Rapid Coprecipitation Technique with Hybrid Hydroxide System Using Ytterbium(III), Gallium(III), and Magnesium(II) for Simultaneous Concentration of 13 Elements in Concentrated Salt Solution Prior to Their Inductively Coupled Plasma Atomic Emission Spectrometric Determination

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Beryllium(II), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), arsenic(V), selenium(IV), cadmium(II), antimony(III), and lead(II) ions in concentrated salt solutions, such as seawater or sodium chloride and sulfate solutions, were collected quantitatively by coprecipitation with hydroxides of ytterbium(III), gallium(III), and magnesium(II). In this method, a rapid coprecipitation technique combined with internal standardization was applied to simplify the operation; yttrium was used as an internal standard. The 13 elements collected were readily determined by inductively coupled plasma atomic emission spectrometry using internal standardization. The detection limits (3σ, $n = 10$) were in the range of 0.003 µg (for beryllium(II)) to 0.13 µg (for zinc(II)) in the initial sample solution (up to 150 mL). The proposed method was applied to the analyses of some commercially available salts and an effluent as well as the certified reference materials; the elements ranging from 0.03–0.14 $\mu g\,g^{-1}$ in the salts, 0.004–0.041 $mg\,L^{-1}$ in the effluent, or 0.006–0.30 $mg\,L^{-1}$ in the certified reference materials could be determined with the relative standard deviation of 7–33, 0.3–3, or 2–17%, respectively. The time required for the preconcentration was approximately 20 min.

In Japan, the discharge of some elements, including chromium, manganese, iron, copper, zinc, arsenic, selenium, cadmium, and lead, through effluents from industrial facilities is strictly regulated by the National Effluent Standards.[1] The effluents often contain large amounts of matrix ions such as sodium, chloride, and sulfate ions, which are often added during the wastewater treatment process. Therefore, analytical methods with which matrix ions do not interfere are required for the detection of the regulated elements in effluents. Furthermore, a method that can simultaneously determine various regulated elements is attractive because it can save time and work.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is an effective tool for multi-element analysis.[2] For water analysis, however, the sensitivity to some elements is insufficient in ICP-AES; therefore, various preconcentration techniques have been combined.[2] Coprecipitation with metal hydroxide is one of the most useful techniques for the simultaneous concentration of various elements;[3–5] hydroxides of magnesium(II),[6–10] aluminum(III),[8] gallium(III),[9–14] indium(III),[15] iron(III),[16,17] and lanthanum(III)[18,19] have been applied as coprecipitants for water analysis by ICP-AES. Each of these coprecipitants can collect many elements; however, no application has been reported for the simultaneous concentration of all of the above-mentioned regulated elements.

In this work, we sought coprecipitants that have the ability to collect the regulated elements and others as simultaneously as possible in a concentrated salt solution. We found that a hybrid hydroxide system using ytterbium(III), gallium(III), and magnesium(II) is effective for this purpose. Recently, it has been reported that ytterbium(III) hydroxide, which is a new coprecipitant, is useful for the concentration of cadmium(II) ions in spring water prior to its graphite furnace atomic absorption spectrometric determination.[20] This coprecipitant can also quantitatively recovered tin(IV), lead(II), bismuth(III), copper(II), chromium(III,VI), manganese(II), cobalt(II), and nickel(II) ions;[20] however, there is no information of the coprecipitation behavior of the elements in a concentrated salt solution and the application to the ICP-AES determination. We found that ytterbium(III) hydroxide is able to recover not only chromium(III), copper(II), and lead(II) ions but also beryllium(II), iron(III), zinc(II), arsenic(V), antimony(III), and selenium(IV) ions in spiked seawater or sodium chloride and sulfate solutions within 10% error. Although the recoveries of manganese(II), cobalt(II), nickel(II), and cadmium(II) ions from the sample solutions were insufficient with only ytterbium(III) hydroxide, the recoveries were considerably improved when gallium(III) hydroxide associated with magnesium(II)[9–14] was used in combination with ytterbium(III) hydroxide. Gallium(III) hydroxide with magnesium(II) is an excellent collector for a number of elements in seawater; however, the recoveries of some elements such as copper(II),[13] cadmium(II),[11–13] and antimony(III)[11,13,14] ions were insufficient. The coprecipitation method with a hybrid hydroxide system using ytterbium(III), gallium(III), and magnesium(II) simultaneously concentrated 13 elements, including the 9 regulated elements mentioned above, in concentrated salt solutions. The concentrated elements were determined by ICP-AES without

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Table 1. Operating Conditions for ICP-AES

Radio frequency output	1.3 kW		
Argon gas flow rate			
Plasma gas	15 L min^{-1}		
Auxiliary gas	0.5 L min^{-1}		
Neblizing gas	0.8 L min^{-1}		
Pump parameter			
Sample flush time	10 s		
Sample flush flow rate	4.0 mL min^{-1}		
Sample flow rate	1.2 mL min^{-1}		
Read delay time	30 s		
Reading time	auto (min. 0.2 s–max. 20 s)		
Analytical wavelength/nm			
	Be, 313.107	Cr, 206.149	Mn, 257.610
	Fe, 238.204	Co, 228.616	Ni, 221.647
	Cu, 324.754	Zn, 213.856	As, 188.979
	Se, 196.026	Cd, 214.438	Sb, 206.833
	Pb, 220.353	Y, 371.030 (internal standard)	

any interference. In addition, a rapid coprecipitation technique[21–26] was applied to this method. By using centrifugation combined with decantation in the separation of the precipitate, which is a tedious and time-consuming process in coprecipitation, the time required for the concentration of the elements was shortened.

This paper describes the fundamental conditions for the coprecipitation of some elements in concentrated salt solutions with a hybrid hydroxide system using ytterbium(III), gallium(III), and magnesium(II) and the application of a rapid coprecipitation technique to this coprecipitation. The availability of this coprecipitation technique for the concentration of 13 elements in some water samples, including the certified reference materials, prior to their ICP-AES determination is also evaluated.

Experimental

Apparatus. For measurements of elements, a Perkin-Elmer Optima 3000XL inductively coupled plasma atomic emission spectrometer was used; the operating conditions are summarized in Table 1. The pH was measured by using a Horiba F-22 pH meter. A Kubota model 5400 centrifuge was used for separation of the precipitate.

Reagents. The water used for all of the experiments was purified by distillation and ion exchange, and then was passed through a Millipore Milli-Q purification system. A 10 g L^{-1} ytterbium(III) solution was prepared by dissolving ytterbium(III) oxide (99.95%, Kanto Kagaku) in 30 mL of concentrated hydrochloric acid (for poisonous metal analysis, Kanto Kagaku) and diluting the mixture to 500 mL with Milli-Q water. Gallium metal (99.9999%, Nacalai Tesque) was dissolved with 10 mL of concentrated hydrochloric acid and 0.5 mL of concentrated nitric acid (for poisonous metal analysis, Kanto Kagaku), and the solution was then diluted to 100 mL with Milli-Q water for the preparation of a 10 g L^{-1} gallium(III) solution. A solution containing 10 g L^{-1} of the magnesium(II) ion was prepared by dissolving magnesium(II) oxide (guaranteed reagent grade, Wako Pure Chemical Industries) with 50 mL of concentrated hydrochloric acid and diluting the solution to 500 mL with Milli-Q water. A solution containing 5 g L^{-1} of the indium(III) or aluminum(III) ion was also prepared by dissolving indium(III) sulfate (99.9%, Mitsuwa Chemicals) or aluminum(III) chloride hexahydrate (guaranteed reagent grade, Kanto Kagaku) in a small amount of concentrated hydrochloric acid and diluting the solution with Milli-Q water. The commercially available ICP multi-element standard solution XVI, which contains beryllium(II), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), arsenic(V), selenium(IV), molybdenum(VI), cadmium(II), antimony(III), lead(II), and some other ions (100 mg L^{-1} each, Merck), as well as a stock solution of the yttrium(III) ion (1000 mg L^{-1}, Kanto Kagaku), was used. The standard solution was diluted to the desired concentration in each experiment. The other reagents, including sodium hydroxide, were of guaranteed or analytical reagent grade.

Table 2. Ranges of Calibration Curves and Detection Limits for 13 Elements

Element	Range of calibration curve$^{a)}$/μg	Detection limit$^{b)}$ /μg
Be(II)	0.01–100	0.003
Cr(III)	0.05–100	0.017
Mn(II)	0.2–100	0.039
Fe(III)	0.2–100	0.051
Co(II)	0.3–100	0.077
Ni(II)	0.3–100	0.086
Cu(II)	0.1–100	0.025
Zn(II)	0.5–100	0.13
As(V)	0.2–100	0.041
Se(IV)	0.4–100	0.12
Cd(II)	0.1–100	0.018
Sb(III)	0.4–100	0.12
Pb(II)	0.5–100	0.11

a) The amount in the initial sample solution. b) 3σ. $n = 5$.

Recommended Procedure. To a sample solution (up to 150 mL) containing the 13 elements shown in Table 2, 5 mL of the ytterbium(III) solution, 1 mL of the gallium(III) solution, and, when the content of the magnesium(II) ion in the sample solution is small, 5 mL of the magnesium(II) solution as carriers, and 100 μL of the yttrium(III) solution as an internal standard were added. Through the use of a pH meter, the pH of the solution was adjusted to 9 with approximately 1 and 0.1 mol L^{-1} sodium hydroxide solutions. After the solution containing formed precipitate stood

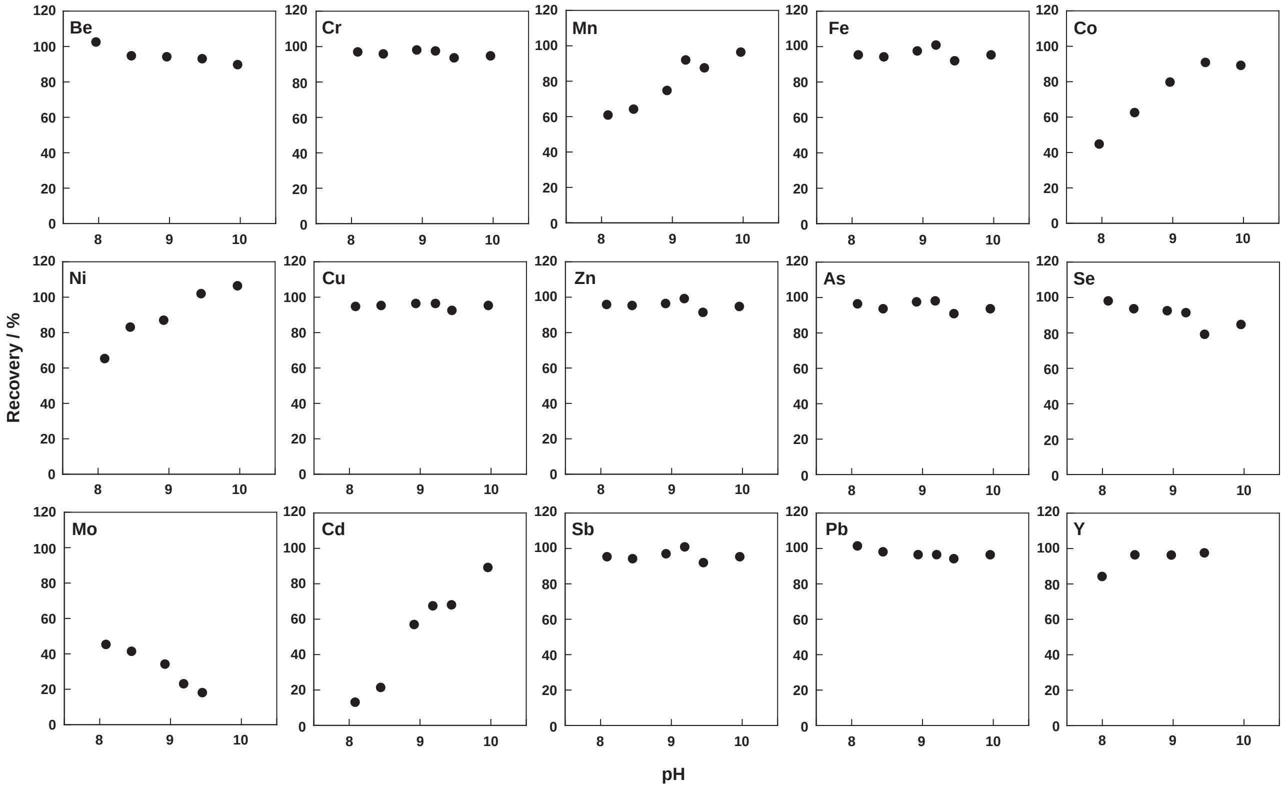

Fig. 1. Effect of pH on the recoveries of some elements by ytterbium(III) hydroxide. Sample, seawater (100 mL); each element, 5 µg (except for Y(III), 100 µg); Yb(III), 50 mg.

for approximately 5 min, a portion of the supernatant solution was discarded by decantation; in this operation, some loss of the precipitate is permitted. The solution containing the precipitate was transferred to a 50-mL polyethylene centrifuge tube, and the precipitate was centrifuged at 3500 rpm for 5 min. After the supernatant solution was discarded, the precipitate was washed by adding approximately 10 mL of Milli-Q water to the tube and then shaking it. The suspension was centrifuged again, and the separated precipitate was dissolved with 3 mL of approximately 1 mol L^{-1} hydrochloric acid. The amounts of the elements were determined by ICP-AES using internal standardization with yttrium.

A blank, using Milli-Q water as a sample solution, was run using the same procedure as for the sample solution.

Results and Discussion

Coprecipitation with Ytterbium(III) Hydroxide. Recently, some rare earth elements, including samarium(III),[27] erbium(III),[28] and ytterbium(III),[20] have been proposed as carriers for coprecipitation of some trace elements prior to their atomic absorption spectrometric determination. In this work, ytterbium(III) was chosen as a main carrier because the presence of ytterbium has little influence in the ICP-AES determination of the elements investigated.

The recoveries of some elements were investigated using 100 mL of seawater (sampled in Toyama Bay, Toyama, Japan) as a concentrated salt solution; the sample solution was filtered through a membrane filter (Nihon Millipore, Omnipore membrane, pore size of 0.45 µm) before each experiment. In the coprecipitation, the precipitate that formed was filtered by suction using the membrane filter (pore size of 0.2 µm) and dissolved with 2 mL of 6 mol L^{-1} hydrochloric acid; the solution was diluted to 10 mL. For beryllium(II), iron(III), zinc(II), arsenic(V), selenium(IV), and antimony(III) ions as well as chromium(III), copper(II), and lead(II) ions, more than 90% recoveries were obtained at pH 9 by using 30 mg of the ytterbium(III) ion. The recoveries of manganese(II), cobalt(II), nickel(II), molybdenum(VI), and cadmium(II) ions increased with an increase in the added amount of the ytterbium(III) ion; however, the recoveries were less than 90% even when 100 mg of the ytterbium(III) ion was added. The addition of a large amount of the ytterbium(III) ion was sometimes troublesome during the separation of the precipitate because a large amount of precipitate was formed. In this method, 50 mg of the ytterbium(III) ion was added for the coprecipitation.

The added ytterbium(III) ion (50 mg) was precipitated quantitatively in 100 mL of seawater as well as Milli-Q water in a pH range of 8 to at least 12. Beryllium(II), iron(III), zinc(II), arsenic(V), and antimony(III) ions as well as chromium(III), copper(II), and lead(II) ions were quantitatively coprecipitated in the pH range of 8–10 (Fig. 1). For manganese(II), cobalt(II), nickel(II), and cadmium(II) ions, the recoveries increased with an increase in the pH. The recoveries of molybdenum(VI) and selenium(IV) ions, which were present as oxo anions in the aqueous solution, decreased with an increase in the pH; for the selenium(IV) ion, more than 90% recoveries were obtained at pH 9 or below. On the other hand, the amount of the precipitate increased when the pH was adjusted to more than 9.5. In this method, the coprecipitation was carried out at pH 9, the objective being the efficient coprecipitation of the selenium(IV) ion and the easy separation of the precipitate.

Use of Another Carrier Combined with Ytterbium(III). To improve the recoveries of manganese(II), cobalt(II), nickel(II), molybdenum(VI), and cadmium(II), the use of another carrier in combination with the ytterbium(III) ion was investigated. Aluminum(III),[8] gallium(III),[9–14] and indium(III)[15] ions were examined as potential carriers because they have been applied to ICP-AES determination. The addition of 10 mg of the indium(III) ion improved the recoveries of manganese(II), cobalt(II), and nickel(II) ions; however, the recovery of the cadmium(II) ion was less than 90% at pH 9. By adding 10 mg of the aluminum(III) or gallium(III) ion, manganese(II), cobalt(II), nickel(II), and cadmium(II) ions were recovered at 93–102%. It is well known that the precipitation of the magnesium(II) ion in seawater is induced by the precipitation of aluminum(III)[8] and gallium(III)[9–14] ions. The amount of the precipitate increased greatly when the aluminum(III) ion was added, although a slight increase of the precipitate amount was observed when the gallium(III) ion was added. The recovery of molybdenum(VI) from seawater was less than 40% even when the aluminum(III), gallium(III), or indium(III) ion with the ytterbium(III) ion was added. In this method, the gallium(III) ion was selected as another carrier in combination with the ytterbium(III) ion, and the concentration of the molybdenum(VI) ion was reluctantly abandoned.

The necessary amount of the gallium(III) ion in combination with 50 mg of the ytterbium(III) ion was then investigated for the quantitative recoveries of manganese(II), cobalt(II), nickel(II), and cadmium(II) ions from 100 mL of seawater. For the quantitative coprecipitation of the cadmium(II) ion, more than 7.5 mg of the gallium(III) ion was required, although 92–105% recoveries of the other elements were obtained by adding at least 1 mg of the gallium(III) ion. From these results, 10 mg of the gallium(III) ion was added in this method.

The recoveries of 13 elements at pH 9 from spiked seawater by adding only the ytterbium(III) ion, gallium(III) ion, and both ytterbium(III) and gallium(III) ions are summarized in Fig. 2. When both 50 mg of the ytterbium(III) ion and 10 mg of the gallium(III) ion were added, the recoveries of the 13 elements ranged from 94–102%. In this case, approximately 10.5 mg of magnesium(II) in 100 mL of seawater, which contained approximately 74 mg of the magnesium(II) ion, was precipitated with ytterbium(III) and gallium(III). The recoveries of selenium(IV) and antimony(III) ions were very low when only the gallium(III) ion was added. Since the amount of magnesium(II) precipitated with ytterbium(III) hydroxide was approximately 0.5 mg, the quantitative coprecipitation of selenium(IV) and antimony(III) ions was due to the collection ability of ytterbium(III) hydroxide. Both the recoveries of cobalt(II) and nickel(II) ions, which were insufficient with only ytterbium(III) hydroxide, were 102% when only 10 mg of the gallium(III) ion was added to the solution; in this case, approximately 9.9 mg of the magnesium(II) ion was precipitated with gallium(III) hydroxide. When 100 mL of 10%w/v sodium chloride or 2.5%w/v sodium sulfate solution was used as a sample solution and both ytterbium(III) and gallium(III) ions were added, the recoveries of cobalt(II) and nickel(II) ions ranged from 98–104%. This result seems to indicate that the quantitative recoveries of cobalt(II) and nickel(II) ions are greatly facilitated by the collection ability of gallium(III) hydroxide. On the other hand, the recovery of the cadmium(II) ion from the sodium chloride solution was reduced to 74%, and that of manganese(II) from the sodium sulfate solution was also decreased to 76%, although the recoveries of the cadmium(II) ion from the sodium sulfate solution and the manganese(II) ion from the sodium chloride solutions were 107 and 95%, respectively. However, the recoveries were improved by the addition of 50 mg of the magnesium(II) ion with ytterbium(III) and gallium(III) ions; in this case, approximately 11.1 or 5.9 mg of magnesium(II) was precipitated with ytterbium(III) and gallium(III) in the sodium chloride or sodium sulfate solution, respectively. These results suggest that not only hydroxides of ytterbium(III) and gallium(III), but also the precipitated magnesium(II) contributes to the quantitative coprecipitation of manganese(II) and cadmium(II) ions. In this method, 50 mg of the magnesium(II) ion was also added to the sample solution, which did not contain a large amount of the magnesium(II) ion.

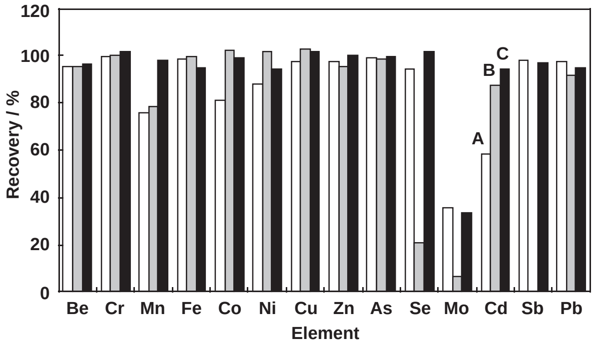

Fig. 2. Recoveries of some elements by coprecipitation with hydroxides of ytterbium(III) and/or gallium(III) associated with magnesium(II). Sample, seawater (100 mL); each element, 5 µg; Yb(III), 50 mg; Ga(III), 10 mg; pH, 9. Only ytterbium(III) ion (A), only gallium(III) ion (B), and both ytterbium(III) and gallium(III) ions (C) were added to the sample solution.

The recoveries of the 13 elements reached 90–110% within 5 min after the formation of the precipitate, and remained almost constant for at least 3 h.

Application to Rapid Coprecipitation Technique. In order to simplify the coprecipitation operation, a rapid coprecipitation technique[21–26] was applied to the coprecipitation with a hybrid hydroxide system using ytterbium(III), gallium(III), and magnesium(II).

Selection of Internal Standard: In the rapid coprecipitation technique, the amount of the coprecipitant in the final solution after coprecipitation must be determined or estimated, because the contents of the desired elements in the initial sample solution are calculated based on the ratio of the amount of added coprecipitant to a part of the amount of precipitated coprecipitant. An internal standardization is conveniently available for the estimation of the amount of the coprecipitant.[25,26] In this method, yttrium was selected as the internal standard because this element is widely utilized for internal standardization in ICP-AES determination.[29] The element used for the internal standard in the rapid coprecipitation technique must satisfy four requirements:[25,26] 1) The amount of the internal standard element in the sample solution must be negligibly small, 2) the internal standard element must be quantitatively coprecipitated, 3) the loss of the internal standard element must be proportional to the loss of the precipitate and the desired elements in the precipitate separation process, and 4) the internal standard element must be readily determined. In general, the concentration of the yttrium(III) ion in a concentrated salt solution such as seawater is extremely low.[30] The quantitative recovery of the yttrium(III) ion was obtained over a wide pH range as shown in Fig. 1. The amount of the yttrium(III) ion in solution was easily determined by ICP-AES. Thus, the relationship between the emission intensity of ytterbium or gallium and that of yttrium after coprecipitation was investigated. In this experiment, the precipitate was formed in 100 mL of a seawater sample containing 100 µg of the yttrium(III) ion, 50 mg of the ytterbium(III) ion, 10 mg of the gallium(III) ion, and 5 µg of the 13 elements at pH 9. A part of the solution containing the precipitate was discarded by decantation before the separation of the precipitate. The amounts of ytterbium, gallium, and yttrium in the final solution were measured by ICP-AES after the filtration and subsequent dissolution of the precipitate. Since proportional relationships were obtained, the amount of coprecipitant can be estimated by measuring yttrium. For the relationships between the emission intensity of yttrium and those of the 13 elements, good correlations were also obtained. From these results, the third requirement mentioned above was satisfied. The rapid coprecipitation technique combined with the internal standardization can be applied to the coprecipitation of the 13 elements with a hybrid hydroxide system using ytterbium(III), gallium(III), and magnesium(II).

Separation and Dissolution of Precipitate: In the proposed method, centrifugation combined with decantation was adopted for the separation of the precipitate. When the solution after the pH adjustment stood for approximately 5 min to settle down the formed precipitate and then the supernatant solution was discarded by decantation, a significant amount of the precipitate could be transported to a 50-mL polyethylene centrifuge tube. The recovery of the yttrium(III) ion, nearly equal to the recovery of the coprecipitant, reached approximately 80% for more than 5 min at 3500 rpm, the maximum speed of the centrifuge used. The centrifuged precipitate was readily dissolved with 3 mL of 1 mol L^{-1} hydrochloric acid; in this case, the final volume of the solution was approximately 5 mL. The recoveries of some elements decreased by using centrifugation combined with decantation instead of filtration. This result might have been due to the interference of matrix ions in the residual mother liquor in the centrifuge tube after the supernatant solution was discarded. However, the interference was effectively reduced by washing the precipitate after centrifugation. The quantitative recoveries of the 13 elements were obtained by washing with 10 mL of Milli-Q water and then re-centrifuging at 3500 rpm for 5 min.

In this method, since the amount of the formed precipitate was larger than those in the methods using ytterbium(III) hydroxide[20] and gallium(III) hydroxide with magnesium(II),[11–14] the time required for the filtration (the membrane filter, pore size of 0.2 or 1.0 µm, diameter of 25 mm) was approximately 1 h or more. The filtration time could be shortened by increasing the diameter of the filter; however, the adjustment of the final volume was troublesome. The method proposed here did not require the complete collection of the precipitate or the strict adjustment of the final volume, so the operation was quite simple and rapid.

Initial Volume of Sample Solution: The recoveries of the 13 elements were investigated using 150–750 mL of seawater samples spiked with 5 µg of these elements. The recoveries of beryllium(II), chromium(III), iron(III), copper(II), and lead(II) ions from 750 mL ranged from 94–103%; the hybrid hydroxide system using ytterbium(III), gallium(III), and magnesium(II) was effective for the coprecipitation of these elements. More than 90% recoveries were obtained from 500 mL for cobalt(II) and nickel(II) ions, 200 mL for manganese(II), arsenic(V), selenium(IV), and cadmium(II) ions, and 150 mL for the antimony(III) ion. From these results, up to 150 mL of the sample solution was utilized in the proposed method; it was attractive that the 13 elements including selenium(IV) and antimony(III) ions could be collected simultaneously from the concentrated salt solution, although the concentration factor was less than those in the methods using ytterbium(III) hydroxide[20] and gallium(III) hydroxide with magnesium(II).[11]

Calibration Curves. The relationships between the amount of each element in the initial sample solution and the emission intensity ratio of each element to yttrium were investigated. Straight lines were obtained for all of the elements over the ranges summarized in Table 2. The detection limits, defined as 3 times the standard deviations obtained from 10 replicate determinations of the blank, are appended in Table 2; the obtained values were much lower than the allowable levels for the elements in the National Effluent Standards.[1] The blank values (mean ± standard deviation, $n = 5$) were $0.40 \pm 0.00_6$ µg for manganese(II), $0.70 \pm 0.00_7$ µg for iron(III), 0.16 ± 0.04 µg for cobalt(II), and 0.38 ± 0.08 µg for zinc(II) when ytterbium(III), gallium(III), and magnesium(II) ions were added; with the addition of only ytterbium(III) and gallium(III) ions, the values were $0.35 \pm 0.00_7$ µg for manganese(II), $0.21 \pm 0.00_9$ µg for iron(III), 0.15 ± 0.03 µg for cobalt(II), and 0.24 ± 0.06 µg for zinc(II). The blanks for the other elements could be neglected in most instances because those were extremely small. From these results, the calibration curves were prepared using the same carriers added to the sample solutions, although the difference of the slopes with or without the addition of the magnesium(II) ion was not significant.

Recoveries of 13 Elements from Spiked Water Samples. The recoveries of 13 elements were investigated using 100 mL of spiked Milli-Q water, seawater, a 10%w/v sodium chloride solution, and 2.5%w/v sodium sulfate solution according to the recommended procedure. For the investigations using the sodium chloride and sodium sulfate solutions, the magnesium(II) ion was added with ytterbium(III) and gallium(III) ions. The recoveries of the elements ($n = 5$) ranged from 92–103% with the relative standard deviation range of 2–6% for Milli-Q water, 94–102% with 1–4% for seawater, 91–110% with 1–3% for sodium chloride solution, and 91–109% with 1–5% for sodium sulfate solution. The relative standard deviations obtained were nearly equal to those in the methods using ytterbium(III) hydroxide[20] and gallium(III) hydroxide with magnesium(II),[11,14] in which the precipitate was separated by

Table 3. Results of Determination of 13 Elements in the Certified Reference Materials[a]

Element	EU-L-1 (Wastewater)		ES-L-1 (Ground water)	
	Found[b] /mg L^{-1}	Consensus value /mg L^{-1}	Found[b] /mg L^{-1}	Consensus value /mg L^{-1}
Be(II)	$0.034 \pm 0.000_4$	0.03	0.055 ± 0.002	0.052
Cr(III)	0.154 ± 0.002	0.15	0.021 ± 0.001	0.020
Mn(II)	0.274 ± 0.006	0.30	0.094 ± 0.003	0.096
Fe(III)	0.104 ± 0.002	0.11	0.020 ± 0.001	0.021
Co(II)	0.216 ± 0.003	0.20	0.055 ± 0.002	0.051
Ni(II)	0.211 ± 0.004	0.20	0.011 ± 0.001	0.010
Cu(II)	0.262 ± 0.016	0.26	0.021 ± 0.001	0.020
Zn(II)	0.056 ± 0.001	0.06	$0.020 \pm 0.000_4$	0.021
As(V)	0.217 ± 0.003	0.21	0.009 ± 0.001	0.011
Se(IV)	0.070 ± 0.002	0.07	N.D.[d]	(0.001)[c]
Cd(II)	0.069 ± 0.001	0.06	$0.011 \pm 0.000_2$	0.010
Sb(III)	0.054 ± 0.001	0.06	0.006 ± 0.001	0.006
Pb(II)	0.101 ± 0.002	0.10	(0.002 ± 0.001)[e]	(0.002)[c]

a) Sample volume, 100 mL. b) Mean ± standard deviation ($n = 5$). c) The values are not certified; they are listed for information only. d) N.D.: Not detected. e) The result was estimated by the extrapolation of the calibration curve.

Table 4. Results for Determination of 13 Elements in Some Commercially Available Salts

Element	Added /µg	Salt 1[a]			Salt 2[b]		
		Conc.[c] /µg g^{-1}	Found[d] /µg	Recovery /%	Conc.[c] /µg g^{-1}	Found[d] /µg	Recovery /%
Be(II)			N.D.[e]			N.D.[e]	
	5		5.0 ± 0.2	101		4.7 ± 0.2	94
Cr(III)			N.D.[e]			N.D.[e]	
	5		5.2 ± 0.3	103		4.8 ± 0.1	95
Mn(II)		0.04	$0.4_0 \pm 0.1_0$		0.05	$0.2_4 \pm 0.0_8$	
	5		5.7 ± 0.1	105		5.0 ± 0.2	95
Fe(III)		(0.00_8)	$(0.0_8 \pm 0.0_6)$[f]		0.07	$0.3_5 \pm 0.0_9$	
	5		5.5 ± 0.3	108		5.4 ± 1.0	102
Co(II)			N.D.[e]			N.D.[e]	
	5		5.2 ± 0.1	103		4.7 ± 0.2	93
Ni(II)		0.03	$0.2_6 \pm 0.0_5$			N.D.[e]	
	5		5.2 ± 0.2	99		4.8 ± 0.1	95
Cu(II)		0.14	$1.3_7 \pm 0.0_9$		(0.0_1)	$(0.0_6 \pm 0.1_4)$[f]	
	5		6.8 ± 0.5	108		5.0 ± 0.2	98
Zn(II)			N.D.[e]		(0.0_3)	$(0.1_6 \pm 0.1_0)$[f]	
	5		5.2 ± 0.4	106		4.8 ± 0.2	93
As(V)		(0.00_7)	$(0.0_7 \pm 0.0_1)$[f]		0.03	$0.1_7 \pm 0.0_5$	
	5		5.4 ± 0.3	106		5.0 ± 0.1	96
Se(IV)			N.D.[e]			N.D.[e]	
	5		5.1 ± 0.2	104		4.7 ± 0.1	95
Cd(II)			N.D.[e]			N.D.[e]	
	5		4.8 ± 0.3	97		4.6 ± 0.1	93
Sb(III)			N.D.[e]			N.D.[e]	
	5		5.4 ± 0.2	107		4.8 ± 0.1	98
Pb(II)			N.D.[e]			N.D.[e]	
	5		5.0 ± 0.3	100		4.6 ± 0.1	91

a) Sample, 10.00 g in 100 mL. b) Sample, 5.00 g in 100 mL. c) Conc.: Concentration. d) Mean ± standard deviation ($n = 3$). e) N.D.: Not detected. f) The result was estimated by the extrapolation of the calibration curve.

filtration. These results indicate that coprecipitation with a hybrid hydroxide system using ytterbium(III), gallium(III), and magnesium(II) would be applicable to the analyses of these concentrated salt solutions.

Determination of 13 Elements. According to the recommended procedure, the determination of the 13 elements in the certified reference materials, *Enviro*MAT™ wastewater (EU-L-1, SCP Science) and ground water (ES-L-1, SCP Science),

Table 5. Results for Determination of 13 Elements in Effluent[a)]

Element	Added /µg	Conc.[b)] /$\mathrm{mg\,L^{-1}}$	Found[c)] /µg	Recovery /%
Be(II)			N.D.[d)]	
	5		5.2 ± 0.1	105
Cr(III)			N.D.[d)]	
	5		4.9 ± 0.1	98
Mn(II)		(0.002)	$(0.1_8 \pm 0.0_1)$[e)]	
	5		5.4 ± 0.1	104
Fe(III)		0.041	$4.0_7 \pm 0.0_6$	
	5		9.2 ± 0.2	103
Co(II)			N.D.[d)]	
	5		5.1 ± 0.1	102
Ni(II)		0.032	$3.2_1 \pm 0.0_1$	
	5		7.9 ± 0.1	94
Cu(II)		0.004	$0.4_3 \pm 0.0_1$	
	5		5.5 ± 0.2	101
Zn(II)		0.025	$2.4_9 \pm 0.0_8$	
	5		7.6 ± 0.2	103
As(V)		(0.001)	$(0.1_2 \pm 0.1_0)$[e)]	
	5		5.1 ± 0.1	99
Se(IV)			N.D.[d)]	
	5		5.1 ± 0.2	104
Cd(II)			N.D.[d)]	
	5		4.9 ± 0.1	99
Sb(III)		(0.001)	$(0.1_4 \pm 0.0_3)$[e)]	
	5		5.0 ± 0.1	98
Pb(II)			N.D.[d)]	
	5		4.9 ± 0.1	101

a) The effluent was sampled at University of Toyama (Toyama prefecture, Japan). Sample volume, 100 mL. b) Conc.: Concentration. c) Mean ± standard deviation ($n = 3$). d) N.D.: Not detected. e) The result was estimated by the extrapolation of the calibration curve.

was attempted. The consensus values of the magnesium(II) ion were 1.24 $\mathrm{mg\,L^{-1}}$ for EU-L-1 and 0.110 $\mathrm{mg\,L^{-1}}$ for ES-L-1, so 50 mg of the magnesium(II) ion was added for each investigation. The results are shown in Table 3; for all elements, the obtained results were nearly equal to the consensus values. The time required for the preconcentration was approximately 20 min.

The determination of the 13 elements in some commercially available salts and an effluent was also attempted. For the analysis of effluent, 5 mL of concentrated hydrochloric acid was added, and the solution was then boiled for 10 min before coprecipitation.[29] The obtained results are summarized in Tables 4 and 5. Some elements were determined, and all of the spiked elements were recovered within 10% error.

Conclusion

Coprecipitation with a hybrid hydroxide system using ytterbium(III), gallium(III), and magnesium(II) has been shown to be an effective technique for the simultaneous preconcentration of 13 elements in a concentrated salt solution. Beryllium(II), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), arsenic(V), selenium(IV), cadmium(II), antimony(III), and lead(II) were collected quantitatively from seawater and from sodium chloride and sulfate solutions without any interference by matrix ions at pH 9. By applying a rapid coprecipitation technique combined with internal standardization using yttrium, the operation was simplified, and the time required for the preconcentration was approximately 20 min. The collected elements were readily determined by ICP-AES using internal standardization. Although only up to 150 mL of the sample solution was available for the simultaneous concentration of the 13 elements, the detection limits in this method were in the range of 0.003 µg (for beryllium(II)) to 0.13 µg (for zinc(II)). The proposed method was applied to the analyses of the certified reference materials (EU-L-1 and ES-L-1), and good results were obtained. The method could also contribute to the analyses of effluents from industrial facilities as well as some salt samples.

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