CHEMISTRY LETTERS, pp. 2157-2160, 1992.

Preconcentration of Trace Metal Ions by Coprecipitation with Gallium Phosphate for Flameless Atomic Absorption Spectrometry

Shigehiro KAGAYA, Shiro KOSUMI, and Joichi UEDA*
Department of Chemistry, Faculty of Education, Kanazawa University, Marunouchi, Kanazawa 920

Gallium phosphate was a useful coprecipitant for the preconcentration of lead(II), tin(IV), antimony(III), and bismuth(III) on the flameless atomic absorption spectrometry. The determination of trace amount of lead(II) in water was demonstrated.

Coprecipitation is a useful method for concentrating trace metals and a lot of coprecipitants,[1-3] including metal phosphates,[4-20] have been proposed. The majority of them, however, has not been used for the preconcentration prior to the determinations of trace elements by flameless atomic absorption spectrometry, because of the interference caused by the coprecipitant itself or a large quantities of alkali and alkaline earth metals coprecipitated simultaneously together with the trace elements to be collected. We have been investigating a new coprecipitant for trace metals and have found that gallium phosphate is an effective collector for lead(II), tin(IV), antimony(III), and bismuth(III) on the flameless atomic absorption spectrometry; it is the selective collector for these ions and coprecipitates few or no matrix ions such as alkali or alkaline earth elements, and a large amount of gallium does not interfere in the atomic absorption spectrometric determination. Recovery percentages of some metal ions by gallium phosphate are shown in Table 1.

In this letter, we investigated in detail the optimum conditions for the coprecipitation and the flameless atomic absorption spectrometric determination of lead(II), and evaluated the potential of this method measuring recoveries of lead(II) from distilled and tap water samples spiked with lead(II).

Measurements were carried out with Hitachi 170-70 Zeeman-effect atomic absorption spectrometer with Hitachi hollow cathode lamp. A gallium solution was prepared by dissolving 5 g of gallium metal (99.9999%) with 50 cm^3 of hydrochloric acid and diluting with distilled water. All the other

reagents used were of guaranteed reagent grade.

Although it is troublesome to precipitate gallium as hydroxide because of redissolution of the precipitate, it is easy to precipitate gallium almost completely as phosphate in the wide pH range, 2.5-6.0. In addition, gallium phosphate coprecipitated lead(II) quantitatively over the relatively wide pH range as shown in Fig.1. In this figure, the results of the examinations about tin(IV), antimony(III), and bismuth(III) were also appended. The recovery of lead(II) reached its maximum value at a few minutes after gallium phosphate was formed and this value remained almost constant for at least 3 h. For the dissolving the precipitate, hydrochloric acid was preferred to other mineral acids because this acid gave the highest peak height of atomic absorption of lead(II).

Table 1. Recoveries of some ions by gallium phosphate

Ion[a]	Added	Recovery
	μg	%
Sn^{4+}	25.0	100.6
Pb^{2+}	2.5	100.8
Sb^{3+}	12.5	98.3
Bi^{3+}	25.0	94.8
Cu^{2+}	12.5	23.1
Au^{3+}	1.25	10.0
Cd^{2+}	0.25	22.5
Cr^{3+}	5.0	42.5
Mn^{2+}	0.25	2.6
Co^{2+}	25.0	8.7
Ni^{2+}	25.0	5.8
Na^{+}	500.0	0.0[b]
K^{+}	75.0	0.0[b]
Be^{2+}	1.25	56.3
Mg^{2+}	50.0	0.0[b]
Ca^{2+}	375.0	4.3[b]

a) Coprecipitated at pH about 3 using 10 mg of Ga from about 100 cm^3 of aqueous solution.
b) Flame atomic absorption spectrometry was used for the measurement.

Table 2. Recovery of lead(II) from spiked water samples

Sample	Sample volume	Pb(II) added	Pb(II) found	RSD
	cm^3	μg	μg	%
Distilled water	100	2.0	2.02	0.9
	250	1.0	0.95	4.1
	500	1.0	0.94	2.1
Tap water[a]	100	2.0	1.94	1.3
	500	1.0	0.97	12.4
Tap water[b]	500	1.0	0.98	5.2

The recoveries obtained are the average of five replicate determinations.
RSD : Relative standard deviation.
Location of tap water: a) Kanazawa. b) Nonoichi.

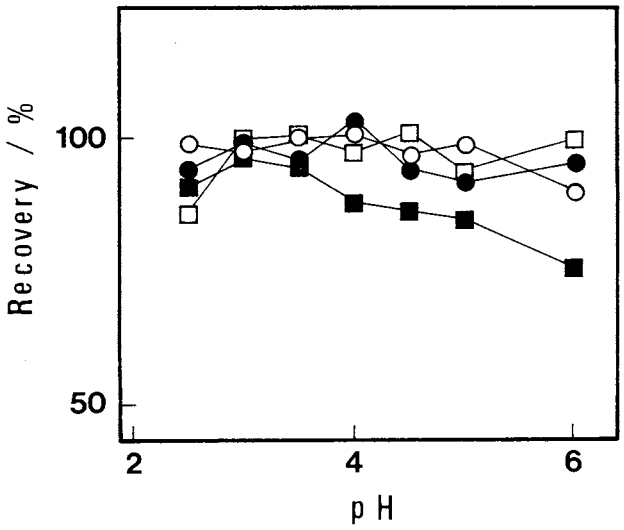

Fig.1. Effect of pH on the recovery of lead(II), tin(IV), antimony(III), or bismuth(III)
Each ion was coprecipitated from about 100 cm^3 of sample solution. Ga, 15 mg ; PO_4^{3-}, 1.5×10^{-3} mol ; concd HCl, 2 cm^3 ; final volume, 25 cm^3. □)Sn(IV),20 μg. ●)Pb(II), 2 μg. ○)Sb(III),15 μg. ■)Bi(III), 50 μg. Wavelength(nm) —— Sn(IV), 286.3 ; Pb(II),283.3 ; Sb(III), 217.5; Bi(III),306.7.

From these results, the following recommended procedure for the lead(II) determination can be proposed. To a sample solution (100-500 cm^3) containing 0.25-4.0 μg of lead(II), 15 mg of gallium and 3 cm^3 of 0.5 mol dm^{-3} phosphoric acid are added. Then gallium phosphate is precipitated at pH about 3 using diluted aqueous ammonia. After allowed the solution to stand for about 10 min, the precipitate is filtered by suction using a 3G4 glass filter and dissolved with 2 cm^3 of concentrated hydrochloric acid. The solution is then diluted to 25 cm^3 with distilled water and the atomic absorbance of lead(II) is measured. As the calibration curve, a straight line passing through the origin was obtained over the concentration range 0.01-0.16 μg cm^{-3} of lead(II). The relative standard deviation of this method which was obtained from five repeat determinations was 0.54% for 4.0 μg of lead(II) in 100 cm^3 of sample solution. The detection limit (signal to noise ratio = 2) was 0.20 ng cm^{-3} of lead(II) in 500 cm^3 of initial sample solution. The influence of each of 32 diverse ions on the determination of 2.0 μg lead(II) was examined by coprecipitating it from about 100 cm^3 of sample solutions containing each ion. Any ions did not give the serious effects on the determination and lead(II) can be determined within 5% error in the presence of 1 mg each of Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, In^{3+}, Tl^{3+}, Sn^{4+}, As(V), Sb^{3+}, Bi^{3+}, Se(IV), Cu^{2+}, Zn^{2+}, Cd^{2+}, La^{3+}, Ti^{4+}, Zr^{4+}, Hf^{4+}, Th^{4+}, V(V), Cr^{3+}, Mo(VI), W(VI), Mn^{2+}, Fe^{3+}, Co^{2+}, and Ni^{2+}. To investigate the reliability of this method, the recoveries of lead(II) from distilled and tap water samples spiked with lead(II) were examined. As shown in Table 2, the good results were obtained.

From these results, it can be seen that gallium phosphate has an excellent collecting ability for lead(II). This collector was also recognized to be the effective coprecipitant for tin(IV), antimony(III), and

bismuth(III) on the flameless atomic absorption spectrometric determination. Furthermore, it seems that gallium phosphate may be applicable for the preconcentration of these four metal ions on the other various determination techniques.

References

1) A.Mizuike, "Enrichment Techniques for Inorganic Trace Analysis," Springer-Verlag, Berlin(1983), pp.56-66.
2) T.Takahashi and H.Daidogi, "Furnace Genshikyuko-bunseki," Gakkai Shuppan Center, Tokyo(1984), p.143.
3) K.Fuwa, S.Shimomura, S.Toda, and T.Kumamaru, "Saishin Genshikyuko-bunseki," Hirokawa Pub., Tokyo(1989), pp.1035-1045.
4) C.L.Luke, Anal. Chem., 31, 572(1959).
5) F.L.Moore, Anal. Chem., 43, 487(1971).
6) N.Zurlo, A.M.Griffini, and G.Colombo, Anal. Chim. Acta, 47, 203(1969).
7) I.Bacić, N.Radaković, and P.Strohal, Anal. Chim. Acta, 54, 149(1971).
8) R.D.Rodabaugh and G.T.Upperman, Anal. Chim. Acta, 60, 434(1972).
9) H.F.Zhang, J.Holzbecher, and D.E.Ryan, Anal. Chim. Acta, 149, 385 (1983).
10) M.Hara and S.Suzuki, Bull. Chem. Soc. Jpn., 48, 1431(1975).
11) S.Taguchi, M.Taga, H.Yoshida, and S.Hikime, Bunseki Kagaku, 24, 26 (1975).
12) H.Kawamoto, S.Abe, and N.Iijima, Bunseki Kagaku, 31, 341(1982).
13) T.Okutani, Bunseki Kagaku, 33, 443(1984).
14) K.H.Reinhardt and H.J.Müller, Fresenius Z. Anal. Chem., 292, 359(1978).
15) Z.Hölgye, Fresenius Z. Anal. Chem., 315, 247(1983).
16) Z.Hölgye, Fresenius Z. Anal. Chem., 320, 181(1985).
17) S.A.Reynolds and T.G.Scott, Radiochem. Radioanal. Lett., 23, 269(1975).
18) V.T.Chuiko, F.A.Chmilenko, N.V.Kovaleva, A.A.Kravtsova, and V.S.Smirnaya, Tr. Khim. Khim. Tekhnol., 1973, 112; Chem. Abstr., 81, 85494j(1974).
19) E.B.Sandell, "Colorimetric Determination of Trace Metals," Interscience Pub., New York(1959), pp.252, 282, 323, 561, 914.
20) J.Minczewski, J.Chwastowska, and R.Dybczynski, "Separation and Preconcentration methods in Inorganic Trace Analysis," John Wiley & Sons, New York(1982), p.50.

(Received July 22, 1992)