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Preconcentration of Indium(III) by Coprecipitation with Gallium Phosphate for Electrothermal Atomization Atomic Absorption Spectrometry

Shigehiro KAGAYA and Joichi UEDA*
Department of Chemistry, Faculty of Education, Kanazawa University, Kakuma-machi, Kanazawa 920-11
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Synopsis. Gallium phosphate coprecipitates quantitatively 0.5—7.5 μg of indium(III) from 100—500 cm^3 of water at pH 2.5—6.0 and from the same volume of sea water at pH 3.5—6.0. The detection limit (signal/noise=2) is 0.3 $ng\,cm^{-3}$ of indium(III) in 500 cm^3 of the initial sample solution.

The coprecipitation method is widely used for the concentration of trace metal ions. A variety of coprecipitants have been examined.[1—3] For the preconcentration of indium (III) prior to the electrothermal atomization atomic absorption spectrometric determination, hydroxides of hafnium[4] and lanthanum[5] have been proposed. However, these coprecipitants have some disadvantages; hafnium is expensive and lanthanum does not give a linear calibration curve.

Previously, we suggested that gallium phosphate is effective as a collector of trace amounts of lead[6] and tin(IV).[7] In this work, we report that gallium phosphate also coprecipitates indium(III) quantitatively and that the coprecipitated indium(III) can be measured satisfactorily by the electrothermal atomization atomic absorption spectrometry. During the measurement of atomic absorbance, the use of a graphite furnace impregnated with hafnium lowered the interferences from diverse ions and improved the sensitivity and the reproducibility of the determination. The method proposed here overcomes the weak points of hafnium and lanthanum mentioned above and is applicable to the analyses of water and sea water which contain down to 1.0 $ng\,cm^{-3}$ of indium(III).

This paper describes the fundamental conditions for the coprecipitation of indium(III) with gallium phosphate and for the electrothermal atomization atomic absorption spectrometric determination of it.

Experimental

Apparatus. All of the apparatus employed in this work were described previously.[7]

Reagents. The reagents were the same as those described previously,[7] except for that mentioned below.

Standard Indium(III) Solution: A solution containing about 1000 $\mu g\,cm^{-3}$ of indium(III) was prepared by dissolving indium(III) nitrate in a small amount of nitric acid and diluting with 0.5 $mol\,dm^{-3}$ nitric acid. The concentration of this solution was determined by the complexometric back titration with a standard thorium solution using Xylenol Orange as an indicator.

Recommended Procedure. To water or sea water (100—500 cm^3) containing 0.5—7.5 μg of indium(III), 15 mg of gallium and 3 cm^3 of 0.5 $mol\,dm^{-3}$ of phosphoric acid are added. Gallium phosphate is then precipitated at a pH of about 3 for water or 3.5 for sea water using 7 $mol\,dm^{-3}$ ammonia solution. After the precipitate is allowed to settle, the solution is filtered by suction using a 3G4 glass filter. The collected precipitate is dissolved in 1 cm^3 of concentrated nitric acid and the solution is diluted to 25 cm^3 with distilled water. The atomic absorbance of indium(III) is then measured at 325.6 nm.

Results and Discussion

Optimum Conditions for Coprecipitation. The required amount of gallium for the quantitative recovery of indium(III) was more than 5 mg for both 100 and 500 cm^3 of the sample solution. Although the presence of gallium decreased the peak height of indium(III), almost constant peak heights of indium(III) were obtained over a gallium concentration range from 0.4 to 0.8 $mg\,cm^{-3}$ (Fig. 1). The necessary amount of phosphoric acid for the quantitative coprecipitation of indium(III) was more than 0.1×10^{-3} mol for 100 cm^3 of the sample solution and 0.5×10^{-3} mol for 500 cm^3, and the presence of phosphate did not influence the determination of indium(III).

Indium(III) was coprecipitated quantitatively by gallium phosphate from water at a pH range from 2.5—6.0 and from sea water at pH 3.5—6.0. Almost 100% recovery of indium(III) was obtained within a few minutes after the formation of gallium phosphate and the

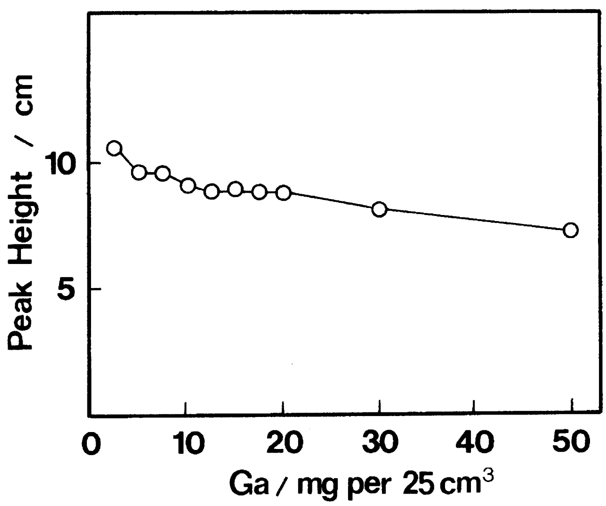

Fig. 1. Effect of the gallium amount on the peak height of indium(III). In(III), 5 μg; 0.5 $mol\,dm^{-3}$ H_3PO_4, 3 cm^3; concd HNO_3, 1 cm^3; final volume, 25 cm^3.

Table 1. Effect of Diverse Ions on the Determination of Indium(III)

Ion	Amount added	Recovery[a)]/%		Ion	Amount added	Recovery[a)]/%	
	mg	A	B		mg	A	B
Li^+	1.0	97.9	97.2	Bi^{3+}	1.0	106.7	100.0
Na^+	1200.0	107.5	101.0	Se(IV)	1.0	105.9	99.5
K^+	100.0	100.0	96.1	Te(IV)	1.0	91.5	96.6
Be^{2+}	1.0	100.0	98.3	Cu^{2+}	1.0	99.0	101.3
Mg^{2+}	200.0	114.4	98.0	Zn^{2+}	1.0	99.0	98.7
Ca^{2+}	250.0	110.6	99.0	Cd^{2+}	1.0	100.0	97.6
Sr^{2+}	1.0	99.0	98.9	La^{3+}	1.0	103.5	98.4
Ba^{2+}	1.0	101.4	96.1	Ti^{4+}	1.0	109.2	96.3
Al^{3+}	1.0	103.6	98.3	V(V)	1.0	112.9	100.0
Tl^+	1.0	96.4	99.4	Cr^{3+}	1.0	105.8	100.8
Tl^{3+}	1.0	97.9	98.9	Mo(VI)	1.0	107.1	102.1
Ge(IV)	1.0	97.4	95.6	W(VI)	1.0	107.6	101.6
Sn^{4+}	1.0	81.5	101.0	Mn^{2+}	1.0	101.8	96.5
Pb^{2+}	1.0	102.6	100.5	Fe^{3+}	1.0	106.0	96.0
As(V)	1.0	99.5	100.6	Co^{2+}	1.0	101.3	96.0
Sb^{3+}	1.0	101.6	98.3	Ni^{2+}	1.0	101.3	100.0

a) A: In(III), 10 μg. A non-impregnated graphite furnace was used. B: In(III), 5 μg. A graphite furnace impregnated with hafnium was used.

recovery remained almost constant on standing for at least 24 h.

For the dissolution of gallium phosphate, nitric acid was preferred to hydrochloric acid because the latter suppressed the peak height of indium(III) seriously, although gallium phosphate dissolved readily in either acid. In this method, 1 cm^3 of concentrated nitric acid was used.

Optimization of Operating Conditions. During the drying stage, almost constant peak heights were obtained with 21 to 25 A of heating current and 20 to 35 s of heating time. In the ashing stage, the maximum peak height was obtained at 110 A and remained almost constant from 20 to 50 s. In the atomizing stage, the peak height became higher with an increase of the atomizing current and reached a maximum at 310 A, which is the highest current obtainable in this apparatus. This peak height remained almost constant from 2.5 to 7.5 s of heating time.

Calibration Curve. A straight line through the point of origin was obtained over the concentration range from 0.02 to 0.30 $\mu g\,cm^{-3}$ of indium(III). The sensitivity and the reproducibility of this method were improved by the use of a graphite furnace impregnated with hafnium; that is, the detection limit (signal to noise ratio=2) and the relative standard deviation of the peak heights obtained from five repeated determinations were 0.3 $ng\,cm^{-3}$ in 500 cm^3 of initial sample solution and 1.3% for 5 μg of indium(III) in 100 cm^3 of sample solution respectively, although the detection limit and the reproducibility were 0.7 $ng\,cm^{-3}$ and 4.2% for 10 μg of indium(III) when a non-impregnated graphite furnace was used.

Interference. The influence of each of 32 diverse ions on the determination of indium(III) in 100 cm^3 of distilled water was examined according to the recommended procedure. The results obtained are summarized in Table 1. Some foreign ions interfered with the determination when non-impregnated graphite furnace was used, but their interferences could be reduced remarkably by the use of a graphite furnace impregnated with hafnium; that is, large amounts of sodium, magnesium, and calcium, and up to 1 mg of tin(IV), bismuth(III), selenium(IV), tellurium(IV), titanium(IV), vanadium(V), chromium(III), molybdenum(VI), tungsten(VI), and iron(III) do not give any serious interferences.

Recoveries of Indium(III) from Spiked Water Samples. Using a recommended procedure, we examined the recovery of indium(III) from 250—500 cm^3 of water samples spiked with 0.5—5.0 μg of indium(III). Almost 100% of indium(III) was recovered from distilled, tap, or river water within the relative standard deviation range of 1.0—5.3%. In the case of sea water, 97—101% recoveries were obtained within the relative standard deviation range of 2.1—4.7%.

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