

## Multielement Determination of Trace Elements in Coastal Seawater by ICP-MS and ICP-AES after Aluminum Coprecipitation Associated with Magnesium

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(Received October 18, 1995)

An analytical method for multielement determination of trace and ultratrace elements in seawater has been investigated by using ICP-MS. Trace and ultratrace elements were preconcentrated by 10- or 20-times with addition of aluminum into seawater and then the elements were determined by ICP-MS. In this procedure, aluminum was added as the carrier for coprecipitation; it precipitated together with magnesium in seawater. Some trace elements were also measured by ICP-AES after coprecipitation. In addition, major and minor elements in seawater were determined by ICP-AES after dilution with acidified water. As the result, 37 elements in total could be determined in coastal seawater. The present results are compared with the concentrations of the elements in open seawater.

In general, the concentrations of most elements in seawater are extremely low, at the ppb ( $\text{ng ml}^{-1}$ ) or ppt ( $\text{pg ml}^{-1}$ ) level, although many elements in seawater have been determined by various analytical methods.<sup>1–12</sup> In the determination of the elements, the sensitive analytical methods such as atomic absorption spectrometry (AAS),<sup>1,3,4</sup> inductively coupled plasma atomic emission spectrometry (ICP-AES),<sup>2,5,9–11</sup> inductively coupled plasma mass spectrometry (ICP-MS),<sup>6,7,12</sup> and neutron activation analysis<sup>8</sup> have been employed. In spite of the use of such sensitive methods, it is often required to perform the preconcentration of trace elements in seawater by some appropriate chemical methods because of their extremely low concentrations. As the preconcentration methods, the solvent extraction,<sup>1,2</sup> chelating resin,<sup>3–7</sup> adsorption,<sup>6</sup> and coprecipitation techniques<sup>7–12</sup> have been used in seawater analysis. Among them, it appears that the coprecipitation method is one of most suitable techniques for simultaneous multielement preconcentration because of less selectivity. Hiraide et al.<sup>9</sup> applied the indium coprecipitation method to the determination of trace elements in seawater by ICP-AES. The present authors have reported the gallium coprecipitation method for the determination of trace elements by ICP-AES<sup>10,11</sup> and ICP-MS.<sup>12</sup> However, aluminum has not been used for such a purpose in trace analysis by ICP-AES and ICP-MS, although it was used for the determination of rare earth elements in spring and lake water by neutron activation analysis.<sup>13</sup> In the present paper, hence, the coprecipitation method using aluminum has been investigated for preconcentration of trace and ultratrace el-

ements in seawater and their determination by ICP-MS. At the same time, ICP-AES was also used for the determination of major and minor elements in seawater. Consequently, 37 elements including all rare earth elements, U and Th have been determined for coastal seawater sample.

### Experimental

**Apparatus:** An ICP-MS instrument of model SPQ 8000 (Seiko Instrument Inc., Tokyo) was used for the determination of trace and ultratrace elements; it consisted of a quadrupole-type mass spectrometer. An ICP-AES instrument of model Plasma Atom Comp MkII (Jarrell-Ash, Franklin, MA, USA) was also used for the simultaneous multielement determination of major and minor elements as well as of some trace elements in seawater. The instrumental components and operating conditions are shown in Table 1. In the ICP-MS measurement, an internal standard method, similar to that in the previous work,<sup>12</sup> was employed to correct matrix effects due to major elements in seawater. In the internal standard method, Ge, In, and Bi were used as the internal standard elements.

**Samples and Chemicals:** The coastal seawater samples used for analysis were collected near Nagoya Port (Aichi Prefecture). The seawater samples were filtered first with a glass fiber filter and then with a membrane filter (pore size  $0.45 \mu\text{m}$ ) from Nippon Millipore Ltd. (Tokyo). The filtered seawater sample was acidified to pH 1–2 by adding  $\text{HNO}_3$  and used for analysis. Thus, only the elements dissolved in seawater were determined in the following experiment.

All the chemicals used were of analytical reagent grade. The multielement standard solutions were prepared by mixing the commercially-available 1000 ppm ( $1 \text{ ppm} = 1 \mu\text{g ml}^{-1}$ ) standard solutions of the examined elements for atomic absorption spectrometry. The standard solutions for Re were prepared by dissolving pure metals (99.99%, from Nacalai Tesque Co., Kyoto) in  $\text{HNO}_3$ . The sodium hydroxide aqueous solution of Ultrapur grade was obtained from Kanto Chemical Co. (Tokyo). The pure water used throughout the present experiment was prepared by a Milli-Q system (Nippon

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

ICP-MS: Seiko SPQ 8000	
Plasma conditions	
Incident power	1.2 kW
Coolant gas flow rate	16 l min <sup>-1</sup>
Auxiliary gas flow rate	1.0 l min <sup>-1</sup>
Carrier gas flow rate	0.50 l min <sup>-1</sup>
Sample uptake rate	0.7 ml min <sup>-1</sup>
Nebulizer	Concentric type
Sampling conditions	
Sampling orifice diameter	1.1 mm
Skimmer orifice diameter	0.35 mm
Sampling position	15 mm from load coil
Data acquisition	
Dwell time	10 ms/channel
Data points	3 points/peak <sup>a)</sup>
No. of scans	100
ICP-AES: Jarrell-Ash Plasma Atom Comp MkII	
Plasma conditions	
Incident power	1.0 kW
Coolant gas flow rate	17 l min <sup>-1</sup>
Auxiliary gas flow rate	1.0 l min <sup>-1</sup>
Carrier gas flow rate	0.5 l min <sup>-1</sup>
Sample uptake rate	1.2 ml min <sup>-1</sup>
Observation height	18 mm above load coil
Nebulizer	Cross-flow type
Polychromator	
Mounting	Paschen-Runge
Focal length	75 cm
Grating	2400 grooves/mm
Entrance slit width	25 $\mu$ m
Exit slit width	50 $\mu$ m

a) Assumed peak center and  $\pm 0.125$  u from the center.

Millipore Ltd.).

**Preconcentration Procedure:** In the preconcentration procedure, 5 ml of 100 ppm Al solution was added to 500 ml of the acidified seawater sample. The pH of the seawater sample was adjusted to pH 9.5 with 1 M and 0.1 M sodium hydroxide aqueous solutions ( $1 \text{ M} = 1 \text{ mol dm}^{-3}$ ) to produce the precipitate. The precipitate was kept standing for 24 h, and then it was filtered with a membrane filter (pore size  $0.45 \mu\text{m}$ ). After washing with a small amount of water, the precipitate on the filter was dissolved with 3.4 ml of concentrated  $\text{HNO}_3$ , and then 5 ml of a mixed solution of Ge, In, and Bi (100 ppb each) was added. The solution was finally diluted to 50 ml (10-fold preconcentration) with water and used for the ICP-MS measurement. In the case of 20-fold preconcentration,  $1 \text{ dm}^3$  seawater and the same amount of Al as the carrier were used in the experiment.

## Results and Discussion

**pH Dependence of Precipitation of Aluminum:** The pH dependence of the recovery of aluminum in precipitation, which was added as the coprecipitation carrier, was examined first because a recovery of the carrier gave large influences to the recoveries of trace elements in seawater. The seawater sample was preconcentrated by 10-fold, according to the

procedure described in the experimental section. The result is shown in Fig. 1. As is seen in the figure, the recovery of Al was about 90% at pH 6 and once decreased close to 60% at pH 9. However, it increased again to be almost 100% above pH 9.5. It should be noted here that aluminum hydroxide formed partly dissolved above pH 6, but aluminum may coprecipitate with Mg in solution above pH 9. As the result, Al may be recovered quantitatively above pH 9.5. In Fig. 1, pH dependences of the concentrations of Na, K, and Mg in the analysis solution in the case of 10-fold preconcentration are also shown, where the analysis solution means the final solution after preconcentration procedure. These results indicate that the precipitation of Mg significantly increases at the pH above 9, although Na and K do not precipitate. This fact supports the conclusion that Al added as the carrier coprecipitates with or is adsorbed on the precipitate of magnesium hydroxide. A similar phenomenon, i.e., coprecipitation of the carrier with magnesium, has been known in gallium coprecipitation in seawater.<sup>12,14)</sup> Then, it is noted that Al in the present coprecipitation produces the precipitate cooperated with Mg above pH 9.5, which is one of the major constituents in seawater. Consequently, the present method should be considered as aluminum coprecipitation associated with magnesium.

**pH Dependences of Recoveries of Trace Elements in Seawater:** In order to obtain the accurate and precise results in the ICP-MS analysis, it is desirable to have better recoveries for the elements of interest in the coprecipitation procedure. Thus, the pH dependences of the recoveries for trace elements in seawater were investigated by adding the analyte elements (10 ppb each) into the real seawater sample. As some of the examples, the recovery curves for Fe, Cu, Zn, Ni, Mn, Sr, and Ba are shown as a function of the pH in Fig. 2. For other elements, pH dependences were quite similar to those in the case of gallium coprecipitation reported in the previous works.<sup>10,12)</sup> The alkaline earth elements (Sr and Ba)

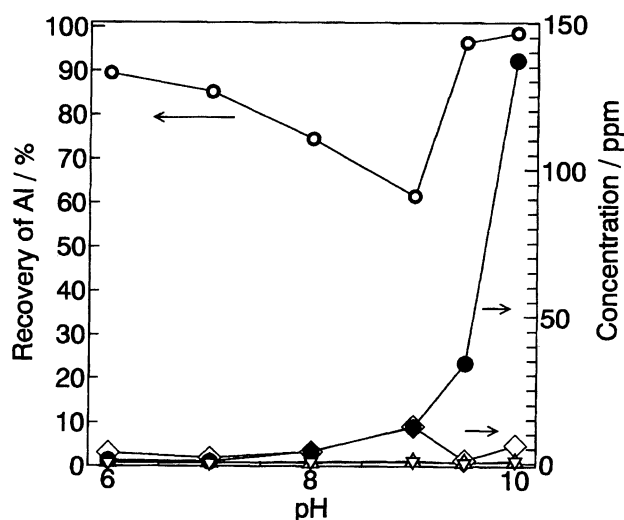


Fig. 1. Recovery of Al and concentration of major elements in the analysis solution after Al coprecipitation (10-fold preconcentration).  $\odot$ : Al,  $\bullet$ : Mg,  $\diamond$ : Na,  $\triangle$ : K,  $\nabla$ : Ca.

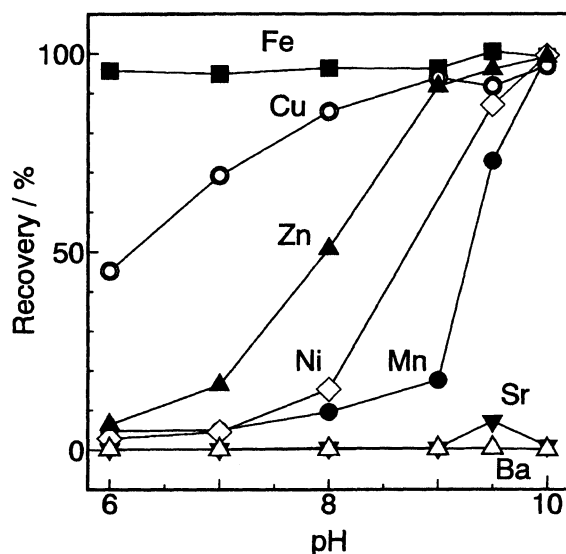


Fig. 2. The recoveries of trace elements in seawater as the pH function. ●: Mn, ■: Fe, ◇: Ni, ○: Cu, ▲: Zn, ▼: Sr, △: Ba

did not precipitate in the pH range examined, but other heavy elements were well recovered up to almost 100% at pH 10. However, as mentioned earlier, the significant amount of Mg precipitates at pH 10, which may cause serious matrix effects to the analyte elements in the ICP-MS measurement. Therefore, pH in the coprecipitation procedure was adjusted at 9.5 to reduce Mg contained in the analysis solution, keeping the recoveries of trace elements as high as possible, and the total coprecipitation procedure described in the experimental section was finally proposed in the present experiment. The recovery values of the analyte elements at pH 9.5 in 10-fold preconcentration are summarized in Table 2.

Furthermore, 20-fold preconcentration for the analyte elements was also examined. In this case, 1 dm<sup>3</sup> of seawater was used as the sample. All other experimental parameters including the amount of Al added into the sample were the same as those for 10-fold preconcentration procedure. In order to avoid the high concentration of Al in the analysis solution, the amount of Al added as the carrier was kept the same as that for the 10-fold preconcentration procedure, even though the sample volume was 2-times more. The recoveries of trace elements obtained by the 20-fold preconcentration are also summarized in Table 2.

The recoveries obtained in the 20-fold preconcentration were in general lower than those obtained in 10-fold preconcentration. The slightly poorer recoveries may be attributed to the lower concentration of Al in the treated solution. The amount of Al added into the sample in the 20-fold preconcentration procedure, however, is considered to be appropriate, because the concentration of Mg in the analysis solution after the 20-fold preconcentration could be at the same level as that of Mg after the 10-fold preconcentration, although the concentration factor was larger by 2-times.

The recoveries of alkali (Rb, Cs) and alkaline earth (Sr, Ba) elements were of course extremely poor. Those of Cr,

Mo, Sb, and W were also poor. These results suggest that these elements exist as the oxo-anion forms in seawater. In addition, fairly poor recoveries were obtained for Cd and Hg. This may be attributed to their dissolved forms in chloro-complexes with a large amount of chloride ions in seawater. The recovery of U was also not so good. The main chemical form of U in seawater may be in the form of  $\text{UO}_2^{2+}$ , which is much less adsorbed on the mixed hydroxide precipitates of Al and Mg.

**Concentration of Major Elements in Preconcentrated Solutions:** Since major elements in seawater cause matrix effects in the ICP-MS measurements, the concentrations of major elements such as Na, Mg, K, and Ca in the analysis solution after coprecipitation in the pH range of 6–10 were determined by ICP-AES. The results are shown in Fig. 1. As mentioned earlier, the concentration of Mg significantly increased at the pH value above 9.5, while the concentrations of Na, K, and Ca were kept negligibly low in the examined pH range. The Mg concentration at pH 10 was more than 100 ppm, which was too high to correct the matrix effect of Mg in the ICP-MS measurement even by internal standard method. At pH 9.5, the concentrations of Na, K, Mg, and Ca in the solution after the Al coprecipitation preconcentration (10-fold) were 1.0, 0.23, 34, and 0.10 ppm, respectively. The matrix effects caused by the major elements at these concentration levels could be corrected by an internal standard method, as will be described later.

**Correction of Matrix Effects by Internal Standard Method:** As mentioned earlier, the concentrations of alkali and alkaline earth elements in seawater could be significantly reduced by the present coprecipitation method, but they still remained in the final solution for analysis. In particular, the concentration of Mg in the analysis solution was sometimes quite high, depending on the coprecipitation conditions. Thus, the matrix effects of Mg on the analyte elements caused by Mg and their correction by the internal standard method were examined to optimize the pH value in the coprecipitation procedure.

In internal standard correction, various concentrations of Mg were added in the blank, test and standard solutions along with the internal standard elements (Ge, In, and Bi). Internal standard correction was made in a manner similar to that in the previous work.<sup>12)</sup> In Figs. 3(A) and 3(B), the uncorrected and corrected results, respectively, are shown for a number of the elements over a wide mass range, where Mg of 10, 50, 100, and 200 ppm was added as the matrix element in the test solution. Figure 3(A) shows that significant degradation of sensitivity was observed for all the analytes examined, depending on the Mg concentration. On the contrary, the matrix effect due to Mg was quite well corrected by internal standard correction, as is seen in Fig. 3(B), although the internal standard correction was not so good when the Mg concentration was larger than 100 ppm. Thus, in the following experiments, pH in the coprecipitation procedure was adjusted to 9.5 so that the Mg concentration in the analysis solution was kept lower than 50 ppm.

In the analysis solution, about 10 ppm of Al was contained.

Table 2. Instrumental and Analytical Detection Limits Obtained by ICP-MS by Al Coprecipitation Preconcentration

Element	Mass of isotope	Instrumental limit detection	10-fold preconcentration		20-fold preconcentration	
			Recovery	Analytical detection limit	Recovery	Analytical detection limit
	u	ppb	%	ppb	%	ppb
Sc	45	0.015	78.7	0.0019	77.3	0.00097
Ti	49	0.095	81.7	0.012	80.3	0.0059
Cr	53	0.025	24.0	0.010	42.4	0.0029
Co	59	0.017	73.7	0.0023	71.3	0.0012
Ni	60	0.029	67.9	0.0043	61.5	0.0024
Ga	71	0.0033	67.9	0.00049	46.4	0.00036
Rb	85	0.0078	1.7	— <sup>a)</sup>	0.8	— <sup>a)</sup>
Sr	88	0.0032	4.3	— <sup>a)</sup>	1.2	— <sup>a)</sup>
Y	89	0.0027	81.7	0.00033	80.3	0.00017
Zr	90	0.242	79.2	0.031	77.3	0.016
Mo	98	0.0027	0.4	— <sup>a)</sup>	0.3	— <sup>a)</sup>
Cd	111	0.0151	37.5	0.0040	26.3	0.0029
Sn	120	0.068	86.7	0.0079	82.6	0.0041
Sb	121	0.016	0.5	— <sup>a)</sup>	0.2	— <sup>a)</sup>
Cs	133	0.0014	0.05	— <sup>a)</sup>	0.03	— <sup>a)</sup>
Ba	138	0.015	0.8	— <sup>a)</sup>	1.3	— <sup>a)</sup>
La	139	0.0060	82.7	0.00073	80.6	0.00037
Ce	140	0.0056	87.4	0.00064	85.8	0.00033
Pr	141	0.0041	86.8	0.00047	84.9	0.00024
Nd	146	0.0050	86.8	0.00058	84.5	0.00030
Sm	152	0.0029	90.4	0.00032	88.8	0.00016
Eu	153	0.0024	89.4	0.00027	86.7	0.00014
Gd	158	0.0043	90.6	0.00047	88.3	0.00024
Tb	159	0.0036	89.6	0.00040	88.5	0.00020
Dy	163	0.0028	87.5	0.00032	86.8	0.00016
Ho	165	0.0027	88.7	0.00030	87.2	0.00015
Er	166	0.0065	89.6	0.00073	88.1	0.00037
Tm	169	0.0022	89.3	0.00025	87.5	0.00013
Yb	174	0.0030	92.7	0.00032	91.1	0.00016
Lu	175	0.0031	92.1	0.00034	89.1	0.00017
W	184	0.10	6.5	— <sup>a)</sup>	5.5	— <sup>a)</sup>
Hg	202	0.37	18.6	0.20	26.7	0.070
Pb	208	0.046	90.0	0.0051	82.8	0.0028
Th	232	0.011	97.0	0.0011	93.5	0.00059
U	238	0.0017	62.4	0.00027	31.3	0.00027

a) The analytical detection limits were not estimated because of poor recoveries less than 10%.

However, since the concentration of Al at this level was lower than that of Mg, the matrix effect due to Al may be corrected by the present internal standard correction method.

**Detection Limits Obtained by ICP-MS:** In Table 2, the instrumental detection limits obtained for pure standard solutions and the analytical detection limits for analysis solution are summarized. The instrumental detection limits were defined as the concentration corresponding to 3-fold of the standard deviation of the background intensity for the blank solution (0.1 M HNO<sub>3</sub>), where the standard deviation was calculated from the 10-times repeated measurements at each mass number in ICP-MS. The analytical detection limits for cases of both 10- and 20-fold preconcentrations were calculated from the instrumental detection limits, taking into account the concentration factors and the recoveries listed in Table 2. As is seen in Table 2, the analytical detection limits at the sub-ppt level were obtained for more than 20 elements in the present experiment.

In Table 2, the detection limits were not obtained for the elements whose recovery values were lower than 10%. The detection limits for Cr, Cd and Hg in Table 2 should be considered as a kind of reference value because their recoveries were lower than 50%.

**Multielement Analysis of Seawater by ICP-MS after Aluminum Magnesium Coprecipitation:** Trace and ultratrace elements in coastal seawater were preconcentrated by 10- and 20-fold, according to the recommended preconcentration procedure of the coprecipitation method described in the experimental section. Their concentrations were determined by ICP-MS. In addition, 10-fold preconcentration at pH 10 was also carried out for simultaneous determination of Mn, Fe, Cu, and Zn by ICP-AES. Since the concentrations of these elements in coastal seawater were relatively high, these elements could be determined by ICP-AES. Further, it was no problem in the ICP-AES measurement to introduce the analysis solution which contained 200 ppm of Mg into

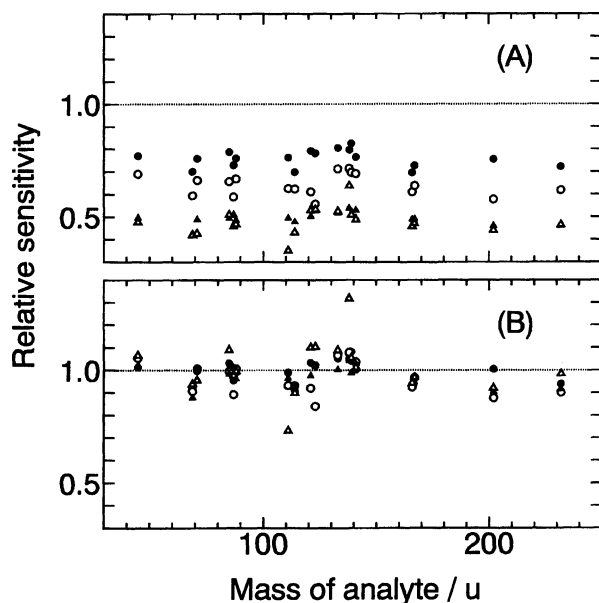


Fig. 3. Internal standard correction of matrix effect due to magnesium. Mg concentration (ppm): 10 (●), 50 (○), 100 (▲), 200 (△). Signal intensities were normalized to those for the test solution without Mg. Internal standard elements: Ga, In, and Bi at 1 ppb each. (A) not corrected, (B) corrected.

the plasma, and thus preconcentration was performed at pH 10 so as to obtain better recoveries for Mn, Fe, Cu, and Zn.

In Table 3, the results for the elements whose recoveries were lower than 50% are shown in parentheses. These values should be considered as reference values, which indicate the dissolved levels of those elements in coastal seawater. The concentration of Ti could not be determined in 10-fold preconcentration. In addition, the analytical results obtained after both 10- and 20-fold preconcentration are shown in Table 3. In the table, the ratios of the concentration obtained are also estimated from the analytical results. As is seen in Table 3, the analytical results for most of the elements obtained in 10- and 20-fold preconcentration are at almost the same concentration level, and thus the concentration ratios given in Table 3 are between 0.25 (Eu, Tb)—2.71 (Hg). Since the concentrations of the elements determined are extremely low at the ppt level, such differences of the analytical values obtained are often unavoidable when a large variety of elements are determined by the multielement separation/preconcentration and measurement methods. Of course, the analytical methods for multielement determination should be improved from the viewpoint of accuracy and precision.

Furthermore, polyatomic interferences are often prone to the errors in the determination of rare earth elements by ICP-MS. For example,  $^{135}\text{Ba}^{16}\text{O}^+$  interferes with  $^{151}\text{Eu}^+$ , and oxides of Ce and Nd do with Gd. In the present experiment, such interferences due to polyatomic ions were not corrected, which may cause the analytical errors by a maximum of 5% in the cases of Eu and Gd.

In the present experiment, 32 elements in coastal seawater

Table 3. Analytical Results for Trace Elements in Coastal Seawater Determined by ICP-MS and ICP-AES after Aluminum Coprecipitation.

Element	Al coprecipitation <sup>a)</sup>			Ga coprecipitation <sup>c)</sup>
	10-fold ppb	20-fold ppb	Concentration ratio <sup>b)</sup>	10-fold ppb
Sc	0.032	0.024	1.3	
Ti	—	0.063	—	0.082
Cr	(0.61)	(0.33)	1.9	0.25
Mn	63.0 <sup>d)</sup>	— <sup>e)</sup>	—	54
Fe	5.0 <sup>d)</sup>	— <sup>e)</sup>	—	4.0
Co	0.29	0.24	1.2	0.33
Ni	3.1	2.3	1.3	11
Cu	1.0 <sup>d)</sup>	— <sup>e)</sup>	—	1.0
Zn	3.0 <sup>d)</sup>	— <sup>e)</sup>	—	5.7
Ga	0.053	(0.073)	0.73	
Y	0.029	0.036	0.81	0.013
Zr	0.041	0.051	0.80	0.49
Cd	(0.024)	(0.026)	0.92	
Sn	0.057	0.047	1.2	8.0
La	0.013	0.026	0.50	0.0056
Ce	0.012	0.019	0.63	
Pr	0.004	0.013	0.31	
Nd	0.010	0.015	0.67	
Sm	0.003	0.007	0.43	
Eu	0.001	0.004	0.25	
Gd	0.003	0.008	0.38	
Tb	0.001	0.004	0.25	
Dy	0.004	0.007	0.57	
Ho	0.002	0.004	0.50	
Er	0.008	0.011	0.73	
Tm	0.002	0.004	0.50	
Yb	0.006	0.009	0.67	
Lu	0.002	0.004	0.50	
Hg	(0.19)	(0.070)	2.7	
Pb	0.11	0.24	0.46	0.088
Th	0.002	0.005	0.40	0.0085
U	1.9	2.1	0.90	2.1

a) Aluminum-added coprecipitation method. Data in parentheses are the results for the elements of which the recoveries were lower than 50%. b) The ratios of the concentrations determined after 10-fold preconcentration to those after 20-fold preconcentration. c) Cited from Ref. 12. d) Determined by ICP-AES after Al-added coprecipitation at pH 10. e) Not determined.

could be determined by ICP-MS and ICP-AES after preconcentration by the coprecipitation method; the results are summarized in Table 3. In addition, major elements and Sr were determined by ICP-AES after 100-fold dilution of the sample seawater with acidified water. The results were as follows; Na 5060 ppm, Mg 643 ppm, K 193 ppm, Ca 205 ppm, and Sr 4.0 ppm. Thus, 37 elements in total could be determined in coastal seawater examined in the present study. In Table 3, the analytical results obtained by Ga coprecipitation and ICP-MS<sup>12)</sup> are also presented for comparison. The sampling site of seawater in the previous work<sup>12)</sup> was also in the Nagoya port, but it was about 10 km apart from the present sampling site. Although the sampling sites were not exactly the same, the results obtained by two different preconcentration methods were almost at the same concentration

level.

In Fig. 4, the concentrations of the elements in coastal seawater determined in the present experiment are plotted together with those in open seawater<sup>15)</sup> in order to compare the elemental concentration levels. The concentrations of the elements determined were in the ranges from several thousand ppm level to a few-ppt level. They are summarized as follows:

ppm ( $\mu\text{g ml}^{-1}$ ) level: Na, Mg, K, Ca, Sr

ppb ( $\text{ng ml}^{-1}$ ) level: Mn, Fe, Ni, Cu, Zn, U

ppt ( $\text{pg ml}^{-1}$ ) level: Sc, Ti, Cr, Co, Ga, Y, Zr, Cd, Zn, REEs, Hg, Pb, Th

In order to figure out the difference between coastal seawater and open seawater, the concentration ratios of the elements in coastal seawater (present study) to those in open

seawater<sup>15)</sup> are plotted as is seen in Fig. 5. The concentrations of major elements (Na, K, Mg, and Ca) as well as Cd and U were much lower in coastal seawater. This indicates that these elements are diluted with river water in coastal areas. On the other hand, the concentrations of many trace elements were much higher in the coastal seawater, compared to those in open seawater. In particular, the concentrations of Mn, Fe, Co, Sn, Hg, Sc, Ga, Pb, and Th in coastal seawater were higher than those in open seawater by more than 10 fold. The concentrations of rare earth elements (REEs) were also higher in coastal seawater than those in open seawater. Terrigenous components, which are transferred by river water, may be main source of Mn, Fe, REEs, and Th in coastal seawater. In the present study, as described in the experimental section, "dissolved components (elements)" were

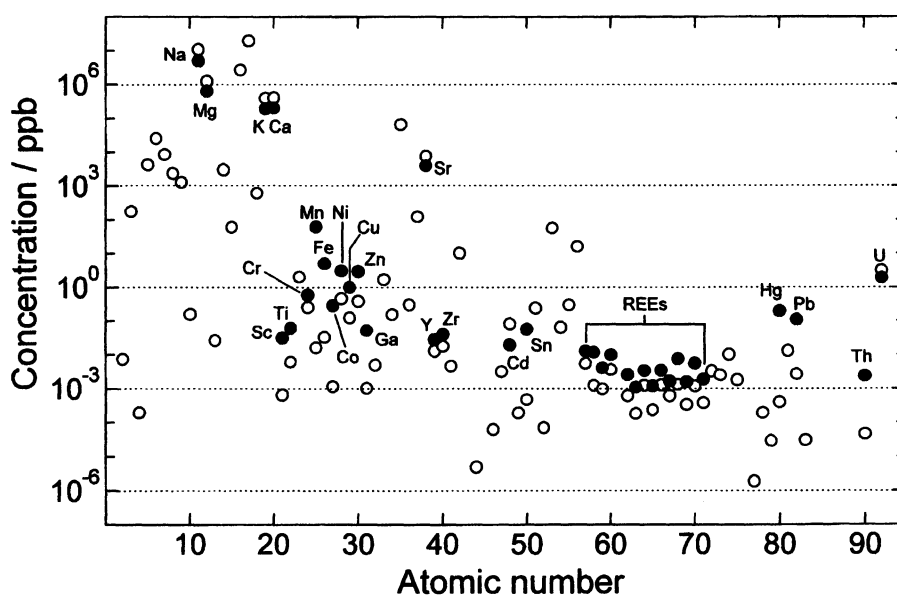


Fig. 4. Comparison of the concentrations of elements in coastal seawater (present study) and open seawater (Ref. 15).  
●: coastalseawater, ○: open seawater.

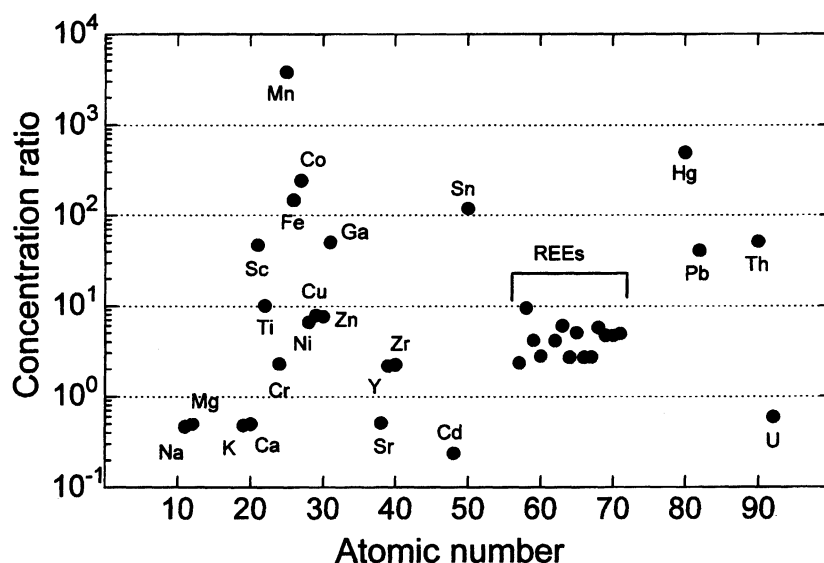


Fig. 5. Concentration ratios of the elements in coastal seawater (present study) to those in open seawater (Ref. 15).

determined after filtration with a membrane filter. Even so, it should be taken into consideration that some parts of these elements determined here possibly existed in suspended particles smaller than the pore size (0.45  $\mu\text{m}$ ) of the filter, which resulted in their high concentrations in coastal seawater. The high concentrations of Co, Ni, Cu, Sn, and Hg in coastal seawater may be caused by human activities, because the concentrations of these elements in common rocks and soils are generally not so high.

### Conclusion

With use of Al-added coprecipitation, 37 kinds of trace elements in coastal seawater could be determined by ICP-MS and ICP-AES. Coprecipitation at pH 9.5 was appropriate for the determination of trace elements by ICP-MS measurement because major elements in seawater was effectively removed. Thus, the Mg concentration in the analysis solution after preconcentration was sufficiently low, and thus matrix effects of Mg to trace elements in the ICP-MS measurement could be corrected by internal standard correction. The concentration of Mn, Fe, Cu, and Zn were determined by ICP-AES after coprecipitation at pH 10. The use of Al as the coprecipitation carrier may have some advantages over other similar methods due to the smaller amount of Al added and its small mass number. These are important in the ICP-MS measurements because the former helps to reduce impurity contamination and matrix effect, and the latter avoid spectral interferences due to polyatomic ions of matrix elements. As a result, many elements at the  $\text{pg ml}^{-1}$  concentration could be determined for coastal seawater. The multielement determination of trace elements in coastal seawater, as shown in the present

experiment, may help us to understand their kinetic behaviors as well as their sources in coastal seawater from the viewpoint of geochemical and environmental science.

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