ノート

〔衛 生 化 学〕
EISEI KAGAKU
35 (4) 297-300 (1989)

— Notes —

Investigation of Interference by Inorganic Phosphate on Coprecipitation of Cadmium, Copper, Manganese and Lead in Water with Zirconium Hydroxide

TAKAKO OSANAI, KUMI HAYAKAWA, NAOMI KIKUCHI, SHIGEKO KONNO, KOTA ITO,
NOBUYUKI SHIBATA and SHIGEO SUZUKI

*Second Department of Hygienic Chemistry, Tohoku College of Pharmacy,
Sendai 981, Japan*

(Received January 5, 1989)

The interference effect of PO_4^{3-} on the recovery of Cd, Cu, Mn and Pb in water during determination by coprecipitation with $\text{Zr}(\text{OH})_4$ followed by flame atomic absorption spectrometry (FAAS) was investigated. Free PO_4^{3-} in water, from 0.125 to 1.5 mg/ml, exhibited weak interference on the recovery of these metals, giving rise to errors of a few to several percent in the direct FAAS analysis. In the coprecipitation method, Zr^{4+} showed an unfavorable property to FAAS, forming a precipitate of phosphate which was insoluble to both water and (1+1) HCl. The above problems were solved by precipitating PO_4^{3-} with Zr^{4+} followed by washing the precipitate with (1+1) HCl, solubilizing the coprecipitated metals quantitatively, and removing PO_4^{3-} by centrifugation as acid-insoluble Zr^{4+} salt.

Keywords — quantitative determination; cadmium; copper; manganese; lead; coprecipitation; zirconium hydroxide; atomic absorption spectrometry; phosphate

In an earlier paper by Abe *et al.*,¹⁾ it was reported that coprecipitation of metal ions with zirconium hydroxide ($\text{Zr}(\text{OH})_4$) was quite effective in concentrating Cd, Cu, Mn, and Pb existing in water. In the presence of PO_4^{3-} , however, there is a problem in the recovery of metal by this method due to the formation of water-insoluble precipitate with Zr^{4+} . As PO_4^{3-} is an anion present in various samples collected for metal analysis, we investigated the interference behavior of PO_4^{3-} on the determination of these four metals in deionized water by the sequential adoption of coprecipitation with $\text{Zr}(\text{OH})_4$ and flame atomic absorption spectrometry (FAAS).

Materials and Methods

Reagents and Water — Zirconium solution

(aqueous 3.53 (w/v%) solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and the standard solution of Cd, Cu, Mn and Pb were the same as in the earlier paper.¹⁾ Water used in the present study was tap water deionized by passing through an Organo Puric GA-15-B apparatus.

General Operating Procedure — Fifty ml of a standard solution of Cd, Cu, Mn and Pb, 25 $\mu\text{g/l}$, in a 100-ml glass centrifuge tube was acidified with (1+1) HCl to pH 1.0. To the solution was added zirconium solution, 1.0 ml, and the pH was adjusted to 10.0 by dropwise addition of 4 N NaOH. In the presence of PO_4^{3-} , the precipitate formed at pH lower than 3.0. The reaction mixture was then centrifuged at 2000 rpm for 10 min. The supernatant was discarded, and the sediment was washed by centrifuging with 80 ml of deionized water. To the residue was added 4 ml of (1+1) HCl, the mixture was stirred for 30 s at room

temperature on a magnetic stirrer, and deionized water was added to make it 20 ml. If any insoluble materials including zirconium phosphate remained, the mixture was centrifuged at 2000 rpm for 10 min. The metal content in the supernatant was then analyzed by FAAS using a Hitachi Z-6100 polarized Zeeman atomic absorption spectrophotometer. Determination was repeated 3 times. Chart 1 summarizes the above process. The analytical conditions of FAAS for Cd, Cu, Mn and Pb are shown in Table I.

Examination of Interference Caused by PO_4^{3-} — (1) Reaction of PO_4^{3-} with Zr^{4+} : To 50 ml of deionized water, pH 1.0, containing increasing amounts of PO_4^{3-} was added 1.0 ml of zirconium solution, and pH was adjusted to 5.0 with 4 N NaOH with stirring. After centrifugation at 2000 rpm for 10 min followed by washing with 80 ml of water by centrifugation, the residue was stirred with 4 ml of (1+1) HCl, and the total volume was brought up to 20 ml with deionized water. An aliquot of the mixture was centrifuged at 2000 rpm for 10 min, and phosphate content in the supernatant was analyzed by the Ames-Dubin test solution

metal standard solution, 50 ml
pH 1.0 with (1+1) HCl
 ZrOCl_2 solution 1.0 ml (Zr, 10 mg)
pH 10.0 with 4 N NaOH

centrifuge for 10 min at 2000 rpm

precipitate

supernatant

wash with water
dissolve in (1+1) HCl, 4 ml
bring up to 20 ml

centrifuge for 10 min at 3000 rpm

precipitate

supernatant

flame atomic absorption
spectrometry

Chart 1. Determination of Metals by Coprecipitation Method with $\text{Zr}(\text{OH})_4$ in the Presence of Phosphate

method.²⁾

(2) Recovery of Metals in the Presence of PO_4^{3-} : To 50 ml of deionized water, containing increasing amounts of PO_4^{3-} was added 1.0 ml of a standard metal solution, then the mixture was subjected to the coprecipitation method as described in "General Operating Procedure".

Results and Discussion

In the preceding study,¹⁾ we conducted a recovery test of Cd, Cu, Mn and Pb in drinking water by coprecipitation with $\text{Zr}(\text{OH})_4$; we observed that the precipitation of these metals started at pH 6–7, and their recovery was not affected by low concentrations of the various cations and anions contained in drinking water.³⁾ However, with increase in the amount of PO_4^{3-} , the formation of white precipitate was observed even below pH 3, suggesting that PO_4^{3-} forms water-insoluble salt with Zr^{4+} in an acidic medium. The present study was undertaken to examine the influence of PO_4^{3-} of considerably high con-

TABLE I. Operating Condition for Flame Atomic Absorption Spectrometry (Hitachi Z-6100)^{a)}

	Cd	Cu	Mn	Pb
Wave length (nm)	228.8	324.8	279.5	283.3
Lamp current (mA)	6.0	5.0	5.0	7.5
Slit width (nm)	1.3	1.3	0.4	1.3

^{a)} Simultaneous background correction was made by the polarized Zeeman effect method.
acetylene, 0.3 kg/cm². air, 1.6 kg/cm².

TABLE II. Interference by PO_4^{3-} on Recoveries of Cd, Cu, Mn and Pb from Deionized Water

Amount of PO_4^{3-} added (mg/ml)	Extent of interference (%)			
	Cd ^{a)}	Cu ^{b)}	Mn ^{c)}	Pb ^{d)}
0.125	+2.6	+4.9	+0.7	+5.0
0.25	+5.1	+5.9	+3.0	+3.7
0.5	+5.5	+7.0	+2.9	+4.5
1.5	+5.9	+7.6	-0.1	+1.6

^{a)} 50 ng/ml, ^{b)} 200 ng/ml, ^{c)} 50 ng/ml, ^{d)} 200 ng/ml.

centration on the determination of metals. We first examined the direct interference effect of PO_4^{3-} on the recovery of Cd, Cu, Mn and Pb. Table II summarizes the results of this interference test in water containing PO_4^{3-} , 0.125 to 1.5 mg/ml. As seen, PO_4^{3-} with concentration above 0.25 mg/ml can positively interfere with decrease of the recovery of Cd, Cu, and Pb in a few-to several-percent scale. Recovery of Mn was also shown to undergo interference by PO_4^{3-} , although the extent was less than those of other metals. Therefore, the establishment of a procedure to eliminate PO_4^{3-} in metal analysis by FAAS seemed essential. We thus conducted a recovery test of the four metals using coprecipitation with $\text{Zr}(\text{OH})_4$ in the hope of establishing a method of eliminating the PO_4^{3-} interference by the formation of water-insoluble precipitate, followed by the dissolution of $\text{Zr}(\text{OH})_4$ with dilute acid leaving zirconium phosphate as an insoluble residue. Figure 1 shows the relationship between the amount of precipitated PO_4^{3-} with Zr^{4+} and pH of the reaction mixture. It is evident that Zr^{4+} forms an insoluble precipitate with PO_4^{3-} , indicating that the maximum exists at pH 5.0. Therefore, the formation of this precipitate in further recovery tests of PO_4^{3-} was conducted at

Fig. 1. Relationship between Binding Ratio of PO_4^{3-} and pH in Coprecipitation with $\text{Zr}(\text{OH})_4$

this pH. In order to investigate the influence of extremely large amounts of PO_4^{3-} in water, up to 30 mg/50 ml, another series of recovery tests of PO_4^{3-} using a fixed amount of Zr^{4+} was conducted. As shown in Fig. 2 by open circles, the ratio of precipitated PO_4^{3-} in the precipitate decreased rapidly. In other words, Zr^{4+} in 1 ml of zirconium solution can trap quantitatively up to 10 mg of PO_4^{3-} , and the rest of this anion exists in the supernatant. The line with closed circles in the figure indicates the amounts of PO_4^{3-} dissolved from the precipitate by stirring with (1+1)HCl. It is obvious that dissolution of PO_4^{3-} from the precipitate was not quantitative even with the lowest amount of PO_4^{3-} , and that the amounts of PO_4^{3-} precipitated from the solutions of higher concentration than 10 mg/50 ml were entirely retained in the precipitate even when washed with (1+1)HCl. These results led us to the assumption that interference by PO_4^{3-} might be avoidable if $\text{Zr}(\text{OH})_4$ contaminated with a considerable amount of zirconium phosphate can still display the coprecipitating effect of these metals quantitatively. We therefore, conducted a recovery test of the

Fig. 2. Relationship between Amounts of PO_4^{3-} in Sample Water and in Supernatant after Coprecipitation with $\text{Zr}(\text{OH})_4$ Followed by Treatment of the Precipitate with (1+1)HCl

—○—: Amount of precipitated PO_4^{3-} , —●—: Amount of dissolved PO_4^{3-} from zirconium phosphate in precipitate with (1+1)HCl.

Fig. 3. Recovery Tests of Cd, Cu, Mn, and Pb, Each $25 \mu\text{g}/\text{l}$, from Water Containing Less than $1 \text{ mg}/\text{ml}$ PO_4^{3-} by Coprecipitation with $\text{Zr}(\text{OH})_4$ Followed by FAAS

four metals from water containing 5.0 to 50 $\text{mg}/50 \text{ ml}$ of PO_4^{3-} . The results depicted in Fig. 3 clearly indicate that interference by PO_4^{3-} is avoidable by coprecipitation with Zr^{4+} , excepting the case of Pb, in which a slight decrease of the recovery ratio was observed in the concentration range of PO_4^{3-} higher than 25 $\text{mg}/50 \text{ ml}$. The present findings thus demonstrate that interference of PO_4^{3-} on the recoveries of Cd, Cu, Mn, and Pb during determination by the coprecipitation method with $\text{Zr}(\text{OH})_4$ is avoidable with the removal of acid-insoluble zirconium phosphate by centrifugation, and this procedure can then widely be utilized to eliminate direct interference by PO_4^{3-} in FAAS by the determination of various methods in samples containing PO_4^{3-} .

References

- 1) K. Abe, M. Ito, H. Kikuchi, J. Kimura, K. Kumaki, A. Kogawa, E. Kobayashi, K. Sasaki, M. Sakurai, A. Sato, M. Sato, N. Shibata, R. Sugawara, S. Suzuki, Y. Suzuki, T. Seki, M. Takahashi, M. Takeda, I. Chiba, T. Chiba, K. Hiroshima, Y. Mishima, Y. Mihara and K. Yokota, *Eisei Kagaku*, **33**, 258 (1987).
- 2) B.N. Ames and D.T. Dubin, *J. Biol. Chem.*, **235**, 769 (1960).
- 3) M. Ito, M. Sato, N. Shibata and S. Suzuki, *Bunseki Kagaku*, **35**, 802 (1986).