

Multi-Element Determination of Trace Elements in Seawater by Gallium Coprecipitation and Inductively Coupled Plasma Mass Spectrometry

Hideyuki SAWATARI, Eiji FUJIMORI and Hiroki HARAGUCHI†

Department of Applied Chemistry, School of Engineering, Nagoya University,
Nagoya 464-01, Japan

Multi-element determination of trace elements in seawater by inductively coupled plasma mass spectrometry (ICP-MS) has been investigated. Coprecipitation with gallium hydroxide was used for preconcentration of trace elements and elimination of matrix elements. Most trace elements were quantitatively collected at pH 10 with the concentration factor of 10. In the present experimental method, 17 elements (Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Y, Zr, Sn, La, Pb, Th, U) in a coastal seawater sample could be determined by ICP-MS. In addition, 6 elements (Al, Mn, Fe, Ni, Cu, Zn) among them were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The analytical results obtained by ICP-MS and ICP-AES were in fair agreement.

Keywords Seawater, trace elements, gallium coprecipitation, ICP-MS, ICP-AES, internal standardization

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most sensitive analytical methods for the determination of trace metals. The detection limits for most elements in ICP-MS are generally lower by 2 or 3 orders of magnitude than those in inductively coupled plasma atomic emission spectrometry (ICP-AES). The influences of concomitant matrix elements, however, are serious problems in ICP-MS. In seawater analysis, direct introduction of seawater is impossible in ICP-MS, because approximately 3% of salts is contained in seawater. Thus pretreatment procedures are inevitably required to eliminate the salts by various methods such as solvent extraction¹, adsorption on resin after chelating^{2,3}, silica-immobilized 8-hydroxyquinoline⁴, ion exchange⁵, electrochemical deposition⁶, and coprecipitation.⁷ These pretreatment techniques have some characteristic advantages as preconcentration of trace metals in seawater. In general, the techniques other than coprecipitation have been applied to a limited number of trace metals. For example, the electrochemical deposition method suffers from large analytical blanks.⁶ Since ICP-MS makes multi-element analysis feasible, it is desirable to establish a preconcentration method applicable to as wide a variety of trace metals as possible. In the present study, thus, gallium coprecipitation method was investigated from the viewpoint of conventional multi-element determination of trace metals in seawater.

The coprecipitation method has an advantage that many elements other than alkali and alkaline earth

elements are preconcentrated quite effectively under the same experimental conditions, such an advantage allows simultaneous multi-element determination by ICP analysis. Akagi *et al.*^{8,9} developed a coprecipitation method with gallium hydroxide for the determination of trace elements in seawater by ICP-AES, where a concentration factor up to 200-fold was achieved. This method is considered to be suitable also for seawater analysis by ICP-MS because of the following reasons: i) amount of coprecipitation reagent required is smaller than for other coprecipitation methods, and ii) high purity gallium is readily available to avoid contamination. Although the seawater analysis by coprecipitation and ICP-MS was reported previously⁷, the experimental conditions and results were not well described, and only 9 elements were determined by ICP-MS.

In the present study, the gallium coprecipitation method has been examined for the determination of trace elements in seawater by ICP-MS. The coprecipitation characteristics, the limitations and analytical features of the present method are discussed along with the analytical results.

Experimental

Apparatus

The ICP-MS instrument used was Model SPQ-6500 (Seiko Instrument Inc., Tokyo). An ICP-AES instrument of Plasma AtomComp MKII (Jarrell-Ash, Franklin, MA, USA) was also used for the determination

† To whom correspondence should be addressed.

Table 1 Instruments and operating conditions for ICP-MS and ICP-AES

ICP-MS	Seiko SPQ-6500
Plasma conditions	
incident power	1.2 kW
outer gas	15 l min ⁻¹
intermediate gas	1.1 l min ⁻¹
carrier gas	0.45 l min ⁻¹
Nebulizer	glass concentric type (Meinhard TR-30-A2)
sample uptake rate	0.6 ml min ⁻¹
Sampling conditions	
sampling cone	copper 1.1 mm ϕ
skimmer cone	copper 0.35 mm ϕ
sampling depth	15 mm from work coil
Data acquisition	peak jumping
data points per peak ^a	3 points/peak
dwell time	10 ms/point
No. of scans	100
ICP-AES	Jarrell-Ash Plasma AtomComp MKII
Plasma conditions	
incident power	1.2 kW
outer gas	17 l min ⁻¹
intermediate gas	1.0 l min ⁻¹
carrier gas	0.5 l min ⁻¹
observation height	18 mm above work coil
Nebulizer	cross-flow type
sample uptake rate	1.2 ml min ⁻¹
Polychromator	Paschen-Runge (75 cm focal length)
grating	2400 grooves/mm
entrance slit width	25 μ m
exit slit width	50 μ m

a. One point at the assumed peak center and two points at ± 0.125 u from the center.

of matrix elements and some of the trace elements. The instrumental components and typical operating conditions for ICP-MS and ICP-AES are listed in Table 1. These operating conditions were selected after the optimization of each parameter.

Chemicals

Analytical multi-element standard solutions were prepared from commercially-available standard solutions (1000 μ g ml⁻¹) for atomic absorption analysis (Wako Pure Chemical Industries Ltd., Osaka). The standard solution of chromium(III) was prepared by dissolving chromium metal (99.99%; Nacalai Tesque, Kyoto) in hydrochloric acid. Gallium solution as the carrier in coprecipitation was prepared by dissolving gallium metal (99.9999%; Nacalai Tesque) in nitric acid. Nitric acid and hydrochloric acid used were of extra pure grade, purchased from Wako Pure Chemical Industries Ltd., and sodium hydroxide solution was of Ultrapur grade from Kanto Chemical Co. (Tokyo).

Seawater sample

The seawater sample was collected at the Nagoya port; it was acidified to pH 1.2 with nitric acid after filtration with a 0.45 μ m membrane filter. The concentrations of major elements were determined by ICP-AES after diluting seawater by 100-times with 1%(w w⁻¹) nitric acid. The analytical results were as follows: Na 7100 μ g ml⁻¹, Mg 835 μ g ml⁻¹, K 269 μ g ml⁻¹ and Ca 265 μ g ml⁻¹. These values were lower than the typical values for open seawater.¹⁰

Preconcentration procedure

Preconcentration of trace elements in seawater was performed by the following procedure. First, 10 ml of 100 μ g ml⁻¹ gallium solution was added to 200 ml of acidified seawater sample. The pH of the solution was adjusted to the appropriate pH with 1 M and 0.1 M sodium hydroxide solutions. The precipitate was filtered with a 0.45 μ m Omnipore membrane filter (Nippon Millipore Ltd., Tokyo). After washing with about 10 ml of water, the precipitate on the filter was dissolved with 1.5 ml of concentrated nitric acid. A mixed solution of Ge, In and Bi was then added as the internal standard and this mixture was finally diluted to 20 ml with water, which resulted in the concentration factor of 10. The concentration of each internal standard element in the analysis solution was 50 ng ml⁻¹.

Correction of sensitivity drift by internal standard method

In the ICP-MS measurements, the internal standardization was required in order to correct the sensitivity drift of the instrument, which is caused mainly by unstableness of the resolution of the quadrupole mass spectrometer. Since the magnitude of such drift is generally correlated with the masses of the analytes, three internal standards, Ge-74, In-115 and Bi-209, were employed for correction of the drift in the present experiment. The correction was made as follows, based on a procedure similar to that of Doherty.¹¹

The raw count rate, C_{raw} , measured for the calibration standard was corrected to obtain the corrected count rate, C_{cor} , by using a sensitivity correction factor, F :

$$C_{\text{cor}} = C_{\text{raw}} \times F. \quad (1)$$

The correction factors, F_1 , F_2 , F_3 and F_4 , were obtained by Eqs. (2), (5), (6) and (7), depending on the mass number of the analyte. When the mass number of the analyte, M , was smaller than 74,

$$F_1 = S(\text{Ge, sample})/S(\text{Ge, std}) \quad (2)$$

where

$$S(\text{Ge, sample}) = \frac{\text{raw count rate at } m/z = 74 \text{ for sample}}{\text{concentration of Ge in sample}} \quad (3)$$

and

$$S(\text{Ge, std}) = \frac{\text{raw count rate at } m/z = 74 \text{ for standard}}{\text{concentration of Ge in standard}} \quad (4)$$

When $74 < M < 115$,

$$F_2 = \frac{\frac{S(\text{Ge, sample})}{S(\text{Ge, std})}(115 - M) + \frac{S(\text{In, sample})}{S(\text{In, std})}(M - 74)}{115 - 74} \quad (5)$$

When $115 < M < 209$,

$$F_3 = \frac{\frac{S(\text{In, sample})}{S(\text{In, std})}(209 - M) + \frac{S(\text{Bi, sample})}{S(\text{Bi, std})}(M - 115)}{209 - 115} \quad (6)$$

When $M > 209$,

$$F_4 = S(\text{Bi, sample}) / S(\text{Bi, std}) \quad (7)$$

In the above equations, $S(\text{In, sample})$, $S(\text{In, std})$, $S(\text{Bi, sample})$ and $S(\text{Bi, std})$ are defined as in Eqs. (3) and (4). The calibration curves were made by using the C_{cor} values.

Results and Discussion

Spectral interferences from gallium in ICP-MS

Since gallium is used as the carrier element in the present coprecipitation method, gallium in the analysis solution may cause spectral interference with other trace elements. Thus, the ICP-MS spectrum of gallium was first examined by nebulizing Ga $100 \mu\text{g ml}^{-1}$ solution into the plasma, as is shown in Fig. 1. The peak assignment of polyatomic ions and the possible interfered elements are summarized in Table 2. Among these interfered elements, Ag, Cd and Nd can be determined with other isotopes (Ag-107, Cd-114, Nd-143), and Rb, Sr and Ba are not of interest in the present coprecipitation method. However, since Rh is a monoisotopic element, and Ce isotopes of Ce-136 and Ce-138 are in much lower abundance than Ce-140 and Ce-142 and further overlap with Ba isotopes, the determination of Rh and Ce at the ultratrace level by the present method is generally difficult. Even so, the present method is applicable to the determination of many other trace elements in seawater by ICP-MS.

pH dependence of gallium precipitation in seawater

The recovery of gallium added into the seawater at various pH values was examined by ICP-AES ($\lambda = 294.3 \text{ nm}$). As reported elsewhere⁸, gallium precipitates at lower pH (4–6) and at higher pH (>8), while it does not precipitate at pH values between 6–8. Akagi *et al.*⁸ reported that 100% recovery of Ga was obtained at pH 9. In the present experiment, however, gallium was

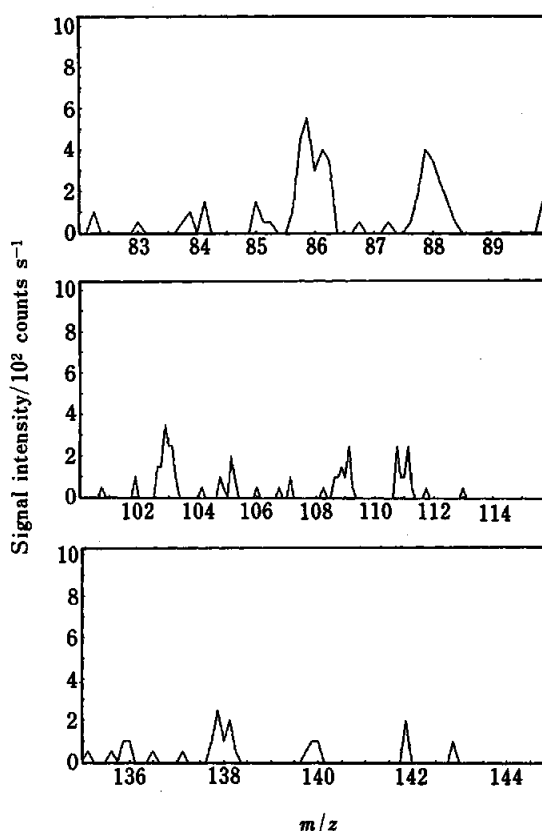


Fig. 1 ICP-MS spectrum observed by nebulizing Ga $100 \mu\text{g ml}^{-1}$ solution.

Table 2 Polyatomic ions observed in the ICP-MS spectrum of gallium and possible interfered elements^a

m/z	Polyatomic ion	Interfered element
85	GaO^+	Rb
86	GaOH^+	Sr
87	GaO^+	Rb, Sr
88	GaOH^+	Sr
103	$\text{Ga}(\text{OH})_2^+$	Rh
105	$\text{Ga}(\text{OH})_2^+$	Pd
109	GaAr^+	Ag
111	GaAr^+	Cd
138	Ga_2^+	Ba, Ce
140	Ga_2^+	Ce
142	Ga_2^+	Ce, Nd

a. In the measurement of the ICP-MS spectrum, the $100 \mu\text{g ml}^{-1}$ Ga solution was nebulized into the plasma.

recovered quantitatively at pH values higher than 9.6. The slightly different result obtained may be due to a difference of the Mg concentration in the seawater samples used. As pointed out by Akagi *et al.*¹², the recovery of Ga depends on the concentration of Mg in the sample. In fact, the concentrations of major elements in the coastal seawater samples used in the present study were lower than those used by Akagi *et al.*⁷

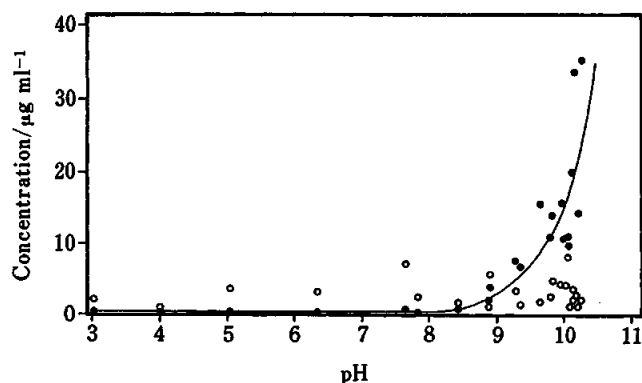


Fig. 2 pH dependences of the concentrations of Mg (●) and Na (○) in the analysis solution after coprecipitation (Concentration factor was 1).

Elimination of matrix elements

In the ICP-MS measurements, it is well known that the major elements in the sample solution often cause matrix effects which reduce the analytical sensitivity. Thus, in general, it is desirable to eliminate the major elements from the sample solution to minimize such matrix effects. Figure 2 shows the pH dependence of the concentrations of Na and Mg in the treated seawater sample solutions after gallium coprecipitation pretreatment. These concentrations for Na and Mg are the values obtained at the concentration factor of 1, which means no preconcentration. As can be seen in Fig. 2, the sodium concentration was less than $10 \mu\text{g ml}^{-1}$, while the magnesium concentration markedly increased at higher pH. At pH 10, the concentrations of major elements in the treated seawater solution were Mg $15 \mu\text{g ml}^{-1}$, Ca $0.2 \mu\text{g ml}^{-1}$, Na $5 \mu\text{g ml}^{-1}$ and K $< 1 \mu\text{g ml}^{-1}$; these values were determined by ICP-AES. We note that the concentrations of these elements in the analysis solution of seawater were low enough to neglect their matrix effects in the ICP-MS measurement. Under these conditions, the chlorine concentration was also very low, which allowed us to determine arsenic at the sub-ppb level without interference due to ArCl^+ .

Concentration factor in gallium coprecipitation

When the concentration factor was 1, the sample solution precipitated at pH 10 usually contained Ga $5 \mu\text{g ml}^{-1}$ along with Mg $15 \mu\text{g ml}^{-1}$, Na $5 \mu\text{g ml}^{-1}$ and Ca $0.2 \mu\text{g ml}^{-1}$, as described above. In practical analyses of seawater, a larger concentration factor is desirable to determine as many trace elements as possible. In general, however, the concentrations of matrix elements also become higher in proportion to the concentration factor, and thus matrix effects due to matrix elements including gallium may become more serious in the ICP-MS measurement.

In order to estimate matrix effects, the sensitivity dependence of each analyte element on matrix elements was examined. In this experiment, the test solution

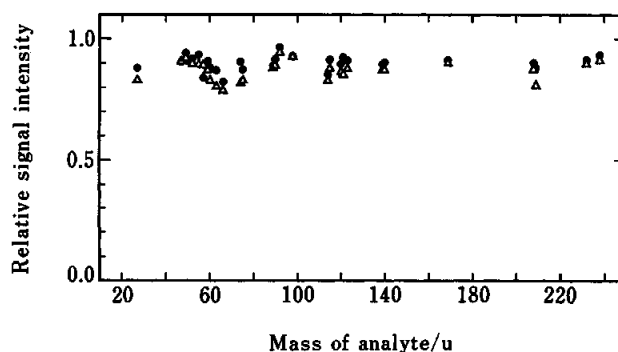


Fig. 3 Sensitivity dependences of the analyte elements in the presence of matrix elements. Concentrations of matrix elements in the test solution; Mg $200 \mu\text{g ml}^{-1}$, Na $50 \mu\text{g ml}^{-1}$, Ca $10 \mu\text{g ml}^{-1}$, K $5 \mu\text{g ml}^{-1}$, Ga $50 \mu\text{g ml}^{-1}$. The relative signal intensities without matrix elements were normalized to be 1.0. The experiment was carried out at the carrier argon gas flow rate of 0.45 l min^{-1} (●) and 0.47 l min^{-1} (△).

contained 50 ng ml^{-1} of each analyte element together with Mg $200 \mu\text{g ml}^{-1}$, Na $20 \mu\text{g ml}^{-1}$, Ca $5 \mu\text{g ml}^{-1}$, K $5 \mu\text{g ml}^{-1}$ and Ga $50 \mu\text{g ml}^{-1}$ as the matrix elements. These concentrations of matrix elements were chosen, presuming that the concentration factor in gallium coprecipitation was 10-times. The relative sensitivities of analyte elements in the cases with and without major elements were observed in the m/z range from 27 to 238. The results are shown in Fig. 3. In Fig. 3, ● and △ indicate the results at the carrier gas flow rate of 0.45 ml min^{-1} and 0.47 ml min^{-1} , respectively, which were observed on different days. As is seen in Fig. 3, the relative sensitivities were varied within ca. 20% in the whole mass range examined. From a practical point of view, these extents of matrix effects could be corrected by the internal standard method described in the experimental section. Consequently, 10-times of preconcentration was performed in the present gallium coprecipitation. Preconcentration of 200-times, which was obtained in seawater analysis by ICP-AES⁷, could not be practically carried out in the present ICP-MS measurement because of severe matrix effects.

Analytical figures of merit

Since the pH dependence of gallium precipitation in the present study was slightly different from the result reported by Akagi *et al.*⁷, the recoveries of trace elements in gallium coprecipitation were also investigated at various pH values in the present study. In the recovery test, all trace elements were spiked in 20 ml of the seawater sample to be 25 ng ml^{-1} . After adding 1 ml of $100 \mu\text{g ml}^{-1}$ gallium solution, we adjusted the pH to appropriate values with sodium hydroxide solution. After filtration, the precipitate on the filter was dissolved with nitric acid, in which internal standard elements (Ge, In, Bi) were added. Finally, the solution was diluted to 20 ml; thus the concentration factor was 1 in this case. The concentrations of trace elements in the test solution

were determined by ICP-MS.

The recoveries of trace elements at various pH values are shown in Fig. 4. In general, it was found that the better recovery values were obtained at the higher pH values. Thus, the pH was adjusted to 10 in the coprecipitation procedure. The recovery values obtained at pH 10 are summarized in Table 3. As is seen in Table 3, many elements were recovered almost quantitatively at pH 10, although the recoveries of Cd, Cu and U were somewhat lower than 90%. The recoveries of Mo, V and Sb, however, were very poor. Therefore, these elements in the seawater sample could not be determined by the present method.

We note here that the value for Sn in Table 3 was obtained in the case where the precipitate after gallium coprecipitation was dissolved with hydrochloric acid to avoid hydrolysis. When nitric acid was used for the dissolution of the precipitate in the determination of Sn, the recovery value of Sn fluctuated in the range from 60% to 80%. Hydrochloric acid usually produces many polyatomic ions in the argon plasma which interfere with many analyte ion peaks. Hence, nitric acid is generally recommended for use in multi-element determination by ICP-MS. Even so, when the determination of Sn in seawater is required, the seawater samples should be treated separately by using hydrochloric acid.

In Table 3, the detection limits and analytical detection limits for 23 elements are also summarized. The detection limits were the concentrations corresponding to 3σ (σ is the standard deviation of the blank signal at m/z of the analyte), which were obtained by nebulizing the multi-element standard aqueous solution of the analytes. Actually, the detection limits should be obtained by using saline standard solution and coprecipitation technique. However, model seawater containing the analyte elements at the trace level cannot be prepared because of the impurities in the reagents used. In the present work, therefore, the analytical detection limits were calculated by using the recovery values after 10-times preconcentration in the present coprecipitation method. The results in Table 3 show that the analytical detection limits for most elements are at a few ng ml^{-1} (ppt) level and those for rare earth elements at the sub-ppt level.

Determination of trace elements in seawater

Trace elements in the coastal seawater sample collected in the Nagoya port were determined by ICP-MS and ICP-AES after preconcentration by the gallium coprecipitation method established in the present experiment. The results are summarized in Table 4, together with the values cited from the previous papers.^{8,10} In the case of 10-times preconcentration, 17 elements could be determined by ICP-MS and 6 elements among them were determined by ICP-AES. As can be seen in Table 4, the analytical values obtained by both ICP-MS and ICP-AES were in good agreement. In the previous paper⁸, as is also shown in Table 4, only 12 elements could be determined by ICP-AES, even when 200 times preconcentration was achieved with gallium coprecipitation.

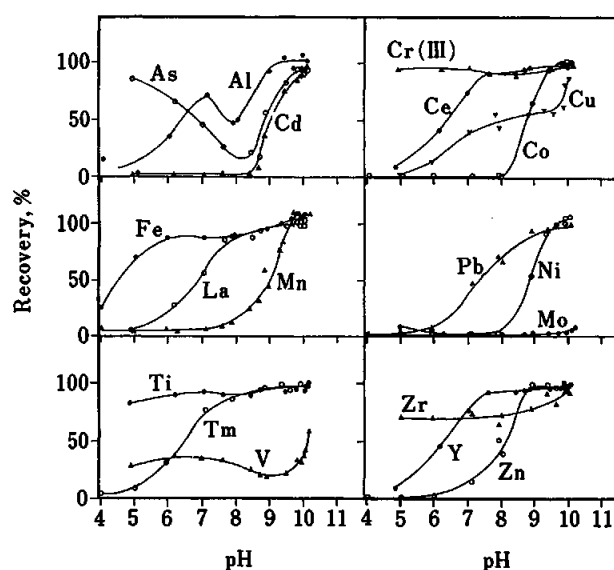


Fig. 4 pH dependences of the recoveries for various analyte elements in gallium coprecipitation.

Table 3 Recoveries and detection limits of trace elements obtained by ICP-MS with gallium coprecipitation at pH 10

Isotope (m/z)	Recovery, %	Detection limit ^b / ng ml^{-1}	Analytical detection limit ^c / ng ml^{-1}
Al	27	101	0.12
Ti	49	96	0.057
V	51	32	0.009
Cr	52	98	0.020
Mn	55	104	0.010
Fe	57	104	0.74
Co	59	101	0.013
Ni	60	103	0.009
Cu	65	83	0.021
Zn	66	100	0.061
As	75	95	0.014
Y	89	99	0.001
Zr	91	94	0.012
Mo	98	1	0.003
Cd	114	87	0.019
Sn	120	97 ^a	0.056
Sb	121	1	0.006
La	139	97	0.001
Ce	140	100	0.002
Tm	169	100	0.001
Pb	208	96	0.020
Th	232	99	0.006
U	238	82	0.008

a. The recovery value was obtained by dissolving the coprecipitate with HCl. See text.

b. Detection limit obtained for the standard solutions without preconcentration.

c. Detection limit calculated by using the recovery value after 10-times preconcentration in the coprecipitation method.

Table 4 Analytical results for trace elements in coastal seawater obtained by ICP-MS and ICP-AES

Element	ICP-MS		ICP-AES		Reference value	
	Isotope (<i>m/z</i>)	Concentration/ ng ml ⁻¹	Wavelength ^a / nm	Concentration/ ng ml ⁻¹	Tokyo Bay ^b / ng ml ⁻¹	Open sea ^c / ng g ⁻¹
Al	27	5.6	308.2 I	9.5	6.5	1
Ti	49	0.082			0.20	<0.001
Cr	52	0.25			0.07	0.350
Mn	55	54	257.6 II	54	36.1	0.010
Fe	57	4.0	259.9 II	4.3	14.4	0.040
Co	59	0.33			0.14	0.002
Ni	60	11	231.6 II	10	1.5	0.48
Cu	65	1.0	324.7 I	1.2	0.31	0.12
Zn	66	5.7	213.8 I	5.7	2.0	0.39
As	75	0.71				2
Y	89	0.013			0.005	0.013
Zr	91	0.49				<1
Sn	120	8.0				0.0005
La	139	0.0056			0.05	0.004
Pb	208	0.088			1.7	0.001
Th	232	0.0085				<0.0007
U	238	2.1				3.2

a. I and II indicate atomic and ionic emission lines, respectively. b. Taken from Ref. 8: the concentrations of trace elements in seawater from Tokyo Bay, which was acidified just after sampling. c. Taken from Ref. 10: mean concentration in seawater taken from open sea.

In the present work, although the preconcentration factor was limited to 10-times because of matrix effect, 17 elements including U and Th were determined by ICP-MS. This indicates that the present preconcentration method is quite useful in marine chemistry.

In summary, inductively coupled plasma mass spectrometry with aid of gallium coprecipitation for preconcentration was successfully applied to the determination of trace elements in coastal seawater. In the present method, the concentration factor was limited to 10-times because of matrix effects, although the larger concentration factor was desirable to determine more trace elements at the lower concentration level in seawater. However, since the present gallium coprecipitation/ICP-MS method enables us to determine more trace elements compared to the similar method using ICP-AES, it is useful for the study of the behavior of trace elements in marine environment.

The present research was supported by the Grants-in-Aid for Scientific Research (04202115) and for Creative Fundamental Research (02NP0204) from the Ministry of Education, Science and Culture, Japan.

References

1. M. B. Shabani, T. Akagi, H. Shimizu and A. Masuda, *Anal. Chem.*, **62**, 2709 (1990).
2. M. R. Plants, J. S. Fritz, F. G. Smith and R. S. Houk, *Anal. Chem.*, **61**, 149 (1989).
3. M. B. Shabani, T. Akagi and A. Masuda, *Anal. Chem.*, **64**, 737 (1992).
4. D. Beauchemin and S. S. Berman, *Anal. Chem.*, **61**, 1857 (1989).
5. K. K. Falkner and J. M. Edmond, *Anal. Chem.*, **62**, 1477 (1990).
6. N. S. Chong, M. L. Norton and J. L. Anderson, *Anal. Chem.*, **62**, 1043 (1990).
7. J. W. McLaren, K. W. M. Siu, J. W. Lam, S. N. Willie, P. S. Maxwell, A. Palepu, M. Koether and S. S. Berman, *Fresenius' J. Anal. Chem.*, **337**, 721 (1990).
8. T. Akagi, K. Fuwa and H. Haraguchi, *Anal. Chim. Acta*, **177**, 139 (1985).
9. T. Akagi and H. Haraguchi, *Anal. Chem.*, **62**, 81 (1990).
10. M. S. Quinby-Hunt and K. K. Turekian, *EOS*, **64**, 130 (1983).
11. W. Doherty, *Spectrochim. Acta*, **44B**, 263 (1989).
12. T. Akagi, K. Fuwa and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **62**, 3823 (1989).

(Received January 9, 1995)

(Accepted March 22, 1995)