseki Kagaku)" Nankodo, (1964), pp. 482.

21 I. Roduskin and T. Ruth, *J. Anal. At. Spectrom.*, **12**, 1181 (1997).

22 G. Chapple and J. P. Byrne, *J. Anal. At. Spectrom.*, **11**, 549 (1997).

23 Y. Sohrin, M. Matsui, and E. Nakayama, *Geochim. Cosmocim. Acta*, **63**, 3457 (1999).

24 T. Akagi and H. Haraguchi, *Geochem. J.*, **28**, 81 (1994).

25 T. Akagi and H. Haraguchi, *Chikyuukagaku (Geochemistry)*, **18**, 81 (1984).

26 J. Zhang and Y. Nozaki, *Geochim. Cosmochim. Acta*, **62**, 1307 (1998).