Rapid Coprecipitation Technique Using Yttrium Hydroxide for the Preconcentration and Separation of Trace Elements in Saline Water Prior to Their ICP-AES Determination

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Yttrium hydroxide quantitatively coprecipitated Be(II), Ti(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) at pH 9.6 – 10.0 for seawater and pH 10.5 – 11.4 for a table-salt solution. The coprecipitated elements could be determined by inductively coupled plasma atomic emission spectrometry; yttrium was used as an internal standard element. The detection limits ranged from 0.001₆ µg (Mn(II)) to 0.22 µg (Zn(II)) in 100 mL of sample solutions. The operation time required to separate 11 elements was approximately 30 min.

(Received May 25, 2007; Accepted June 18, 2007; Published August 10, 2007)

It is important to determine trace elements in environmental samples from the viewpoint of environmental management and/or protection from hazardous infection¹ as well as comprehension of the distribution of trace elements in the environment.² Recently, multielement profiling analysis, in which major-to-ultratrace elements are determined and the distribution patterns of the elements are analyzed, has gathered attention to provide information about the elemental cycle in the environment.^{3,4}

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a powerful method for multi-elemental analysis.⁵ For the determination of trace elements in environmental water samples, however, a preconcentration/separation technique is often required because of a lack of sensitivity and interference by matrices in the samples.⁵ Among various preconcentration/separation techniques, coprecipitation with metal hydroxide is widely used for the ICP-AES determination of trace elements.⁶⁻²³ In the coprecipitation method, however, the required quantitative separation of the precipitate is troublesome and time-consuming. To avoid such a quantitative separation process, a rapid coprecipitation technique has been proposed.²³⁻²⁹ In this technique, a carrier element used for coprecipitation also plays a role as an internal standard element. The carrier element is precipitated to coprecipitate trace elements in sample solutions. The precipitate is separated by using a decantation, short-time centrifugation, and so on; in this process, a part of the precipitate might be lost together along with a portion of the coprecipitated trace elements. However, the total amounts of trace elements in the sample solution can be determined by using the carrier element as an internal standard element, because the loss of trace elements is generally proportional to that of the carrier element.

Yttrium hydroxide³⁰⁻³² has been used as a coprecipitant for the separation of some impurities, including tin³⁰ and manganese³¹ in zinc and copper metals. It is of great advantage for trace elemental analysis that yttrium compounds with high purity are commercially available. Yttrium as a carrier element has an insignificant spectral interference for the ICP-AES determination

of many elements. However, to our knowledge, no application of yttrium hydroxide to the preconcentration/separation of trace elements in environmental water samples has been reported.

In this work, we developed a preconcentration/separation method based on a rapid coprecipitation technique using yttrium hydroxide as a coprecipitant for the determination of trace elements in environmental water samples, especially saline water. In this method, 11 trace elements in 100 mL of saline water could be coprecipitated using a small amount of yttrium and a constant amount of sodium hydroxide solution. After separation and dissolution of the precipitate, the amount of trace elements could be determined by ICP-AES; yttrium could be used as an internal standard element. The developed method was simple and rapid, and was satisfactorily applicable to analyses of certified reference material and table salts.

Experimental

Apparatus

A Perkin Elmer Optima 3000DV inductively coupled plasma atomic emission spectrometer was used to measure elements. The emission intensity of each element was measured in the axial view mode at each wavelength summarized in Table 1; the other operating conditions were the same as those reported previously.²³ The pH measurement was carried out by using a Horiba F-22 pH meter. A Kubota Model 5400 centrifuge was used for separating the precipitate.

Reagents

Purified water obtained by a Millipore Milli-Q purification system was used for all experiments. A yttrium solution (1 g L⁻¹) was prepared by dissolving yttrium oxide (99.99%, Nacalai Tesque) in 5 mL of concentrated hydrochloric acid (for poisonous metal analysis, Kanto Chemical) and diluting to 100 mL with purified water. A commercially available ICP multi-element standard solution XVI, which contains 21 elements including Be(II), Ti(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) (100 mg L⁻¹ each, Merck), was

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Table 1 Analytical wavelengths, blank values, detection limits, and ranges of calibration curves for 11 elements

Element	Analytical wavelength/nm	Detection limit ^a / μg in 100 mL	Range of calibration curve/ μg in 100 mL
Be	313.107	0.001 ₈	0.007 – 10
Ti	334.940	0.032	0.10 – 10
Cr	267.715	0.005 ₄	0.02 – 10
Mn	257.610	0.001 ₆	0.015 – 10
Fe	239.562	0.029	0.10 – 10
Co	228.616	0.005 ₅	0.015 – 10
Ni	232.003	0.017	0.070 – 10
Cu	224.700	0.080	0.20 – 10
Zn	206.200	0.22	0.70 – 10
Cd	228.802	0.006 ₃	0.02 – 10
Pb	220.353	0.063	0.20 – 10
Y ^b	371.030		

a. 3σ ($n = 10$).

b. Internal standard element.

used. The standard solution was diluted to a desired concentration in each experiment. The other reagents were of guaranteed or analytical reagent grade.

Sample solutions

For investigating the optimum conditions for coprecipitation, seawater and a table-salt solution was used as sample solutions. Seawater was sampled in Toyama Bay (Toyama, Japan); it was filtered through a membrane filter (Nihon Millipore, Omnipore membrane, pore size of 0.45 μm) before each experiment. A table-salt solution was prepared by dissolving 5.00 g of table salt (Ishikawa, Japan) with 100 mL of purified water. The appropriate amount of the standard solution containing trace elements was added to the seawater and table-salt solutions. For determining trace elements, 5.00 or 10.00 g of each table salt was dissolved with 100 mL of purified water.

Procedure for separation of trace elements

The sample solution (100 mL) was taken into (for seawater) or prepared in (for table-salt solution) a 175 mL of polystyrene centrifuge bottle (Nalgene). To the solution, 5 mL of a 2.0 mol L^{-1} nitric acid solution and 1 mL of a yttrium solution (1 g L^{-1}) were added. A precipitate was formed after adding 3.7 mL of a 3 mol L^{-1} sodium hydroxide solution. The solution was allowed to stand for approximately 10 min. After centrifugation at 3500 rpm for 5 min, the supernatant solution was discarded. Purified water (10 mL) was added to the centrifuge bottle, which was then shaken by hand. The precipitate was re-centrifuged and dissolved with 5 mL of 1 mol L^{-1} nitric acid. The trace elements in these solutions were determined by ICP-AES; yttrium was used as an internal standard element. Solutions for blank tests and calibration curves were also prepared using 100 mL of purified water and purified water spiked with trace elements, respectively, in the same manner for the sample solution.

Results and Discussion

Coprecipitation of trace elements with yttrium hydroxide

Yttrium was quantitatively precipitated at a pH value of more than 11.1 from 100 mL of purified water spiked with 1 mg of yttrium and 5 μg of each trace element. It was found that Be(II), Ti(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Cd(II) were quantitative coprecipitated (within 90 – 111%)

with yttrium hydroxide at pH 11.1 – 12.1. Yttrium hydroxide also quantitatively coprecipitated Zn(II) and Pb(II) at pH 11.1 – 11.3; however, the recoveries of Zn(II) and Pb(II) decreased with increasing the pH above 11.3. In previous reports, yttrium hydroxide was used to coprecipitate some elements, including Sn and Mn in zinc and copper metals by adding aqueous ammonia for pH adjustments.^{30–32} Zn(II) and Cu(II) were quantitatively coprecipitated in our investigations; this would be due to using a sodium hydroxide solution instead of aqueous ammonia.

Yttrium was also almost completely precipitated from 100 mL of seawater, and a table-salt solution at pH more than 9.6. Quantitative recoveries (91 – 106%) were obtained for all 11 elements at pH 9.6 – 10.0 for seawater and at pH 10.5 – 11.4 for the table-salt solution. The difference in the pH ranges for the quantitative precipitation of yttrium and recoveries of trace elements by the different sample solutions was also reported for other coprecipitation systems. In coprecipitation with indium hydroxide,⁶ a quantitative precipitation of indium was achieved at a pH value above approximately 5.5 from artificial seawater, although the precipitation was insufficient at a pH value below approximately 7 from pure water. In gallium coprecipitation,¹³ precipitated gallium increased with increasing the concentration of magnesium ion in solution; the recoveries of trace elements also showed a strong dependence on the concentration of both gallium and magnesium in the solution. In our investigations, the contents of magnesium ions in 100 mL of the seawater and the table-salt solution were 72.4 and 5.8 mg, respectively. The pH ranges of the coprecipitation with yttrium hydroxide would be dependent on the concentration of some constituents, such as magnesium in the sample solutions.

In the coprecipitation method, a pH adjustment using a pH meter was sometimes cumbersome. To simplify the process of adjusting the pH, a constant amount of 3 mol L^{-1} sodium hydroxide solution was added into the sample solutions as an operation in the proposed method. When 3.7 mL of the sodium hydroxide solution was added to 100 mL of purified water, seawater and a table-salt solution containing 5 mL of 2.0 mol L^{-1} nitric acid, 1 mg of yttrium and 5 μg of each trace elements, the solution pH was approximately 11.3, 9.7 and 10.7, respectively. In this case, the recoveries of all 11 trace elements were quantitative. Therefore, 3.7 mL of the sodium hydroxide solution was used for the pH adjustment.

The recoveries of the 11 trace elements reached within 93 – 105% for approximately 10 min after formation of the precipitate. No significant change of the recoveries was observed when the solution was left standing for at least 4 h.

Application to rapid coprecipitation technique

A carrier element used for the rapid coprecipitation technique must satisfy the following requirements:^{26–29} 1) the content of the carrier element in the sample solution must be negligibly small, 2) the carrier element added to the solution must be quantitatively precipitated, 3) the loss of the carrier element must be proportional to that of each trace element in the precipitate-separation process, and 4) the carrier element must be readily determined. In general, the yttrium background level in environmental water samples is negligible compared with the added yttrium in the proposed method (1 mg). Yttrium could be quantitatively precipitated in 100 mL of the seawater, and the table-salt solution by adding 3.7 mL of the sodium hydroxide solution, and sensitively determined by ICP-AES. To verify that yttrium would meet the requirement 3), the relationship between the emission intensity of yttrium and that of each element after coprecipitation was investigated as follows. A part of the formed precipitate was discarded together with the

Fig. 1 Relationship between the emission intensity of yttrium and that of each element after coprecipitation. Sample solution, table-salt solution (○) or purified water (●); sample volume, 100 mL; 2.0 mol L⁻¹ HNO₃, 5 mL; Y, 1 mg; each element, 5 µg; 3 mol L⁻¹ NaOH, 3.7 mL.

Table 2 Removal of some matrix ions after coprecipitation and the centrifugation

Matrix ion	Content/mg	
	Sample solution ^a	Solution after coprecipitation ^b
Na ⁺	2950	0.2
K ⁺	24	N.D.
Mg ²⁺	5.8	1.8
Ca ²⁺	4.6	N.D.

a. A table salt (5.00 g) was dissolved with 100 mL of purified water.

b. The solution was prepared according to the procedure for separation of trace elements described in the Experimental section.
N.D., Not detected.

mother liquor by decantation, and the remaining precipitate was collected by filtration. After dissolution of the precipitate, the yttrium and the trace elements were determined by ICP-AES. As shown in Fig. 1, linear relationships were obtained in all of the elements; that is, the loss of each trace element was proportional to that of the precipitate. Based on these results, it can be concluded that yttrium is applicable to the carrier element for the rapid coprecipitation technique.

The amounts of matrix ions removed by the proposed coprecipitation method are summarized in Table 2. Nearly 100% of sodium, potassium, and calcium ions in 100 mL of the table-salt solution were removed when the precipitate was washed with 10 mL of purified water after centrifugation at 3500 rpm for 5 min. Approximately 30% of magnesium contained in the table-salt solution was remained after washing; this was due to the lower solubility of magnesium hydroxide. Even in this case, the trace elements coprecipitated could be determined using yttrium as an internal standard element without any interference by magnesium.

Calibration curves and detection limits

Calibration curves, which are the relationships between the amounts of the trace elements and the emission intensity ratios of the trace elements to yttrium, could be prepared after coprecipitation using 100 mL of purified water spiked with the

Table 3 Results for the determination of 11 elements in a certified reference material, ES-L-1 (ground water)

	Found ^a / mg L ⁻¹	Certified/ mg L ⁻¹		Found ^a / mg L ⁻¹	Certified/ mg L ⁻¹
Be	0.052 ± 0.000 ₃	0.052	Ni	0.010 ± 0.000 ₀	0.010
Ti	N.D.	—	Cu	0.019 ± 0.000 ₃	0.020
Cr	0.019 ± 0.000 ₂	0.020	Zn	0.020 ± 0.000 ₃	0.021
Mn	0.099 ± 0.001	0.096	Cd	0.010 ± 0.000 ₁	0.010
Fe	0.019 ± 0.000 ₃	0.021	Pb	(0.002 ± 0.000 ₀) ^b	(0.002) ^c
Co	0.049 ± 0.000 ₃	0.051			

a. Mean ± standard deviation ($n = 3$).

b. The result was estimated by the extrapolation of the calibration curve.

c. The value is not certified; it is listed for information only.

N.D., Not detected.

trace elements in the same manner as for the sample solution. Straight lines were obtained for all of the trace elements, as summarized in Table 1. Sub µg L⁻¹ levels of Be(II), Cr(III), Mn(II), Co(II), Ni(II) and Cd(II), and µg L⁻¹ levels of the other elements would be detected by combining the proposed coprecipitation method and ICP-AES.

The detection limits, which were defined as 3-times the standard deviations obtained from 10 replicate determinations of a blank solution after coprecipitation, are appended in Table 1. The blank values were 0.024 ± 0.002 µg (mean ± standard deviation, $n = 10$) for Cr(III), 0.003 ± 0.000₅ µg for Mn(II), 0.18 ± 0.01 µg for Fe(III) and 0.038 ± 0.006 µg for Ni(II); the values for the other elements were less than the detection limits.

Determination of trace elements in certified reference material and table salts

To validate the proposed method, 11 elements in the certified reference material, *EnviroMAT*TM ground water (ES-L-1, SCP Science), were determined. As shown in Table 3, the obtained results were nearly equal to the certified values. The 11 elements in 2 kinds of table salts were also determined. As shown in Table 4, Cr(III), Mn(II), Fe(III), and Ni(II) could be detected. The recovery tests were also carried out using a solution spiked with the trace elements; all of the spiked

Table 4 Results for the determination of 11 elements in table salts

Element	Added/ μg	Salt 1 ^a			Salt 2 ^b		
		Found ^c /μg	Conc./μg g ⁻¹	Recovery, %	Found ^c /μg	Conc./μg g ⁻¹	Recovery, %
Be		(0.009 ± 0.001) ^d	(0.002)		(0.014 ± 0.002) ^d	(0.001)	
	5	5.1 ± 0.0 ₆		101	5.1 ± 0.0 ₈		101
Ti		N.D.			N.D.		
	5	5.1 ± 0.2		102	5.1 ± 0.0 ₄		101
Cr		0.59 ± 0.04	0.12		0.28 ± 0.01	0.028	
	5	5.5 ± 0.1		99	5.2 ± 0.0 ₄		99
Mn		0.40 ± 0.01	0.080		(0.037 ± 0.000 ₇) ^d	(0.004)	
	5	5.2 ± 0.1		96	4.9 ± 0.0 ₁		98
Fe		3.2 ± 0.2	0.65		0.89 ± 0.02	0.089	
	5	8.3 ± 0.2		100	5.7 ± 0.2		96
Co		(0.012 ± 0.001) ^d	(0.002)		N.D.		
	5	4.7 ± 0.1		94	4.7 ± 0.0 ₁		95
Ni		0.79 ± 0.06	0.16		0.53 ± 0.02	0.053	
	5	6.1 ± 0.1		107	5.9 ± 0.0 ₃		107
Cu		N.D.			N.D.		
	5	4.6 ± 0.1		92	4.8 ± 0.0 ₄		96
Zn		N.D.			N.D.		
	5	4.9 ± 0.1		98	5.1 ± 0.1		101
Cd		N.D.			N.D.		
	5	5.3 ± 0.2		105	5.0 ± 0.0 ₁		99
Pb		N.D.			N.D.		
	5	4.7 ± 0.1		94	5.2 ± 0.0 ₃		105

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

elements were recovered within 10% error. The operation time required for separating the trace elements was approximately 30 min. These results indicate that the coprecipitation method will be useful for preconcentration/separation of the trace elements in environmental water samples, including saline water, and will also contribute to the analysis of table salt.

Acknowledgements

The authors are grateful for financial support from the Salt Science Research Foundation (No. 0604).

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