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# Separation and Concentration of Tin(IV) by Co-precipitation with Gallium Phosphate for Electrothermal Atomization Atomic Absorption Spectrometry

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(Received November 4, 1992)

Gallium phosphate co-precipitates quantitatively 0.5—5.0 μg of tin(IV) from 100 to 500 $cm^3$ of a sample solution at pH 3.0—6.0. After co-precipitation, tin(IV) can be sensitively determined by electrothermal atomization atomic absorption spectrometry. The atomic absorbance of tin(IV) increases by about 1.7 times in the presence of gallium. Although many ions interfere with the determination, interference from the majority can be eliminated by using a graphite furnace impregnated with hafnium, which also improves the sensitivity and reproducibility of the determination. Tellurium(IV) and zirconium(IV) interfere seriously. The calibration curve is linear from 0.02 to 0.20 $\mu g\,cm^{-3}$ for tin(IV), and the detection limit (signal/noise=2) is 0.23 $ng\,cm^{-3}$ of tin(IV) in 500 $cm^3$ of the initial sample solution. This method is applicable to the analyses of water samples for tin(IV).

Electrothermal atomization atomic absorption spectrometry combined with preconcentration and preseparation techniques has been widely used for the determination of trace metal ions. As pretreatment techniques, the co-precipitation method is one of the most useful; various co-precipitants have been proposed.[1—3] We previously proposed gallium phosphate as a new co-precipitant of lead, suggesting that this co-precipitant has the possibility to be a useful collector for tin(IV), antimony(III), and bismuth(III).[4] This time, we investigated the fundamental conditions for the electrothermal atomization atomic absorption spectrometric determination of tin(IV) after co-precipitation with gallium phosphate, and obtained a sensitive and reproductive determination method. In this method, the use of a graphite furnace impregnated with hafnium[5] was effective to eliminate any interference from diverse ions. Until now, hydroxides of lanthanum,[6] zirconium,[7] hafnium,[5] thorium,[8] or yttrium,[9] and manganese dioxide[10] have been reported as co-precipitants of tin(IV) prior to electrothermal atomization atomic absorption spectrometry. However, lanthanum does not give a linear calibration curve, zirconium hydroxide dissolves only slowly in acids, and hafnium and thorium are expensive and radioactive, respectively. The method using manganese dioxide also requires tedious operations. The use of gallium phosphate overcomes these weak points.

## Experimental

**Apparatus.** A Hitachi 170-70 Zeeman-effect atomic absorption spectrometer with a Hitachi tin hollow-cathode lamp was used for atomic absorption measurements. As a graphite furnace, a tube-type cuvette impregnated with hafnium[5] was used. The pH measurements were carried out with a Hitachi-Horiba model M-5 glass electrode pH meter.

**Reagents.** All of the reagents used were of guaranteed reagent grade.

**Standard Tin(IV) Solution:** A solution containing 1000 $\mu g\,cm^{-3}$ of tin(IV) was prepared by diluting NBS SRM 3161 (10.00±0.01 $mg\,cm^{-3}$) with 2 $mol\,dm^{-3}$ hydrochloric acid. This solution was further diluted to the desired concentration with distilled water in each experiment.

**Gallium Solution:** A solution containing 5 $mg\,cm^{-3}$ of gallium 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.

**Recommended Procedure.** To a sample solution (100—500 $cm^3$) containing 0.5—5.0 μg of tin(IV), 15 mg of gallium and 3 $cm^3$ of 0.5 $mol\,dm^{-3}$ phosphoric acid are added. Gallium phosphate is then precipitated at a pH of about 3 using 7 $mol\,dm^{-3}$ ammonia solution. After allowing the solution to stand for about 10 min, the precipitate is filtered by suction using a 3G4 glass filter. The precipitate is dissolved with 2 $cm^3$ of concentrated hydrochloric acid and the solution is diluted to 25 $cm^3$ with distilled water. The atomic absorbance of tin(IV) 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 Co-precipitation.** The necessary amount of gallium or phosphoric acid for the co-precipitation of tin(IV) was studied using a

Table 1. Operating Conditions for the Atomic Absorption Spectrometer

| | |
|---|---|
| Analytical wavelength | 286.3 nm |
| Lamp current | 10 mA |
| Slit width | No. 2 (1.1 nm) |
| Argon flow rate | |
| Sheath gas | 3 $dm^3\,min^{-1}$ |
| Carrier gas | 0 $dm^3\,min^{-1}$ |
| Cuvette | Tube type graphite furnace impregnated with hafnium |
| Drying conditions | 21 A (ca. 100°C), 60 s |
| Ashing conditions | 80 A (ca. 700°C), 30 s |
| Atomizing conditions | 310 A (ca. 2830°C), 5 s |
| Injection volume | 10 μl |

sample solution (100—500 cm$^3$) containing 3 μg of tin(IV). The required amount of gallium for the quantitative recovery of tin(IV) increased with increasing sample volume. By using of more than 15 mg of gallium, however, tin(IV) could be recovered almost completely from 500 cm$^3$ of the sample solution. On the other hand, the presence of gallium increases the sensitivity of the tin(IV) determination; with increasing the amount of gallium, the peak height of tin(IV) gradually increased, and almost constant peak heights were obtained over a concentration range from 0.6 to at least 2.0 mg cm$^{-3}$ of gallium (Fig. 1). From these results, 15 mg of gallium was used for the co-precipitation of tin(IV) in further experiments. The necessary amount of phosphoric acid for the quantitative co-precipitation of tin(IV) was $0.5\times10^{-3}$ to $2.5\times10^{-3}$ mol (Fig. 2). In Fig. 2, a curve showing the effect of the amount of phosphoric acid on the tin(IV) peak height is also appended. In this method, $1.5\times10^{-3}$ mol of phosphoric acid was used.

Gallium phosphate co-precipitated tin(IV) quantitatively from wide pH range, as shown in Fig. 3. In further experiments, the pH was adjusted to about 3 with 7 mol dm$^{-3}$ ammonia solution. The recovery of tin(IV) reached its maximum value a few minutes after gallium phosphate was formed; this value remained almost constant for at least 3 h. For the dissolution of gallium phosphate, hydrochloric acid was preferred to nitric acid, because the former acid gave a higher peak height of tin(IV) than did the latter acid (Fig. 4), although gallium phosphate dissolved readily in either acid.

Concerning the co-precipitation processes of some elements by metal phosphates, several studies have been carried out; the co-precipitaion of americium with zirconium phosphate,[11,12] chromium with zinc phosphate,[13,14] and iron with lead phosphate[14,15] are governed mainly by ion-exchange adsorption, americium with bismuth phosphate,[12] iron or chromium with aluminum phosphate[13,14] by isomorphic co-crystalline, and cobalt with magnesium ammonium phosphate[16] by solid solution formation.

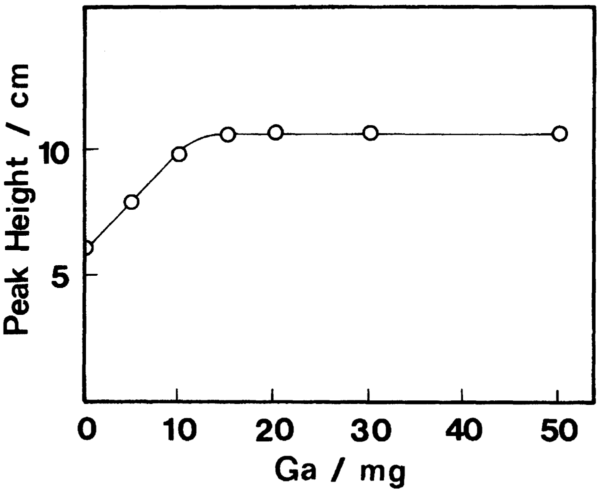

Fig. 1. Effect of the amount of gallium on the peak height of tin(IV). Sn(IV), 3 μg; 0.5 mol dm$^{-3}$ $H_3PO_4$, 3 cm$^3$; concd HCl, 2 cm$^3$; final volume, 25 cm$^3$.

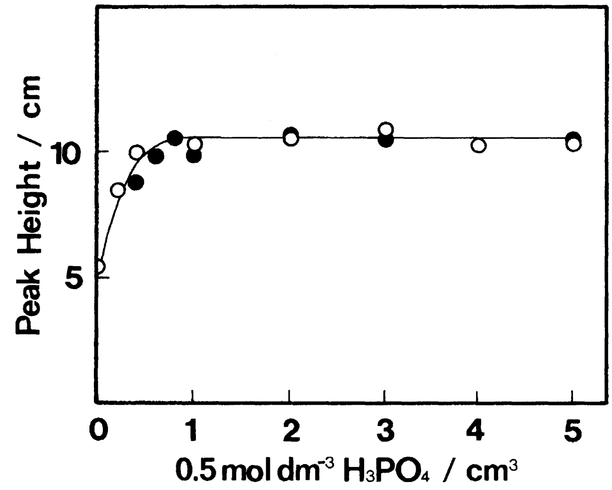

Fig. 2. Effect of the amount of phosphoric acid on the peak height of tin(IV). Sn(IV), 3 μg; Ga, 15 mg; concd HCl, 2 cm$^3$; final volume, 25 cm$^3$. ○) Effect of the amount of phosphoric acid on the peak height of tin(IV). ●) The necessary amount of phosphoric acid for the quantitative co-precipitation of tin(IV).

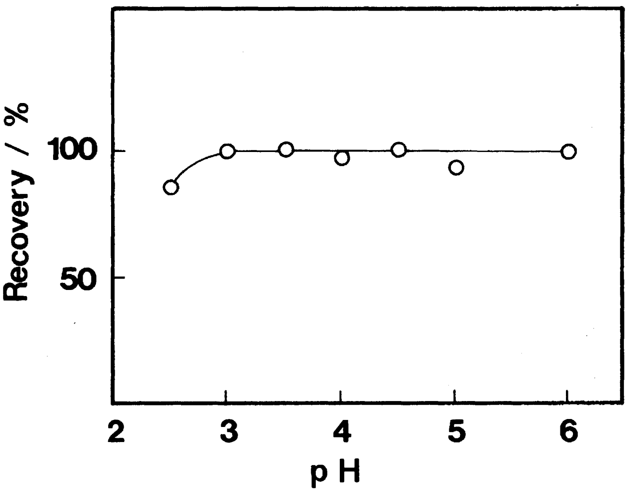

Fig. 3. Effect of the pH on the recovery of tin(IV). Sn(IV), 20 μg; Ga, 15 mg; 0.5 mol dm$^{-3}$ $H_3PO_4$, 3 cm$^3$; concd HCl, 2 cm$^3$; final volume, 25 cm$^3$.

In the case of the co-precipitation of tin(IV) with gallium phosphate, although the concentration process seems to be not so different from those mentioned above, no detailed studies have yet been reported. We will soon examine those in detail.

**Optimization of Operating Conditions.** The optimum conditions for measuring the atomic absorbance of tin(IV) were examined using a solution con-

Table 2. Effect of Diverse Ions on the Determination of Tin (IV)

| Ion | Amount added | Recovery/% | | Ion | Amount added | Recovery/% | |
|---|---|---|---|---|---|---|---|
| | mg | A | B | | mg | A | B |
| $Li^+$ | 1.0 | 102.9 | — | Te(IV) | 1.0 | 30.2 | — |
| $Na^+$ | 1.0 | 96.8 | — | | 0.1 | — | 84.9 |
| $K^+$ | 1.0 | 98.5 | — | $Cu^{2+}$ | 1.0 | 87.1 | 99.7 |
| $Be^{2+}$ | 1.0 | 114.2 | 99.6 | $Zn^{2+}$ | 1.0 | 85.0 | 97.5 |
| $Mg^{2+}$ | 1.0 | 99.5 | — | $Cd^{2+}$ | 1.0 | 97.6 | — |
| $Ca^{2+}$ | 1.0 | 97.2 | — | $La^{3+}$ | 1.0 | 198.3 | 103.4 |
| $Sr^{2+}$ | 1.0 | 115.6 | 98.8 | $Ti^{4+}$ | 1.0 | 130.9 | 97.4 |
| $Ba^{2+}$ | 1.0 | 124.6 | 102.3 | $Zr^{4+}$ | 1.0 | 74.0 | 72.7 |
| $Al^{3+}$ | 1.0 | 132.3 | 98.2 | $Hf^{4+}$ | 1.0 | 99.0 | — |
| $In^{3+}$ | 1.0 | 98.6 | — | $Th^{4+}$ | 1.0 | 113.0 | 101.5 |
| $Tl^{3+}$ | 1.0 | 96.9 | — | V(V) | 1.0 | 137.0 | 99.5 |
| Ge(IV) | 0.1 | 107.4 | 100.7 | $Cr^{3+}$ | 1.0 | 116.4 | 99.8 |
| $Pb^{2+}$ | 1.0 | 103.4 | — | Mo(VI) | 1.0 | 144.2 | 100.0 |
| As(V) | 1.0 | 98.8 | — | W(VI) | 1.0 | 133.2 | 96.1 |
| $Sb^{3+}$ | 1.0 | 121.8 | 103.4 | $Mn^{2+}$ | 1.0 | 114.4 | 101.2 |
| $Bi^{3+}$ | 1.0 | 104.5 | — | $Fe^{3+}$ | 1.0 | 120.1 | 100.8 |
| Se(IV) | 1.0 | 66.2 | — | $Co^{2+}$ | 1.0 | 101.3 | — |
| | 0.1 | — | 95.6 | $Ni^{2+}$ | 1.0 | 103.7 | — |

A: Sn (IV), 15 µg. A non-impregnated graphite furnace was used. B: Sn (IV), 3 µg. A graphite furnace impregnated with hafnium was used.

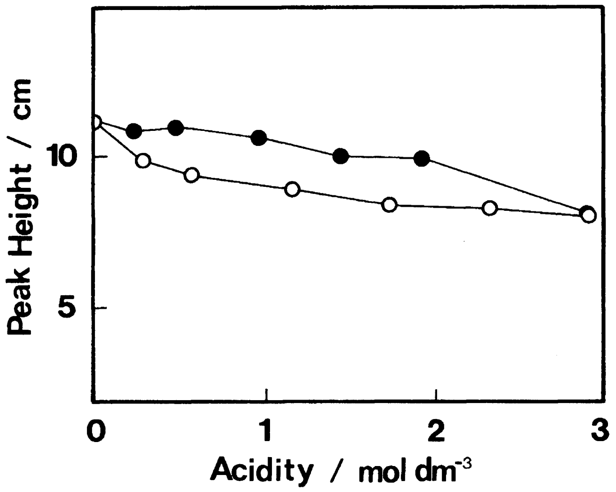

Fig. 4. Effect of the acid concentration on the peak height of tin(IV). Sn(IV), 3 µg; Ga, 15 mg; 0.5 mol dm$^{-3}$ $H_3PO_4$, 3 cm$^3$; final volume, 25 cm$^3$. ●) HCl, ○) $HNO_3$.

taining 3 µg of tin(IV) prepared according to the recommended method.

During the drying stage, almost a constant peak height was obtained within 20—24 A of heating current and 40—80 s of heating time. However, the bumping of the sample solution frequently occurred above 22 A. With an increase in the ashing current, the peak heights became higher and reached a maximum value at 80 A. These peak heights remained almost constant from 20 to 40 s of heating time. At the atomizing stage, the maximum peak height of tin(IV) was obtained at 310 A and from 3—10 s. From these results and other instrumental conditions, such as the analytical wavelength, lamp current, slit width, argon gas flow rate, and injection volume, the optimum measurement conditions for the atomic absorption of the tin(IV) were determined, as summarized in Table 1.

**Calibration Curve.** The relationship between the peak height and the concentration of tin(IV) was examined using the recommended procedure. A straight line through the point of origin was obtained over the concentration range 0.02 to 0.20 µg cm$^{-3}$ of tin(IV). The sensitivity and reproducibility of this method were improved by using 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 0.23 ng cm$^{-3}$ in 500 cm$^3$ of initial sample solution and 1.11% for 0.03 µg cm$^{-3}$ of tin(IV) respectively, although the detection limit and the reproducibility were 0.60 ng cm$^{-3}$ and 4.90% obtained using the non-impregnated graphite furnace.

**Interference.** The influence of each of 34 diverse ions on the determination of tin(IV) in 100 cm$^3$ sample solutions was examined according to the recommended procedure. As shown in Table 2, many ions interfered with the determination when a non-impregnated graphite furnace was used. This interference, however, could be reduced remarkably by using a graphite furnace impregnated with hafnium. Tellurium(IV) or zirconium(IV), however, interfered with the determination.

**Recoveries of Tin(IV) from Spiked Water Samples.** Using the recommended procedure, the

Table 3. Recovery of Tin(IV) from Spiked Water Samples

| Sample | Sample volume | Tin(IV) | | |
|---|---|---|---|---|
| | | Added | Found | RSD |
| | $cm^3$ | μg | μg | % |
| Distilled water | 250 | 3.0 | 2.90 | 1.16 |
| | 500 | 3.0 | 2.92 | 1.23 |
| Tap water | 250 | 3.0 | 3.05 | 3.44 |
| | 500 | 3.0 | 3.00 | 2.63 |
| River water | 250 | 3.0 | 3.00 | 1.62 |
| | 500 | 3.0 | 2.89 | 1.34 |
| Sea water | 250 | 3.0 | 2.95 | 4.18 |
| | 500 | 3.0 | 2.93 | 4.34 |

The recoveries obtained are the average of five replicate determinations. RSD: Relative standard deviation.

recovery of tin(IV) from some water samples spiked with tin(IV) was examined. The samples were filtered through a Fuji Photo Film FR-40 membrane filter (pore size of 0.4 μm) as soon as possible after sampling. The results obtained by the calibration method are shown in Table 3; it seems that the proposed method is applicable to analyses of these water samples.

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