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Gallium Coprecipitation Associated with Magnesium for Preconcentration of Trace Metals in Seawater

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The coprecipitation of trace metals with gallium has been investigated in detail especially with respects to the role of magnesium ion in saline or seawater. Gallium does not precipitate even at pH 9 when magnesium ion does not exist. The concentration of gallium in the precipitate increased with increasing that of magnesium in solution. The recoveries of trace metals also showed strong dependence on the concentrations of both gallium and magnesium in the aqueous solution.

Since the concentrations of trace metals in seawater are extremely low, preconcentration prior to analysis is necessary to determine these elements by the convenient analytical measurement method. Among a variety of preconcentration techniques for trace metals in seawater, coprecipitation technique has been widely employed.[1–12] Zirconium,[1] Fe,[2,3,6] Bi,[2,3] Co-APDC,[4,7] In,[8] La,[9] and Mg,[5,10,11] have been used as the coprecipitation reagents for preconcentration of analyte metals from seawater and/or brine samples.

The present authors developed a coprecipitation technique using gallium as a coprecipitation reagent[12] for preconcentration of trace metals in seawater in order to determine them simultaneously by inductively coupled plasma atomic emission spectrometry (ICP-AES). In the study, it was found that gallium precipitates between pH 5—6 and above pH 9 in seawater, while it does not precipitate between pH 7—8. Furthermore gallium did not precipitate in the river water even above pH 9. This characteristic features of gallium precipitation is very helpful for the preconcentration of trace metals in seawater because of negligibly small contamination from chemicals required for pH adjustment.

According to the present authors' survey, the reason why gallium does precipitate at pH 9 in seawater has not been investigated yet. In the present study, hence, the precipitate formation of gallium has been examined by using saline water samples with various compositions so as to elucidate the role of gallium coprecipitation in seawater.

Experimental

Apparatus. An ICP-AES spectrophotometer used for metal analysis was Plasma Atomcomp MK II from Jarrell Ash Co. The operating conditions of the ICP-AES instrument are summarized in Table 1. A double-beam spectrophotometer UV-210A (Shimadzu Co., Ltd.) was used to monitor the formation of the precipitates at the wavelength 660 nm, which was the same wavelength as that for convenient turbidity measurement. The length of the sample cell used was 10 cm and the width of the entrance slit was set at 2 mm. A pH meter model Ionalyzer 407A (Orion Research Inc.) was employed to adjust pH of the test solutions.

Chemicals. The chemicals used were of analytical reagent grade. All acids were of extra pure grade purchased from Wako Chemicals Co. The stock solutions for metals were prepared by dissolving the corresponding metals or oxides in the acids. One g of gallium metal (99.99%; Wako Chemicals Co.) was dissolved in 10 ml of (1+1) nitric acid and diluted to 200 ml with water. Sodium hydroxide solution (9 M; 1 M=1 mol dm^{-3}) used for pH adjustment was prepared from its salt (Suprapur; Merck).

Procedures. The test solution (100 ml) was prepared by dissolving the required amount of magnesium chloride (0, 5, 20, 100, 400 mg Mg/100 ml) in pure water. Then different amounts of gallium (0, 0.02, 0.1, 0.5, 2 mg) were added to all the test solutions. After stirring well, pH of all the test solutions was adjusted to 9 by adding sodium hydroxide solution. The precipitate formation was monitored at 660 nm by measuring turbidity. The precipitate was stood for 24 h, and then filtered with a Nuclepore filter. After washing with 3 ml of pure water, the precipitate collected on the filter was dissolved with 2.5 ml of 1 M hydrochloric acid, and diluted exactly to 5 ml with water. The final solution was supplied to the ICP-AES measurement. In the recovery test, analytes (10 μg for each element) were added to the above solutions.

Table 1. Instrumental Components and Operating Conditions

Spectrometer	Jarrell-Ash Plasma Atomcomp MK II
frequency	27.12 MHz
r.f. output power	1.1 kw
coolant gas	argon 15 l min^{-1}
auxiliary gas	argon 0.5 l min^{-1}
carrier gas	argon 1.0 l min^{-1}
observation height	17 mm above work coil
Nebulizer	Cross-flow type
Polychromater	Paschen-Runge type (75 cm focal length)
grating	2400 grooves/mm
reciprocal linear dispersion	0.54 nm/mm at 270 nm
entrance slit width	25 μm
exit slit width	50 μm
Monochromator	Ebert type (50 cm focal length)

Results and Discussion

pH Dependence of Gallium Precipitation. Since gallium is an amphoteric metallic element, it dissolves in aqueous solution at both low and high pH region. The equilibria and their dissociation constants of gallium hydroxide in solution are as follows.[13]

$$\mathrm{Ga(OH)_3(s)=Ga^{3+}+3OH^-} \qquad K=5\times10^{-37}$$

$$\mathrm{Ga(OH)_3(s)=GaO_2^-+H^++H_2O} \qquad K=10^{-15}$$

The pH dependences of the precipitate formations for the solutions containing gallium and/or magnesium were examined by measuring transmittance at 660 nm. The experimental results are shown in Fig. 1-(a), (b), and (c). As is shown in Fig. 1-(a), gallium formed the precipitate in aqueous solution at the pH range between 4 and 6, which was observed as the slight decrease of the transmittance of the solution. The pH dependence of the precipitate formation of magnesium in aqueous solution, in which the concentration of magnesium is the same as those in natural seawater, i.e., 1300 mg of Mg/l, is shown in Fig. 1-(b). The transmittance of the solution began to decrease markedly from pH 10. At pH 11 the precipitation of magnesium took place so significantly that the transmitted light could be hardly detected.

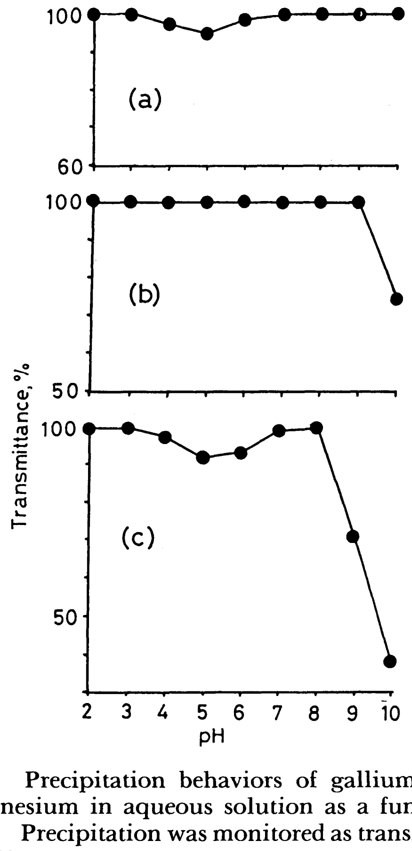

Fig. 1. Precipitation behaviors of gallium and/or magnesium in aqueous solution as a function of pH. Precipitation was monitored as transmittance at 660 nm.
(a); 10 mg of gallium/l, (b); 1300 mg of magnesium/l, (c); 10 mg of gallium/l and 1300 mg of magnesium/l.

The transmittance of the solution containing both gallium (10 mg $\mathrm{l^{-1}}$) and magnesium (1300 mg $\mathrm{l^{-1}}$) at various pH is shown in Fig. 1-(c). Precipitation occurred between pH 4—6 and above pH 9. The precipitation behavior below pH 8 was almost identical to the result obtained for only the gallium solution (see Fig. 1-(a)). On the other hand, above pH 9 the behavior was similar to that of the magnesium solution (Fig. 1-(b)), but the precipitation took place from the lower pH. It should be noted that the mixed solution of magnesium and gallium precipitated at pH 9, where the solution containing only magnesium did not.

pH Dependence of Gallium Precipitation in Seawater Martix Solution. The amounts of seawater-matrix elements (sodium, potassium, calcium, and magnesium) and gallium in the precipitate were analyzed as the pH function, when the gallium coprecipitation was applied to seawater. The compositions of the precipitate were measured by ICP-AES as the relative concentration, where the amount of each element at pH 9 was defined as 1. The experimental results are shown in Fig. 2. In the pH range between 7 and 8, no precipitation took place, and then test was not made. Gallium precipitated almost quantitatively between pH 5 and 6 and above pH 9, as can be seen in Fig. 2. Among the matrix elements in seawater, magnesium and calcium in the precipitate showed a strong dependence on pH around pH 9. The amount of Ca in the precipitate started to increase suddenly above pH 9.3. The amounts of magnesium and gallium in the precipitate at pH 9 were about 5 mg, when 5 mg of gallium is added to 1 l of seawater. They were rather larger than the amounts of calcium, sodium, and potassium in the precipitate (0.05 mg, 0.005 mg, and 0.05 mg, respectively). The strong dependence of the magnesium content in the precipi-

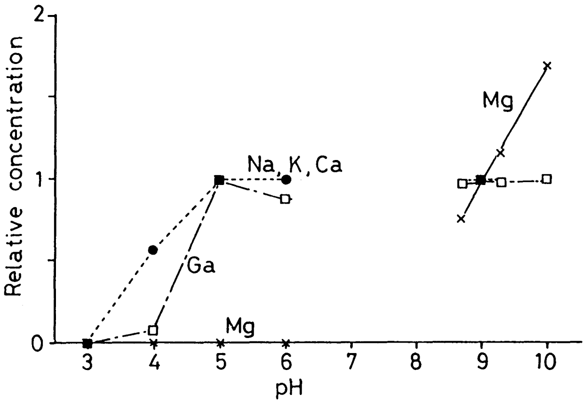

Fig. 2. Concentrations of gallium, alkali and alkaline earth elements in the precipitate at various pH in the case of gallium coprecipitation. Artificial seawater was used. Five mg of gallium was added to 1 l of seawater. The concentrations of all elements at pH 9 are defined as 1.
●: Na, K, Ca, □: Ga, ×: Mg.

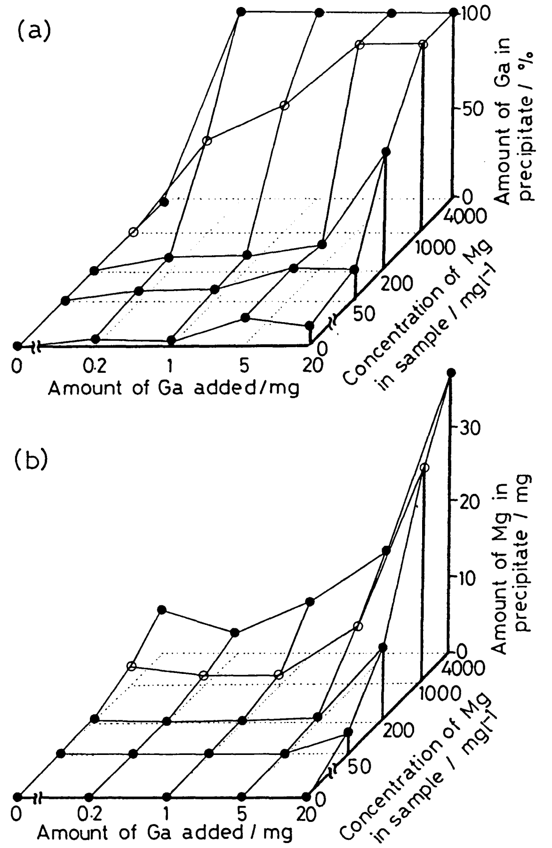

Fig. 3. Dependences of the precipitate compositions on the concentrations of magnesium and gallium at pH 9.0.
(a); amount of gallium in the precipitate (%). (b); amount of magnesium in the precipitate (mg). Open circles indicate the results for the solutions containing magnesium at the seawater level. The experiment was done using 100 ml of test solutions. The values in the figure was converted ones for 1 l of solutions.

tate on pH as well as the precipitate formation of the magnesium and gallium solution (Fig. 1-(c)) suggest the role of Mg in the precipitation of gallium. Therefore, the precipitation behaviors of gallium associated with magnesium in seawater was further investigated at pH 9.

Effect of Amounts of Magnesium and Gallium on Precipitate Formation. The precipitate formation of gallium at pH 9 was investigated using the solutions which contained both gallium and magnesium at various concentrations. The experimental results are shown in Fig. 3. The test solutions were prepared by dissolving required amounts of magnesium chloride in pure water and then different amounts of gallium were added into the solutions, in which the concentrations of magnesium in the test solutions were varied from 0 to 4000 mg l^{-1}, and those of gallium from 0 to 20 mg l^{-1}. The precipitate collected on a filter was dissolved in 1 M HCl solution. The percent recovery of gallium and amount of magnesium in the precipitates are shown in Figs. 3-(a) and -(b), respectively, as the functions of magnesium and gallium concentrations. As is seen in Fig. 3-(a), the percent recovery of gallium in the precipitate showed strong dependence on the concentrations of both gallium and magnesium in the solutions, and it was improved at the higher concentrations of both gallium and magnesium in the solution. When the concentration of magnesium in the sample was 4000 mg l^{-1}, gallium formed completely the precipitate at its concentration larger than 0.2 mg l^{-1}. For the solution containing magnesium at the concentration of seawater level (1000 mg l^{-1}, indicated by open circle in Figs. 3), gallium precipitated quantitatively (100%), when it was added not less than 5 mg l^{-1}. On the other hand, only a few percentage of gallium formed the precipitate when the magnesium concentration was below 50 mg l^{-1}.

Similar dependence was observed for the magnesium precipitation (Fig. 3-(b)). The amount of magnesium in the precipitate increased with the increases of the concentrations of both gallium and magnesium

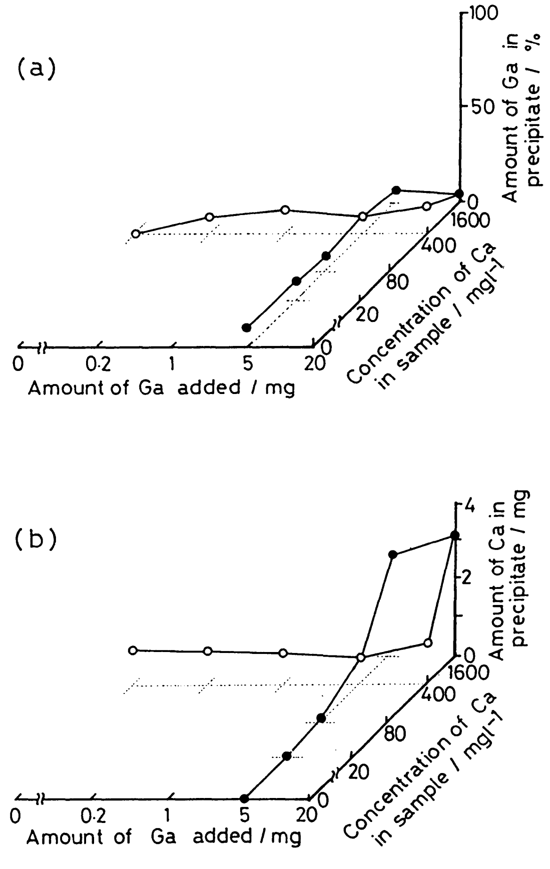

Fig. 4. Dependence of the precipitate compositions on the concentrations of gallium and calcium at pH 9.0.
(a); amount of gallium in the precipitate (%). (b); amount of calcium in the precipitate (mg). Open circles indicate the results for the solutions containing calcium at the seawater level. The experiment was done using 100 ml of test solutions. The values in the figure was converted ones for 1 l of solutions.

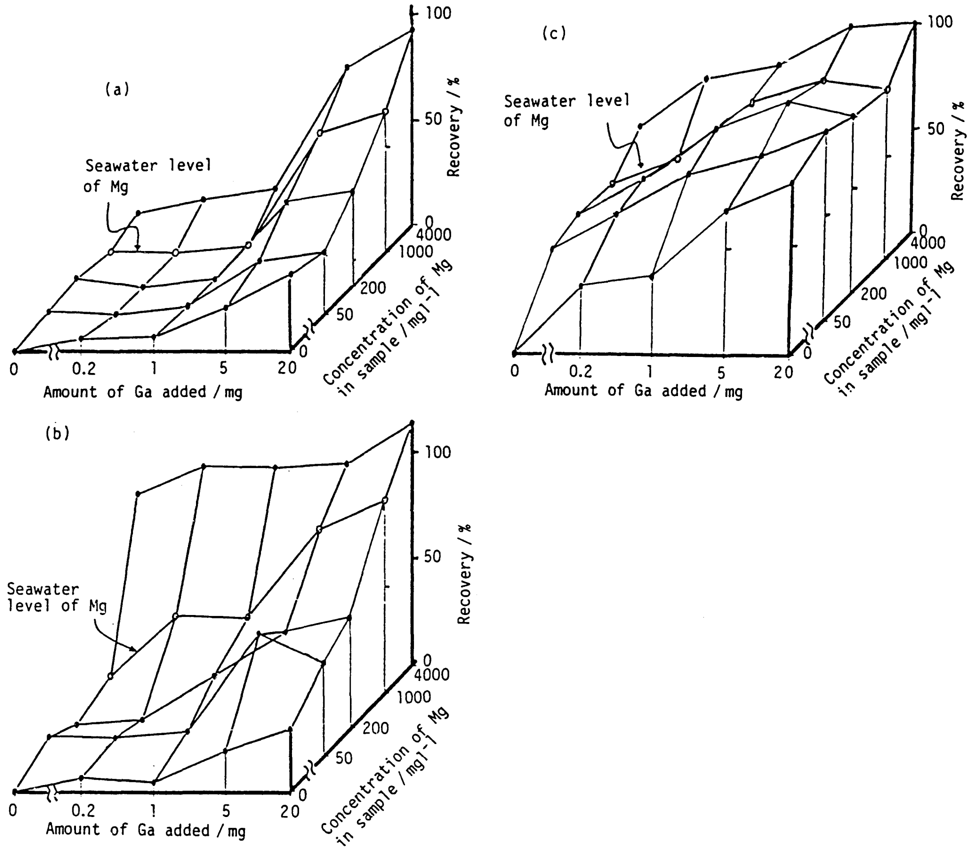

Fig. 5. Recoveries of cadmium (a), manganese (b), and yttrium (c) as the function of both gallium and magnesium concentrations at pH 9.0.
Open circles indicate the results for the solutions containing magnesium at the seawater level.

in solution. However, the amount of magnesium in the precipitate did not show proportionality to neither its concentration nor the added amount of gallium in the solution.

The experimental results described above indicate the interactions between magnesium and gallium in their precipitate formations.

Influence of Calcium on Gallium Precipitation. One 1 of seawater contains about 400 mg of calcium, which is about one third of magnesium content in seawater. The chemical property of calcium is more similar to that of magnesium than those of any other salts in seawater such as sodium and potassium. Thus, it is worthwhile to examine the influence of calcium on gallium precipitation. Such an influence was tested in the same manner as the case of magnesium. The calcium solutions (0—1600 mg l^{-1}) were prepared by dissolving required amounts of calcium chloride in pure water. The concentations of calcium in the test solutions were 0—4 times as large as that in seawater. The pH of the test solutions was adjusted to 9. The experimental results, the percent recovery of gallium and the amount of calcium in the precipitate, are shown in Figs. 4-(a) and (b), respectively. As can be seen in the figures, the percent recovery of gallium was low and did not depend on the gallium amount added or the concentration of calcium in the sample solution. The amount of calcium in the precipitate showed slight dependence on both of them, but it was much lower than that of magnesium (Fig. 4-(b)). Thus it is concluded that calcium had little cooperation in gallium precipitation.

Influence of Anions on Gallium Precipitation. Although large amount of chloride ion is present in seawater, the behavior of magnesium in its precipitation with gallium was investigated, when magnesium ion coexisted with different anion such as nitrate ion. The experiment was carried out by using magnesium nitrate solution. The results obtained for magnesium nitrate were almost similar to those using magnesium chloride. This experimental result may lead to the conclusion that only magnesium ion is responsible for its interaction with gallium in the gallium precipitation. The present result is due to the existence of Mg as the ionic form in high ionic strength solution, according to the calculation by Berner.[14]

Influence of Gallium and Magnesium Matrices on Recoveries of Heavy Metals. The precipitate in the gallium coprecipitation consists of magnesium as well as gallium. So far only magnesium hydroxide has been used as a coprecipitation carrier.[10,11] Therefore, not only gallium hydroxide but also magnesium hydroxide are expected to collect heavy metals in solution. Hence the recoveries of analyte elements were investigated in terms of the added amount of gallium and the concentration of magnesium in solution. The original concentration of each analyte metal was 10 $\mu g\,l^{-1}$. The experimental results for Cd, Mn, and Y are shown in Figs. 5-(a), (b), and (c), respectively. As can be seen in the figures, the recoveries of analyte metals were dependent on both of the added amount of gallium and the concentration of magnesium in the test solution, i.e., the recoveries of such metals were improved with the increases of gallium and magnesium. Slight differences in the recovery patterns were, however, observed, depending on the analyte metals examined. The recovery of Mn was influenced by the concentration of magnesium rather than that of gallium (Fig. 5-(b)), while the recovery of Y depended more largely on the concentration of gallium (Fig 5-(c)). Iron showed a similar tendency to Mn, but Cu, Co, and V had the similar trends to Y. The tendencies of Zn, As, and Cr were similar to that of Cd. The results may be explained by the difference in chemical affinities of analyte metals with gallium and/or magnesium hydroxides.

Conclusion

The gallium coprecipitation method can be efficiently used for trace metal preconcentration in seawater in association with magnesium in solution. It has been elucidated that the cooperative interaction between gallium and magnesium is necessary in the efficient precipitate formation. The presence of magnesium ion in sample solution helped the quantitative precipitation of gallium added as a coprecipitation reagent, although very small portion of magnesium (about 0.3%) in seawater was found in the precipitate at pH 9. To coprecipitate analyte elements, both gallium and magnesium play as the coprecipitation carriers, which provides some unique advantages[12] in seawater analysis by ICP-AES.

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References

1) T. Akagi, H. Nojiri, M. Matsui, and H. Haraguchi, *Appl. Spectrosc.*, **39**, 662 (1985).

2) E. Nakayama, H. Tokoro, T. Kuwamoto, and T. Fujinaga, *Nature (London)*, **290**, 768 (1981).

3) E. Nakayama, T. Kuwamoto, H. Tokoro, and T. Fujinaga, *Anal. Chim. Acta*, **131**, 247 (1981).

4) K. Fujiwara, S. Toda, and K. Fuwa, *Bull. Chem. Soc. Jpn.*, **54**, 3209 (1981).

5) D. S. Lee, *Anal. Chem.*, **54**, 1682 (1982).

6) R. S. S. Murthy and D. E. Ryan, *Anal. Chem.*, **55**, 682 (1983).

7) P. C. Cole, J. M. Eckert, and K. L. Williams, *Anal. Chim. Acta*, **153**, 61 (1983).

8) M. Hiraide, T. Ito, M. Baba, H. Kawaguchi, and A. Mizuike, *Anal. Chem.*, **52**, 804 (1980).

9) K. Himeno, K. Yanagisawa, T. Yuki, and Y. Nakamura, *Bunseki Kagaku*, **33**, T44 (1984).

10) A. Andresen and B. Salbu, *Radiochem. Radioanal. Lett.*, **52**, 19 (1982).

11) A. S. Buchanan and P. Hannaker, *Anal. Chem.*, **56**, 1379 (1984).

12) T. Akagi, K. Fuwa, and H. Haraguchi, *Anal. Chim. Acta*, **177**, 139 (1985).

13) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York (1966), p. 437.

14) R. A. Berner, "Principles of Chemical Sedimentology," McGraw Hill, New York (1971), p. 240.