Determination of Lead(II) by Electrothermal Atomization Atomic Absorption Spectrometry after Coprecipitation with Gallium(III) Phosphate

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Gallium(III) phosphate coprecipitates quantitatively 0.1—2.0 μg of lead(II) from 100—500 cm^3 of a sample solution at pH 2.5—6.0. The coprecipitated lead(II) can be sensitively determined by electrothermal atomization atomic absorption spectrometry without any influence of gallium(III) phosphate. The calibration curve is linear from 4 to 80 $ng\,cm^{-3}$ for lead(II). The detection limit (signal/noise = 2) is 0.095 $ng\,cm^{-3}$ of lead(II) in 500 cm^3 of the initial sample solution. Thirty-four diverse ions tested did not interfere seriously with the determination of lead(II). This method was successfully applied to the determination of lead(II) in tap and river water.

The coprecipitation method is widely used for the concentration of trace metal ions prior to their electrothermal atomization atomic absorption spectrometric determination. A variety of coprecipitants have been investigated.[1—3] We previously proposed gallium(III) phosphate as a new coprecipitant of lead(II),[4] and have suggested that it is an excellent collector equivalent, or superior, to the other coprecipitants of tin(IV),[5] indium(III),[6] and chromium(III)[7] for electrothermal atomization atomic absorption spectrometry. In this paper, we report the details of the fundamental conditions for the coprecipitation of lead(II) with gallium(III) phosphate and for the electrothermal atomization atomic absorption spectrometric determination of it. For the preconcentration of lead(II) prior to the electrothermal atomization atomic absorption spectrometric determination, the following coprecipitants have been proposed: iron(III) tetramethylenedithiocarbamate(TMDTC),[8] ammonium pyrrolidinedithiocarbamate (APDC) complexes of copper and iron,[9,10] cobalt APDC,[11] 8-quinolinolate (8-Q) complexes of magnesium[12,13] and aluminum,[13] nickel diethyldithiocarbamate (DDTC),[14] 3, 5-diphenylpyrazolinedithiocarbamic (3, 5-DPDTC) acid,[15] dimethylglyoxime/nickel/1-(2-pyridylazo)-2-naphthol complex,[16] manganese dioxide,[17] and hydroxides of zirconium,[18,19] thorium,[20,21] iron(III),[22,23] lanthanum,[24] and indium.[25] However, some of these coprecipitants have their own disadvantages. The dissolution of APDC complexes of copper and iron,[9,10] nickel DDTC,[14] and zirconium hydroxide[18] is slow. In the case of aluminum 8-Q,[13] the recovery of lead(II) was incomplete. The presence of manganese,[17] used as a carrier element, is prone to influence the atomic absorption of lead. Thorium[20,21] is radioactive. Gallium(III) phosphate as a coprecipitant overcomes these weak points. This method proposed here is applicable to the determination of lead(II) in tap and river water.

As for the coprecipitation processes of some elements by metal phosphates, several studies have been carried out; the coprecipitation of iron, calcium, or uranium with bismuth phosphate[26] was governed mainly by surface adsorption, americium with zirconium phosphate[27,28] by ion-exchange adsorption, chromium with zinc phosphate[29,30] and iron with lead phosphate[30,31] by adsorption and ion-exchange on the surface layer of the precipitate, americium with bismuth phosphate[28] by formation of isostructural phosphate compoud, chromium or iron with aluminum phosphate[29,30] by isomorphic cocrystallization obeying ion-exchange law, arsenic with magnesium ammonium phosphate[32] by mixed crystal formation, and cobalt with magnesium ammonium phosphate[33] by solid solution formation. This time, we also investigated the distribution of lead(II) between the precipitate of gallium(III) phosphate and the solution after the coprecipitation, and found that the relation between the coprecipitated amount of lead(II) and the amount remaining in the solution after the coprecipitation followed the Freundlich adsorption isotherm[34,35] and the overall distribution of lead(II) obeyed the logarithmic distribution law.[1,34—37] From these results, it seems that lead(II) can adsorb on the precipitate of gallium(III) phosphate and the solid solution can be formed successively in the process of the coprecipitation of lead(II) with gallium(III) phosphate.

Experimental

Apparatus. A Hitachi 170-70 Zeeman-effect atomic absorption spectrometer with a Hitachi lead hollow-cathode lamp was used for atomic absorption measurements.

Reagents. **Standard Lead(II) Solution:** A solution containing about 1000 μg cm^{-3} of lead(II) was prepared by dissolving lead(II) nitrate in a small amount of nitric acid and diluting with distilled water. The concentration of this solution was determined by complexometric titration using Xylenol Orange as an indicator. This solution was further diluted to the desired concentration with distilled water in each experiment.

Gallium(III) Solution: A solution containing 5 mg cm^{-3} of gallium(III) was prepared by dissolving 5 g of gallium metal (99.9999%) with 50 cm^3 of hydrochloric acid and diluting with distilled water.

Phosphoric Acid Solution: An about 0.5 mol dm^{-3} solution was prepared by diluting concentrated phosphoric acid with distilled water.

All of the other reagents used were of guaranteed reagent grade.

Recommended Procedure. To a sample solution (100—500 cm^3) containing 0.1—2.0 μg of lead(II), 15 mg of gallium(III) and 3 cm^3 of 0.5 mol dm^{-3} phosphoric acid are added. Gallium(III) phosphate is then precipitated at a pH of about 3 using about 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 2 cm^3 of concentrated hydrochloric acid and the solution is diluted to 25 cm^3 with distilled water. The atomic absorbance of lead is then measured under the operating conditions shown in Table 1. A blank, using distilled water as a sample solution, is also measured.

Results and Discussion

Optimum Conditions for Coprecipitation. Gallium(III) phosphate coprecipitated lead(II) quantitatively from wide pH range, as shown in Fig. 1. Almost 100% recovery of lead(II) was obtained within a few minutes after the formation of gallium(III) phosphate and the recovery remained almost constant upon standing for at least 3 h.

The required amount of gallium(III) for the quantitative recovery of lead(II) was more than 5 mg for both 100 and 500 cm^3 of the sample solution. The presence of gallium(III) did not affect the determination of lead(II) over the range of 0.1—1.2 mg cm^{-3} of gallium(III) in the final sample solution. The necessary amount of phosphoric acid for the quantitative coprecipitation of lead(II) 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. The presence of phosphate also did not influence the determination of lead(II) up to at least 2.5 × 10^{-3} mol for 100 cm^3 of the sample solution.

Table 1. Operating Conditions for the Atomic Absorption Spectrometer

Analytical wavelength	283.3 nm
Lamp current	10 mA
Slit width	No.2 (1.1 nm)
Argon gas flow rate	
Sheath gas	3 dm^3 min^{-1}
Carrier gas	0 dm^3 min^{-1}
Drying conditions	21 A (ca. 100 °C), 60 s
Ashing conditions	80 A (ca. 700 °C), 30 s
Atomizing conditions	250 A (ca. 2250 °C), 5 s
Graphite cuvette	Cup type
Injection volume	20 mm^3

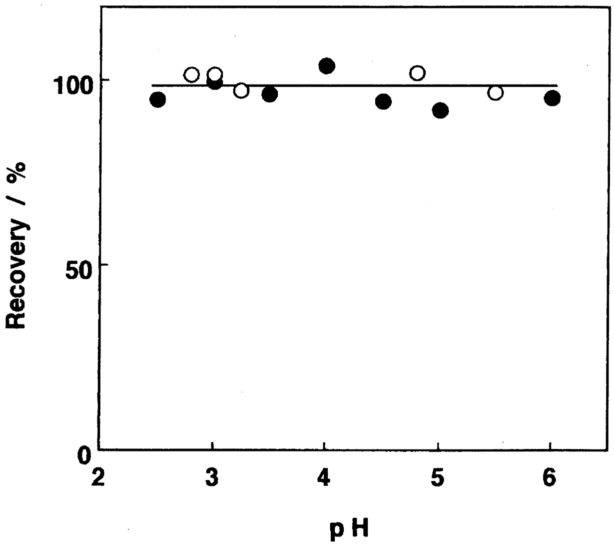

Fig. 1. Effect of the pH on the recovery of lead(II). Pb(II), 1.0 μg (○) or 2.0 μg (●); Ga, 15mg; 0.5 mol dm^{-3} H_3PO_4, 3 cm^3; concd HCl, 2 cm^3; final volume, 25 cm^3.

For the dissolution of gallium(III) phosphate, hydrochloric acid was preferred to nitric acid, because the former acid gave a slightly higher absorbance of lead than did the latter acid (Fig. 2), although gallium(III) phosphate dissolved readily in either acid. In this procedure, 2 cm^3 of concentrated hydrochloric acid was used.

The Distribution of Lead(II) between the Precipitate and the Solution after the Coprecipitation. Using 2.5 mg of gallium(III) and 3 cm^3 of 0.5 mol dm^{-3} phosphoric acid, the 0.01—2 mg range of lead(II) was coprecipitated at pH 3.0 from 60 cm^3 of aqueous solution and; the solution was then kept standing for 5 h at 25.0±0.1 °C. According to the results shown in Fig. 3, the relation between the copre-

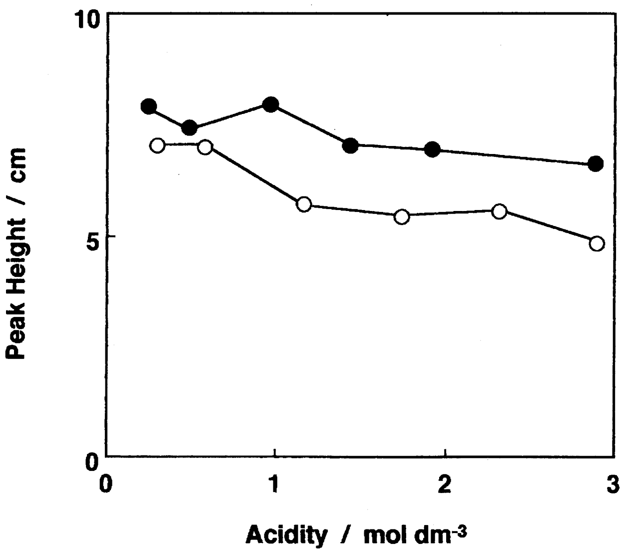

Fig. 2. Effect of the acid concentration on the peak height of lead(II). Pb(II), 1.0 μg; Ga, 15 mg; 0.5 mol dm^{-3} H_3PO_4, 3 cm^3; final volume,.25 cm^3. ●) HCl, ○) HNO_3.

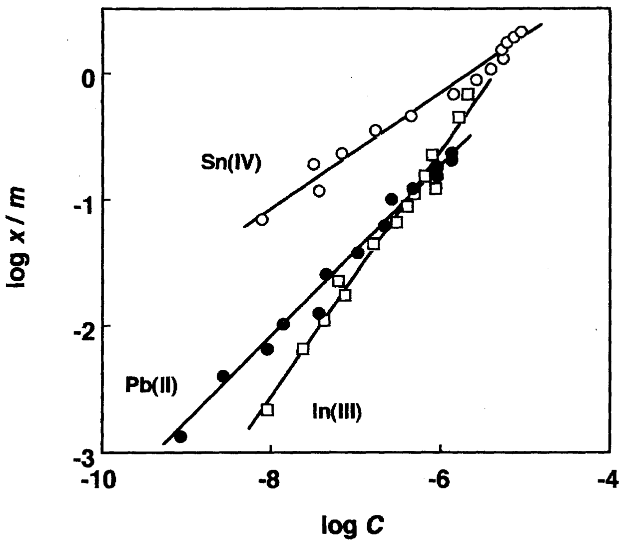

Fig. 3. Relations between the coprecipitated amounts of some metal ions and the remained amounts of them in the solution after the coprecipitation. ●) Pb(II). ○) Sn(IV). □) In(III). Ga(III), 2.5 mg; 0.5 mol dm^{-3} H_3PO_4, 3 cm^3; pH, 3.0; temperature, 25.0±0.1 °C. x: The coprecipitated amount of metal ion (mol). m: The amount of gallium(III) phosphate used for the coprecipitation (mol) C: The concentration of metal ion remaining in the solution after the coprecipitation (mol per 60 cm^3).

cipitated amount of lead(II) and its remaining amount in the solution followed the Freundlich adsorption isotherm,[34,35)]

$$\log (x/m) = (1/n)\log C + \log k, \qquad (1)$$

where x is the coprecipitated amount of lead(II) (mol), m is the amount of gallium(III) phosphate for the coprecipitation (mol), C is the concentration of the remaining lead(II) in the solution (mol per 60 cm^3), and n and k are constants. In this experiment, n and $\log k$ were 1.47 and 3.34, respectively. In Fig. 3, the results of tin(IV) and indium(III), which can be recovered almost 100% at pH about 3 from water,[5,6)] are also appended; n and $\log k$ were 2.23 and 2.52 for tin(IV), and 1.03 and 5.21 for indium(III), respectively.

Then, the effect of the pH adjustment rate on the distribution of lead(II) was investigated, and the distribution obtained at the various rates was compared with that obtained according to the recommended procedure. 0.5 mg of lead(II) was coprecipitated at pH 2.2—2.6 in 60 cm^3 of aqueous solution containing 15 mg of gallium(III) and 3 cm^3 of 0.5 mol dm^{-3} phosphoric acid at 25.0±0.1 °C; in this experiment, the pH was adjusted by the addition of about 2 mol dm^{-3} ammonia solution at a constant rate (20—500 mm^3 min^{-1}) with a μ-HPLC pump while stirring with a magnetic stirrer. At the additional rate of 20—50 mm^3 min^{-1}, the overall distribution of lead(II) between the precipitate and the solution obeyed the logarithmic distribution law :[1,34—37)]

$$\log (\mathrm{Pb_i}/\mathrm{Pb_f}) = \lambda_g(3/2.303)(1/V^{1/3})(\mathrm{Ga_i}^{1/3} - \mathrm{Ga_f}^{1/3}), \qquad (2)$$

where $\mathrm{Pb_i}$ and $\mathrm{Ga_i}$ are the initial amounts of lead(II) and gallium(III) in the solution before the coprecipitation (mol), $\mathrm{Pb_f}$ and $\mathrm{Ga_f}$ are the amounts of them remaining in the solution after the coprecipitation (mol), V is the volume of the solution (dm^3), and λ_g is constant (Fig. 4); this result suggests that the following reaction attains equilibrium on the precipitate of gallium(III) phosphate during the formation of the precipitate,

$$2\mathrm{Ga(III)_{pptn.}} + 3\mathrm{Pb(II)_{sol.}} = 2\mathrm{Ga(III)_{sol.}} + 3\mathrm{Pb(II)_{pptn.}}, \qquad (3)$$

where $\mathrm{Ga(III)_{pptn.}}$ and $\mathrm{Pb(II)_{pptn.}}$ are gallium(III) and lead(II) in the precipitate, and $\mathrm{Ga(III)_{sol.}}$ and $\mathrm{Pb(II)_{sol.}}$ are those in the solution. In this experiment, λ_g was 0.426. At the additional rate of 100—500 mm^3 min^{-1}, however, the λ_g value was decreased with an increase of $\mathrm{Ga_f}$. When lead(II) was coprecipitated according to the recommended procedure, in which the ammonia solution was added by the use of a pipette, the distribution of lead(II) was similar to that at the additional rate of 100—500 mm^3 min^{-1}, as shown in Fig. 4.

From these results, it seems that lead(II) can adsorb on the precipitate of gallium(III) phosphate and the solid solution can be formed successively in the process of the coprecipitation of lead(II) with gallium(III) phosphate.

In the coprecipitation of indium(III) with gallium(III) phosphate, the overall distribution of indium(III) between the precipitate and the solution after the coprecipitation also obeyed the logarithmic distribution law.

Optimization of Operating Conditions. During the drying stage, almost constant peak heights were obtained with 21 to 25 A of heating current and 40 to 80 s of heating time. In the ashing stage, the maximum peak height was

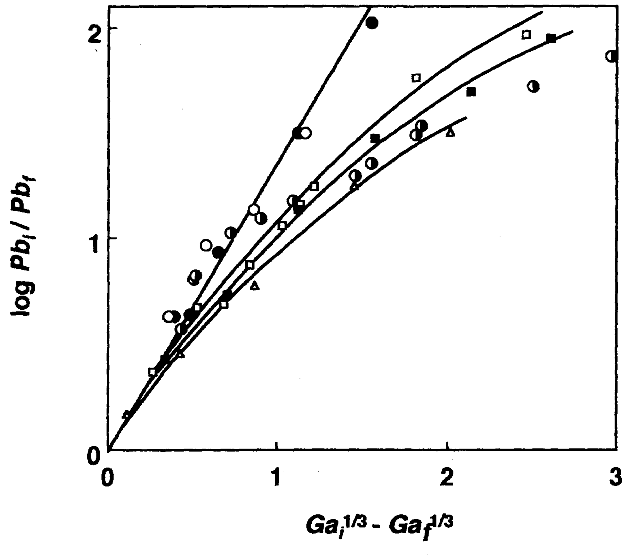

Fig. 4. Distribution of lead(II) between the precipitate and the solution after the coprecipitation. Pb(II), 0.5 mg; Ga(III), 15 mg; 0.5 mol dm^{-3} H_3PO_4, 3 cm^3; temperature, 25.0±0.1 °C. The additional rate of ca. 2 mol dm^{-3} NH_3 solution (mm^3 min^{-1}): ○) 20, ●) 50, □) 100, ■) 250, △) 500. ◑) According to the recommended procedure. $\mathrm{Pb_i}$, $\mathrm{Ga_i}$: The initial amounts of lead(II) and gallium(III) in the solution before the coprecipitation (mol). $\mathrm{Pb_f}$, $\mathrm{Ga_f}$: The amounts of lead(II) and gallium(III) remaining in the solution after the coprecipitation (mol).

obtained at 80 A and remained almost constant from 20 to 40 s. In the atomizing stage, almost constant peak height was obtained with 250 to 310 A and 3 to 10 s. From these results and other instrumental conditions, such as analytical wavelength, lamp current, slit width, argon gas flow rate, and injection volume, the optimum measurement conditions for the atomic absorption of lead were determined, as summarized in Table 1.

Calibration Curve. The relationship between the peak height and the concentration of lead(II) was examined using the recommended procedure. By an increase in the injection volume into the graphite cuvette compared with that reported previously,[4] the sensitivity could be improved; a straight line through the point of origin was obtained over the concentration range from 4 to 80 ng cm^{-3} of lead(II) and the detection limit (signal to noise ratio$=$2) was 0.095 ng cm^{-3} in 500 cm^3 of initial sample solution when 20 mm^3 was injected, although the straight line reached over the range from 10 to 160 ng cm^{-3} and the detection limit was 0.20 ng cm^{-3} for 10 mm^3.[4] The reproducibility of this method, expressed by the relative standard deviation obtained the peak heights from five repeated determinations, was 0.9% for 2.0 µg of lead(II) in 100 cm^3 of sample solution.

Interference. The influence of each of 34 diverse ions on the determination of 1.0 or 2.0 µg of lead(II) in 100 cm^3 of a sample solution was examined according to the recommended procedure. As shown in Table 2, lead(II) could be recovered within a ±5% error in the presence of large amounts of sodium(I), potassium(I), magnesium(II), and calcium(II). The other ions tested also did not cause serious interferences in the determination of lead(II).

Recoveries of Lead(II) from Spiked Water Samples. Using the recommended procedure, almost 100% recoveries were obtained within the relative standard deviation range of 0.9—12.4% from 100—500 cm^3 of distilled and tap water samples spiked with 1.0—2.0 µg of lead(II).[4] From 250 cm^3 of river water samples spiked with 1.0 µg of lead(II), 97% recovery was obtained with 4.1% of the relative standard

Table 2. Effect of Diverse Ions on the Determination of Lead(II)

Ion	Amount added mg	Recovery %	Ion	Amount added mg	Recovery %
Li^{+}	1.0	96.3	Te(IV)	0.5	95.7
Na^{+} a)	1200.0	100.0	Cu^{2+}	1.0	101.8
K^{+} a)	500.0	100.5	Zn^{2+}	1.0	102.1
Be^{2+}	1.0	98.0	Cd^{2+}	1.0	97.5
Mg^{2+} a)	200.0	101.9	La^{3+}	1.0	98.7
Ca^{2+} a)	500.0	104.3	Ti(IV)	1.0	104.3
Sr^{2+}	1.0	98.9	Zr(IV)	1.0	102.4
Ba^{2+}	1.0	98.4	Hf(IV)	1.0	100.3
Al^{3+}	1.0	96.1	Th(IV)	1.0	100.8
In^{3+}	1.0	99.5	V(V)	1.0	98.6
Tl^{3+}	1.0	101.0	Cr^{3+}	1.0	97.2
Ge(IV)	1.0	100.0	Mo(VI)	1.0	103.4
Sn(IV)	1.0	99.2	W(VI)	1.0	100.5
As(V)	1.0	97.1	Mn^{2+}	1.0	95.7
Sb(III)	1.0	99.2	Fe^{3+}	1.0	96.1
Bi(III)	1.0	101.6	Co^{2+}	1.0	97.9
Se(IV)	1.0	100.1	Ni^{2+}	1.0	99.5

Pb(II), 2.0 µg. a) Pb(II), 1.0µg.

Table 3. Results of the Determination of Lead(II) in Tap and River Water

Sample	Sample volume cm^3	Calibration method Found µg dm^{-3}	 RSD %	Standard addition method Found µg dm^{-3}	 RSD %
Tap water					
No.1 a)	100	2.11	2.1	2.04	0.4
	100	3.71	8.0	3.71	3.8
No.2	500	0.51	7.0	0.54	7.8
River water					
	250	1.27	6.7	1.41	8.1

The results obtained are the average of three replicate determinations. a) Sampled on separate days. RSD: Relative standard deviation.

deviation from five repeated determinations.

Determination of Lead(II) in Tap and River Water. Based on the results mentioned above, the determination of lead(II) in tap and river water (located in Ishikawa prefecture) was tried. The samples were filtered through a membrane filter (Fuji Photo Film FR-40, pore size of 0.4 μm) as soon as possible after sampling. As shown in Table 3, the results obtained by the calibration and the standard addition methods were in good agreement with each other. The time required for the determination of lead(II) in 500 cm^3 of the sample solution was about 1 h. The blank value in this method was less than 2.6 ng cm^{-3} of lead(II) in the final sample solution.

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