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# Simultaneous Multielement Determination of Hydride- and Oxoanion-Forming Elements in Seawater by Inductively Coupled Plasma Mass Spectrometry after Lanthanum Coprecipitation

**Tomoki Yabutani, Shan Ji, Fumihiko Mouri, Akihide Itoh, Koichi Chiba, and Hiroki Haraguchi***

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8603

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The simultaneous multielement determination of trace elements in seawater, especially hydride- and oxoanion-forming elements, has been investigated by inductively coupled plasma mass spectrometry with the aid of lanthanum coprecipitation preconcentration. The optimum pH in lanthanum coprecipitation was pH 9.5; at this value, trace elements were well recovered and major constituents of seawater such as Na, Mg, K, and Ca were significantly reduced in the concentrated solutions. The recovery values obtained for V, Cr(III), Mn, As(III), As(V), Se(IV), Y, Sn, Sb(III), Sb(V), W, Bi, and U were more than 85% after lanthanum coprecipitation, while Cr(VI), Se(VI), and Mo(VI) provided poor recoveries of less than 30%. The reproducibility for coprecipitation was within 5% as relative standard deviation. The present method was applied to the determination of trace elements in coastal seawater reference material CASS-3. The analytical values for Mn, As, V, Y, Sb, W, and U were in fairly good agreement with the certified or literature values.

The concentration levels of major elements such as Na, Mg, K, and Ca in seawater are almost constant all over the sea, while those of trace elements often show some local distributions and characteristic behaviors. In addition, the concentration variations of such trace elements often reflect some physicochemical and/or biochemical changes in the sea,[1] even though their concentrations in seawater are extremely low. Thus, the accurate determination of trace elements in seawater is still important to elucidate their roles in the aquatic system or to evaluate environmental pollution in the sea. It is, therefore, desirable to determine as many as possible of major-to-ultratrace elements for comprehensive appreciation of the distributions of trace elements and their multielement correlation in the marine environment.

Inductively coupled plasma mass spectrometry (ICP-MS) has been developed as an analytical method for the determination of trace and ultratrace elements. This method has excellent analytical features, such as simultaneous multielement detection capability, extremely high sensitivity and wide linear dynamic ranges for most metallic elements. Consequently, ICP-MS has been extensively applied to the analyses of various kinds of samples including seawater. However, major elements such as Na, K, Mg, and Ca in seawater often cause serious matrix interferences with trace elements in the ICP-MS measurement.[1,2] Therefore, various pretreatment methods for both preconcentration of trace elements and elimination of major elements have been developed to perform the accurate determination of trace elements at the $\mu g\,dm^{-3}$ or $ng\,dm^{-3}$ level by ICP-MS. As the preconcentration methods for trace elements in seawater, coprecipitation,[2,3] chelating resin preconcentration,[4—8] and solvent extraction method[9,10] have been widely employed so far. The present authors reported that 29 elements in coastal seawater could be simultaneously determined by ICP-MS with the multielement preconcentration method using a chelating resin.[4] However, it was found that the hydride-forming elements (As, Se, Sb, Sn, and Bi) and oxoanion-forming elements (Cr and W) could not be determined by the chelating resin preconcentration method because of the poor recoveries of these elements. Among these elements, some of the hydride-forming elements have been usually determined with a hydride generation method.[11—13] Unfortunately, however, the hydride generation method is not adequate as a pretreatment technique for the simultaneous multielement determination of trace elements in seawater by ICP-MS.

Lanthanum coprecipitation, which has been used for the preconcentration of trace elements in river water[14—16] and industrial waste water[17] in inductively coupled plasma atomic emission spectrometry (ICP-AES) or atomic absorption spectrometry (AAS), can efficiently preconcentrate the hydride-forming elements. However, lanthanum coprecipitation has not been applied to the preconcentration of such elements at the ultratrace level in ICP-MS. In addition, the coprecipitation capability of lanthanum for the elements such as Cr, V, Mo, W, and U, which mostly exist as oxoanion compounds in seawater, has not been examined yet.

In the present study, hence, lanthanum coprecipitation was applied to the preconcentration of hydride- and oxoanion-forming elements for the simultaneous multielement determination by ICP-MS. The pH dependence of the coprecipitation efficiencies, spectral interferences due to lanthanum as a carrier, and analytical figures of merit in lanthanum coprecipitation preconcentration were investigated for the multielement determination of hydride- and oxoanion-forming elements by ICP-MS. The coprecipitation efficiencies for Cr, As, Sb, and Se with the different oxidation states were also examined, because the effects of the oxidation states on the recoveries in lanthanum coprecipitation have not been reported except for Se.[16] In order to evaluate the analytical reliability, the present lanthanum coprecipitation/ICP-MS method was applied to the analysis of coastal seawater reference material (CASS-3) issued from National Research Council of Canada (NRC). In the present experiment, Mn and Y were also determined by the lanthanum coprecipitation/ICP-MS method, because their certified and reference values are provided for CASS-3.

## Experimental

**Instruments.** An ICP-MS instrument model SPQ 8000A (Seiko Instruments Inc., Chiba) was used for the determination of trace elements; it consisted of a quadrudpole-type mass spectrometer. An ICP-AES instrument model Plasma AtomComp MKII (Jarrell-Ash, Franklin, MA, USA) with a polychromator of Paschen–Runge mounting was also used for the simultaneous multielement determination of major and minor elements. The instrumental components and operating conditions are shown in Table 1. These operating conditions were chosen after optimization of each instrumental parameter in the ICP-MS and ICP-AES instruments. A model twin pH meter from Horiba (Kyoto) was used for pH adjustment.

**Chemicals.** Nitric acid and aqueous ammonia solution used were of electronics industry grade (Kanto Chemicals, Tokyo). The multielement standard solutions for standardization of the calibration curves were prepared by mixing the single-element standard stock solutions (1000 $\mu g\ dm^{-3}$) of each element for atomic absorption spectrometry, purchased from Wako Chemicals (Osaka). The standard stock solutions for Cr(III), As(V), Sb(III), Sb(V), and Se(VI) were prepared as follows: The Cr(III) solution was prepared by dissolving high purity metal of guaranteed reagent grade (Nacalai Tesque, Kyoto) in 3 M HCl solution (1 M = 1 $mol\ dm^{-3}$), As(V) solution by dissolving potassium arsenate of chemical grade (Wako Chemicals) in pure water, Sb(III) solution by dissolving dipotassium bis(tartrato) diantimonate(III) of extra grade (Wako Chemicals) in 3 M HCl solution, Sb(V) solution by dissolving potassium hexahydroxoantimonate of guaranteed reagent grade (Nacalai Tesque) in 3 M HCl solution, and Se(VI) solution by dissolving sodium selenate of extra grade (Wako Chemicals) in pure water. The lanthanum solution for the coprecipitation carrier was prepared by dissolving 3 g of $La(NO_3)_3$ (extra grade; Wako Chemicals) in 100 ml of 0.1 M $HNO_3$ so as to provide 10 $g\ dm^{-3}$ of La. Purified water used throughout the present experiment was prepared by a Milli-Q purification system (Nihon Millipore Kogyo, Tokyo).

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

| | |
|---|---|
| ICP-MS: Seiko SPQ 8000A | |
| Plasma conditions: | |
| Incident power | 1.0 kW |
| Coolant gas flow rate | Ar 16 $dm^3\ min^{-1}$ |
| Auxiliary gas flow rate | Ar 1.0 $dm^3\ min^{-1}$ |
| Carrier gas flow rate | Ar 1.0 $dm^3\ min^{-1}$ |
| Sampling depth | 12 mm 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 |
| ICP-AES: Jarrell-Ash Plasma AtomComp MK II | |
| Plasma conditions: | |
| Incident power | 1.0 kW |
| Coolant gas flow rate | Ar 20 $dm^3\ min^{-1}$ |
| Auxiliary gas flow rate | Ar 1.0 $dm^3\ min^{-1}$ |
| Carrier gas flow rate | Ar 0.48 $dm^3\ min^{-1}$ |
| Observation height | 18 mm above load 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 µm |
| Exit slit width | 50 µm |

**Seawater Samples.** Coastal seawater reference material CASS-3 was obtained from the National Research Council of Canada (NRC) for evaluation of the present analytical method. Some coastal seawater samples collected at about 1 km off-shore from Tokoname (Aichi Prefecture) in Ise Bay were also used for the recovery test in the present experiment. The artificial seawater, which was used for the recovery test of Cr, As, Sb, and Se with different oxidation states, was prepared by dissolving 23.4 g of NaCl, 10.6 g of $MgCl_2 \cdot 6H_2O$, 1.40 g of $CaCl_2 \cdot 2H_2O$, and 3.92 g of $Na_2SO_4$ (extra grade; Wako Chemicals) in 1 $dm^3$ of pure water after the reference.[18]

**Preconcentration Procedure.** The following preconcentration procedure for trace elements in the coastal seawater samples was established after optimization, as will be described later. First, 250 ml of the coastal seawater sample was taken in a beaker; into this, 2 ml of the lanthanum solution (10 $g\ dm^{-3}$) was added. Then the solution was stirred with a magnetic stirrer for ca. 5 min. After pH adjustment of the sample solution to 9.5 with aqueous ammonia solution, the sample solution was kept standing for 2 h to complete precipitation. The precipitate which was formed was collected on a PTFE membrane filter (pore size 0.45 µm) by filtration. After washing with 30 ml of pure water, the precipitate was dissolved with 90 ml of 2 M $HNO_3$; into this, 10 ml of mixed solution of Ge, In, Re, and Tl (100 $\mu g\ dm^{-3}$ each) was added as the internal standard elements for correction of matrix effect due to major elements.[3] Consequently, 2.5-fold preconcentration was achieved by the present procedure. This solution was used as the analysis solution to the ICP-MS and ICP-AES measurements.

When the recoveries of Cr, As, Se, and Sb with different oxidation states were investigated, the artificial seawater was used to avoid the disturbances caused by these elements with natural abundances in seawater. Two kinds of recovery test solutions were prepared in order to avoid the oxidation–reduction reactions among the elements. One of them was the solution for the lower oxidation states and the other for the higher oxidation states. Proper amounts of the standard stock solutions of Cr(III), As(III), Sb(III), and Se(IV) were added to the artificial seawater to prepare 250 ml of the test solution for the lower oxidation state, and those of Cr(VI), As(V), Sb(V), and Se(VI) were added to another sample of artificial seawater to prepare 250 ml of the test solution for the higher oxidation state. These two test solutions were subjected to the lanthanum coprecipitation procedure mentioned above.

The polyatomic ion interferences due to Ca, which remained as a matrix element in the analysis solution, were corrected by the interference correction coefficient method.[4]

## Results and Discussion

**pH Dependence of Removal of Major Elements and Recoveries of Trace Elements in Lanthanum Coprecipitation.** The removal of major elements (Na, K, Mg, and Ca), and recoveries of trace elements and La in lanthanum coprecipitation were examined in the pH range of 9.1—9.9, where the preconcentration procedure described in the experimental section was carried out. Since lanthanum hydroxides begin to precipitate near pH 8 and a large amount of Mg precipitates above pH 10,[19] the pH dependence of removal of major elements was examined in the pH range 9—10. The concentrations of major elements such as Na, Ca, and Mg which remained in the analysis solution after lanthanum coprecipitation are shown in Fig. 1. The concentration of Mg was less than 10 mg dm$^{-3}$ below pH 9.5, while it increased to 1000 mg dm$^{-3}$ at pH 9.9, although those of Na and Ca were less than 10 mg dm$^{-3}$ and that of K was below the detection limit in the pH range of 9.1—9.9. Thus, the pH dependence at pH values above 10 was not examined because introduction of the solution containing more than 1000 mg dm$^{-3}$ of Mg into the argon ICP caused serious problems (e.g., cloggings of the plasma torch and the sampling interface) in the ICP-MS instrument.

The recoveries of V, Mn, Sb(V), W, and U as well as La in the pH range of 9.1—9.9 are shown in Fig. 2, as some typical examples. It is seen in Fig. 2 that La was recovered almost 100% in the whole pH range of 9.1—9.9. This result indicates that La is suitable enough as the coprecipitation carrier in the pH range of 9.1—9.9. The recoveries of V, Sb(V), W, and U were almost constant, larger than 85%, while that of Mn provided the maximum value of about 85% near pH 9.5.

In consequence, taking into consideration both the removal efficiencies of major elements and the recoveries of trace elements, we chose pH 9.5 as the optimum pH for lanthanum coprecipitation of trace elements in seawater. Under the optimum conditions, the recoveries of almost all the trace elements examined here were more than 85%, and the total concentration of major matrix elements (Na, K, Mg, Ca) originated from seawater was less than 20 mg dm$^{-3}$ in the analysis solution.

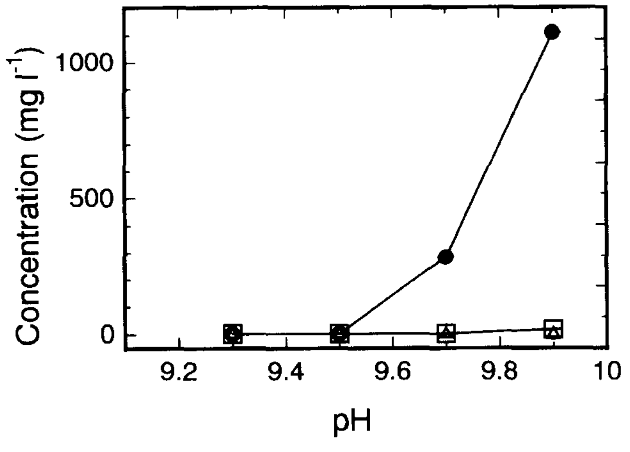

Fig. 1. pH dependence of the concentrations of major elements in the analysis solution after La coprecipitation. ●: Mg, □: Ca, △: Na.

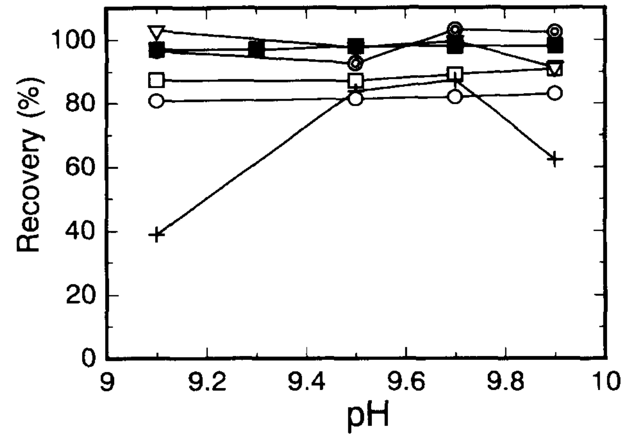

Fig. 2. pH dependence of recoveries of La and trace elements in La coprecipitation. ■: La, □: V, +: Mn, ◎: Sb, ○: W, ▽: U.

**Spectral Interferences of Lanthanum in ICP-MS Measurement.** In the ICP-MS measurement, matrix elements in the analysis solution often cause spectral interference with analyte elements, when they provide some polyatomic and divalent ions. In the present coprecipitation method, the concentration of La used as the coprecipitation carrier was ca. 200 mg dm$^{-3}$ in the analysis solution, and then it became a matrix element in the analysis solution. Thus, possible interferences of polyatomic and divalent ions due to La were examined by measuring the ICP-MS spectrum over the whole mass range. In Fig. 3, the ICP-MS spectra in the *m*/*z* ranges of 65—79 and 141—180 are illustrated, when 200 mg dm$^{-3}$ of lanthanum solution in 2 M $HNO_3$ and the blank solution (2 M $HNO_3$) were introduced into the plasma. The ICP-MS spectrum in the mass range of 80—140 was not shown in Fig. 3, because no significant polyatomic ion peaks due to La were observed in this mass range. The largest peak observed in the mass range of 65—79 is ascribed to the divalent ion of $^{139}La^{2+}$ near *m*/*z* 69, where the major isotope of $^{69}Ga$ (60.11%) is observed. Thus, the determination of Ga by the lanthanum coprecipitation/ICP-MS method is not possible by the measurement of major isotope of $^{69}Ga$, and then Ga should be determined at *m*/*z* 71 with the abundance of 39.89%. In the spectrum in the mass range of 140—180, the polyatomic ions of $^{139}La^{14}N$, $^{139}La^{16}O$, $^{139}La^{17}O$, $^{139}La^{18}O$, and $^{139}La^{16}O^{1}H$ were observed in the mass range between 153 to 158. The peaks observed at *m*/*z* 141 and 142 corresponded to $^{141}Pr$ and $^{142}Ce$, respectively, which were concomitant elements in the lanthanum solution. Two smaller peaks were also observed at *m*/*z* 171 and 179; these were attributed to polyatomic ions of $^{139}La^{16}O_2{}^+$ and $^{139}La^{40}Ar^+$, respectively. The polyatomic ion species of La observed in

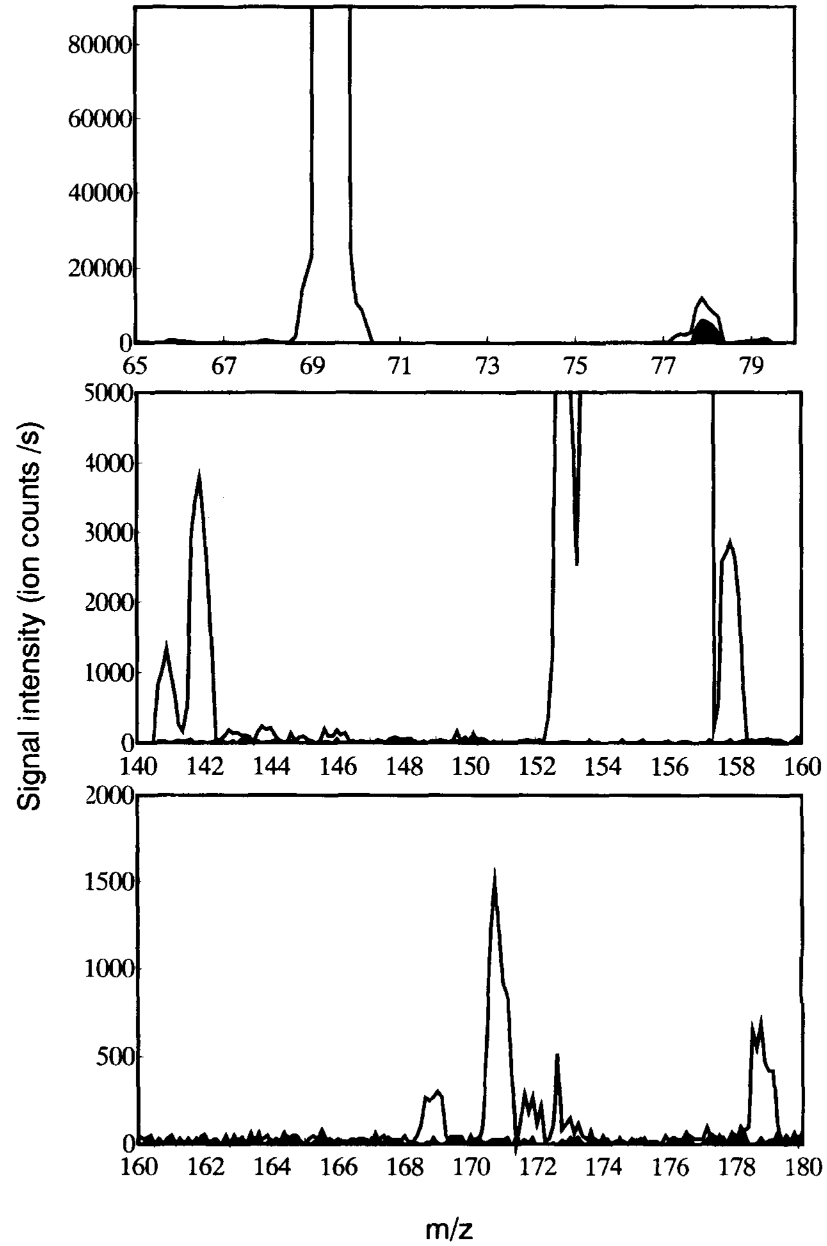

Fig. 3. ICP-MS spectra of 200 mg dm$^{-3}$ La solution in the mass range of *m*/*z* 65—79 and 140—180.
white spectrum: 200 mg dm$^{-3}$ of La solution in 2 M $HNO_3$.
black spectrum: 2 M $HNO_3$ blank solution.

the *m*/*z* range 140—180 caused the interferences with rare earth elements, especially Eu, Gd, and Tb, and thus the lanthanum coprecipitation/ICP-MS method could not be applied to the determination of rare earth elements at the trace level. Since rare earth elements can be effectively preconcentrated with the chelating resin, it is better to use the chelating resin preconcentration/ICP-MS method for the determination of rare earth elements, as reported previously.[4] In consequence, the divalent and polyatomic ions of La were not prone to interfere with the elements listed in Table 2. Furthermore, no severe polyatomic ion interferences of $^{35}Cl^{16}O$ and $^{40}Ar^{35}Cl$ with $^{51}V$ and $^{75}As$, respectively, were observed.

**Analytical Figures of Merit.** In order to evaluate the lower limit of determination by the present method, the analytical detection limits were estimated from the instrumental detection limits, taking into account the concentration factor and the recovery values. The instrumental detection limits of analyte elements were obtained as the concentrations corresponding to 3-fold the standard deviation ($3\sigma$) of the background signal intensities for the blank solution (2 M $HNO_3$), where the standard deviation ($\sigma$) was calculated from the 10-times repeated measurements at each mass number. The analytical detection limits of analyte elements are shown in Table 2. It is seen from Table 2 that the analytical detection limits were in the range from 0.2 μg dm$^{-3}$ for Se to 0.0001 μg dm$^{-3}$ for Bi. The poor detection limit of Se (*m*/*z* 82) may be ascribed to the large background intensity due to polyatomic ion ($Ar_2H_2^+$) and the low isotope abundance ($^{82}Se$

Table 2. Analytical Detection Limits Obtained by La Coprecipitation and ICP-MS Measurements

| Element | m/z | Analytical detection limit[a)] μg dm$^{-3}$ |
|---|---|---|
| V | 51 | 0.005 |
| Cr | 52 | 0.03 |
| Mn | 55 | 0.02 |
| As | 75 | 0.003 |
| Se | 82 | 0.2 |
| Y | 89 | 0.0007 |
| Mo | 95 | 0.04 |
| Sn | 116 | 0.002 |
| Sb | 121 | 0.004 |
| W | 184 | 0.0009 |
| Bi | 209 | 0.0001 |
| U | 238 | 0.05 |

a) Analytical detection limits were calculated from the instrumental detection limits, taking into account the recovery values and concentration factor (2.5) obtained by the present coprecipitation method.

9.2%).

In the lanthanum coprecipitation method, the lanthanum solution with the high concentration (200 mg dm$^{-3}$) added into the sample solution may provide the large blank values. Compared to the detection limits, however, the blank values caused by the lanthanum solution were negligibly small for the analyte elements except for Y. In the case of Y, La provided contamination corresponding to the concentration of Y (0.026 μg dm$^{-3}$) in seawater. The total blank values caused from the whole preconcentration procedure were also examined. They were 0.32 μg dm$^{-3}$ for Cr, 0.031 μg dm$^{-3}$ for Y, 0.009 μg dm$^{-3}$ for Sb, 0.0011 μg dm$^{-3}$ for W, and 0.0004 μg dm$^{-3}$ for Bi, respectively. These blanks might be caused by the contamination introduced at some stages in the preconcentration procedure and/or by the impurities of the lanthanum carrier.

**Recoveries and Coprecipitation Behaviors of Hydride- and Oxoanion-Forming Elements in Seawater.** As mentioned earlier, pH 9.5 was chosen as the optimum pH for lanthanum coprecipitation, and thus the recovery values for trace elements in seawater were estimated by carrying out lanthanum coprecipitation at pH 9.5. The results for the recovery test are summarized in Table 3, where the recovery values of analyte elements obtained by gallium coprecipitation[3] and chelating resin (Chelex 100) preconcentration[4] are also shown. The recoveries of analyte elements except for Cr, As, Se, and Sb were examined using the coastal seawater sample, where the coprecipitation procedure described in the experimental section was carried out. As for Cr, As, Se, and Sb, the artificial seawater sample was used for the recovery test because they have different oxidation states. As reported previously,[3,4] the gallium coprecipitation and chelating resin preconcentration methods have not been applied to the preconcentration of hydride- and oxoanion-forming elements with some exceptions because of their poor recoveries. In gallium coprecipitation, the recoveries of Cr(III), Mn, As(III), Y, Sn, and Sb(III) were much poorer than those in lanthanum coprecipitation. The recoveries of oxoanion-forming elements in gallium coprecipitation were slightly lower than those in lanthanum coprecipitation. As mentioned previously,[5] the chelating resin preconcentration also provided the extremely poor recoveries of the elements listed in Table 3 except for Y. Consequently, the lanthanum copre-

Table 3. Recoveries of Trace Elements in La Coprecipitation at pH 9.5

| Element | Recovery /% | | |
|---|---|---|---|
| | Present work[a)] | Ga coprecipitation[b)] | Chelating resin preconcentration[c)] |
| V | 85.9 ± 0.5 | 32 | 63.9 |
| Cr(III) | 106[d)] | 98 | |
| Cr(VI) | 27.1[d)] | | 8.0 |
| Mn | 100 ± 1 | 104 | 53.9 |
| As(III) | 102[d)] | 95 | |
| As(V) | 100 ± 0.2 | | |
| Se(IV) | 92.0 ± 5.3 | | |
| Se(VI) | 1.4[d)] | | |
| Y | 99.4 ± 4.3 | 99 | 91.3 |
| Mo | 16.0 ± 0.8 | 1 | 57.8 |
| Sn(II) | 98.1 ± 2.8 | 97 | 33.0 |
| Sb(III) | 96.7[d)] | 1 | |
| Sb(V) | 97.6 ± 2.2 | | |
| W | 92.5 ± 0.8 | | 43.2 |
| Bi | 96.2 ± 0.9 | | |
| U | 97.5 ± 1.1 | 82 | 81.1 |

a) The mean values and standard deviations were estimated from 3-times preconcentration procedures. b) The recovery values for Ga coprecipitation, cited from Ref. 3. c) The recovery values for chelating resin (Chelex 100) preconcentration at pH 6, cited from Ref. 4. d) The mean values were estimated from 2-times preconcentration procedures.

cipitation method was more efficient for preconcentration of hydride- and oxoanion-forming elements.

It is seen in Table 3 that the recovery values for V, Cr(III), Mn, As(III), As(V), Se(IV), Y, Sn, Sb(III), Sb(V), W, Bi, and U were larger than 80%, although those for Mo, Cr(VI), and Se(VI) were less than 30%. In the cases of As and Sb, the recoveries were about 100% regardless of their oxidation states. On the other hand, the recoveries of Cr(VI) and Se(VI) were ca. 30% and 1.4%, respectively, while those of Cr(III) and Se(IV) were ca. 100%. The results in the recovery test for Se agreed well with those reported in the reference.[16] Under the oxidizing conditions of coastal seawater, Cr(VI), As(V), Se(VI), and Sb(V) with the higher oxidation state are generally more dominant in seawater than those with the lower oxidation states.[20,21] The excellent recoveries for As(V) and Sb(V) may allow one to determine As and Sb in seawater as their total concentrations by the present method. On the contrary, the poor recoveries for Cr(VI) and Se(VI) in lanthanum coprecipitation unfortunately made it difficult to determine Cr and Se in seawater. The relative standard deviations of the recovery values for V, Mn, As(V), Se(IV), Sn, Sb(V), W, Bi, and U were within 5%. This means that these elements were effectively preconcentrated by lanthanum coprecipitation.

Among the oxoanion-forming elements, Cr(III), V, W, and U were found to be almost completely recovered with lanthanum coprecipitation, but Cr(VI) and Mo were recovered less than 30%. It was reported that oxoanions which have hydroxyl group(s) such as $HM^{VI}O_4^-$ type ion are more efficiently adsorbed on the surface of metal-hydroxide colloids than those with dissociated hydroxyl group(s) (e.g., $M^{VI}O_4^{2-}$ type ions), because the hydroxyl groups in oxoanions may coordinate with metal-hydroxide colloids through hydrogen bondings.[22] At pH 9.5, Cr(VI) and Mo may be in the forms of $CrO_4^{2-}$ and $MoO_4^{2-}$ in the sample solution, while Cr(III), V, W, and U may be in the chemical forms such as $Cr(OH)_3$, $NaHVO_4^-$, $HWO_4^-$, and $UO_2(OH)_3^-$, respectively.[23,24] As a result, Cr(III), V, W, and U can be almost completely coprecipitated with lanthanum hydroxide colloids because their chemical forms have some hydroxyl groups in them. On the contrary, Cr(VI) and Mo are poorly coprecipitated because they have no hydroxyl groups.

The coprecipitation behaviors of As, Sb, and Se in different oxidation states may be explained in analogy to the mechanisms described above. In seawater, As(III), As(V), Se(IV), Sb(III), and Sb(V) may be in the forms of $As(OH)_3$, $HAsO_4^{2-}$, $HSeO_3^-$, $Sb(OH)_3$, and $Sb(OH)_6^-$, respectively.[24] These types of oxo-compounds may be efficiently adsorbed on the hydroxide colloids because they have hydroxyl groups in them. As a result, As(III), As(V), Se(IV), Sb(III), and Sb(V) were completely coprecipitated at all with lanthanum hydroxide colloids. On the other hand, Se(VI), which is in the form of $SeO_4^{2-}$, was hardly coprecipitated with lanthanum hydroxide colloids.

**Determination of Trace Elements in Coastal Seawater Reference Material.** Trace elements in coastal seawater reference material CASS-3 were determined by the present lanthanum coprecipitation/ICP-MS method. The results are summarized in Table 4, along with the certified and literature values. In Table 4, As and Sb were estimated as the total concentrations [As(III+V) and Sb(III+V)] because they provided the same recovery values regardless of their oxidation states although they may exist in the higher oxidation states in seawater.[20,21] Eight elements (Mn, Mo, As, U, V, Y, Sb, and W) in CASS-3 could be determined by the present lanthanum coprecipitation/ICP-MS method. In Table 4, the analytical value of Mo is shown in the parentheses for reference, because its recovery value was poor. Since the concentration levels of Cr, Se, Sn, and Bi in seawater were below the analytical detection limits, they could not be determined by the lanthanum coprecipitation/ICP-MS method. Thus, the larger preconcentration factor is required for lanthanum coprecipitation to determine such elements at the ultratrace level. The relative standard deviations (RSDs) for the elements in Table 4 were less than 10% even at the low concentration level. The analytical results for Mn, As, and U were in fairly good agreement with the certified or information values issued from NRC, although the concentration of U was slightly higher than the information value.

Table 4. Analytical Results for Trace Elements in Coastal Seawater Reference Material CASS-3 Determined by ICP-MS after La Coprecipitation

| Element | Concentration[a] | | Certified value and literature values | |
|---|---|---|---|---|
| | $\mu g\ dm^{-3}$ | | $\mu g\ dm^{-3}$ | |
| Mn | 2.67 | ± 0.05 | 2.51 | ± 0.36 |
| As(III+V) | 1.12 | ± 0.04 | 1.09 | ± 0.07 |
| Mo | (14.4 | ± 1.7) | 8.95 | ± 0.26 |
| U | 3.29 | ± 0.07 | 2.84[b] | |
| V | 1.46 | ± 0.05 | 1.50[c] | |
| Y | 0.0258 | ± 0.0013 | 0.0237[d] | |
| Sb(III+V) | 0.150 | ± 0.004 | 0.12[e] | |
| W | 0.0117 | ± 0.0007 | 0.010[f] | |

a) The means and standard deviation obtained from 3-times independent determination. Data in the parentheses are the results for the elements of which recoveries were lower than 50%. b) Information value issued from NRC. c) Cited from Ref. 25. d) Cited from Ref. 4. e) Cited from Ref. 26. f) Cited from Ref. 27; open seawater.

Since the certified values for V, Y, Sb, and W have not been issued from NRC, their analytical results were compared with the literature values for CASS-3[4,25,26] or the averaged concentration values for open seawater.[27] The analytical results for V, Y, and Sb were in good agreement with the literature values for CASS-3. Furthermore, the concentration of W was almost the same as that in open seawater. This indicates that W is kept almost constant in concentration all over the sea area in the world, since it exists in the stable oxoanions as the dissolved form.

## Conclusion

It has been proved that the lanthanum coprecipitation/ICP-MS method is useful for the multielement determination of hydride- and oxoanion-forming elements as well as some trace elements in seawater. Eight elements (Mn, As, Mo, U, V, Y, Sb, W) in coastal seawater reference material CASS-3 could be determined by the present method, and their analytical values fairly agreed well with the certified or reference values. Since the determination of As, Sb, and W in seawater is not possible by the chelating resin preconcentration/ICP-MS method, the present lanthanum coprecipitation method may be employed as a complimentary method for the chelating resin preconcentration/ICP-MS method.

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