Quantitative Determination of Cadmium, Copper, Manganese, and Lead in Water by Combination of Coprecipitation with Zirconium Hydroxide and Flame Atomic Absorption Spectrometry

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A method for quantitative determination of four harmful metals, Cd, Cu, Mn, and Pb in water by means of coprecipitation with zirconium hydroxide, $Zr(OH)_4$, followed by flame atomic absorption spectrometry has been developed. Because no extraction process of the metal chelates with organic solvents is required, and because Zr shows low toxicity to mammals, this procedure is free from hazard to the health of laboratory workers engaging in metal analysis. The results of recovery tests indicated that the recoveries of the metals by the above procedure are satisfactory (more than 98%).

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

The quantitative determination of metals in drinking water can usually be achieved by atomic absorption spectrometry (AAS) after preconcentration of metal ions or their chelates by extraction with organic solvents. However, this procedure has been shown to involve a serious risk to the health of laboratory workers due to frequent exposure to the solvent vapor. From this viewpoint, the use of the coprecipitation method with water-insoluble metal hydro-

xides seemed to be advantageous, since no hazardous solvent would be required.

Although several metal hydroxides, *i.e.*, those of Fe, La, Th, and Zr have been investigated for ability to coprecipitate other metal ions,¹⁻⁴⁾ zirconium hydroxide, $Zr(OH)_4$, seemed to be the most favorable for our purpose, because zirconium has low sensitivity in AAS, so that chemical and spectrometric interferences with other metals might be small.^{5,6)} The suitability

of $\text{Zr}(\text{OH})_4$ as a coprecipitant for metal analysis in water samples such as deionized water and sea water has been reported by many workers: Satisfactory recoveries of low concentrations of Be, Bi, Ca, Cd, Cu, Fe, Mg, Sn, Pb, and Zn from water samples have been obtained by coprecipitation with $\text{Zr}(\text{OH})_4$.⁶⁻¹⁵ It should also be noted that zirconium shows low toxicity to mammals (LD_{50} of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in rats *p.o.* was found to be 3.5 g/kg¹⁶).

Because there is no established method for application of this coprecipitation procedure to the preconcentration of metals in routine monitoring of water, we attempted to establish suitable analytical conditions for several metals, Cd, Cu, Mn, and Pb, which have been defined as representative harmful metals in the Water Supply Law of Japan. In this paper, we report the usefulness of the coprecipitation method with $\text{Zr}(\text{OH})_4$ for the simultaneous determination of these four metals in water, in combination with flame atomic absorption spectrometry (FAAS).

Materials and Methods

Reagents—Zirconium Solution: Guaranteed reagent grade $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Osaka and Tokyo), 3.53 g, was dissolved in water, and the solution was made up to 100 ml. One milliliter of this solution contains *ca.* 10 mg of Zr.

Standard Metal solutions: Solutions containing each metal at 1 mg/ml were purchased from Wako.

HNO_3 and HCl : These were guaranteed reagents for metal analysis supplied by Wako.

Water—The water sample used in the present study was the tap water of Sendai city. The sample was collected in the laboratory of the Second Department of Hygienic Chemistry, Tohoku College of Pharmacy, on the morning of July 20, 1986, after allowing a large amount of the tap water to flow for 1 h.

Laboratories that Participated in the Inter-laboratory Recovery Test and FAAS Instruments Used

—Abbreviations for the eight participating laboratories and the models of FAAS instruments were as follows: A, Aomori Prefectural Institute of Hygiene (Jarrel-Ash JA 855); B, Fukushima Prefectural Institute of Hygiene (Jarrel-Ash JA 855); C, Iwate Prefectural Institute of Hygiene (Hitachi 170-50 A); D, Miyagi Prefectural Institute of Health and Environment (Hitachi 170-50 A); E, Sendai Municipal Institute of Hygiene and Public Health (Hitachi 170-50 A); F, Tohoku College of Pharmacy, Laboratory I (Hitachi 170-50 A); G, Tohoku College of Pharmacy, Laboratory II (Hitachi 170-50 A); H, Yamagata Prefectural Institute of Hygiene (Varian-Techtron AA-780). These laboratories each received 10 l of the water sample containing fixed amounts of metals and the same water without addition of the metals. The amounts of Cd, Cu, Mn, and Pb added to the sample water were 49.9, 49.9, 47.9, and 98.7 $\mu\text{g/l}$, respectively, as determined by FAAS (direct spray method) after concentration 10 or 20 times.

General Operating Procedure—(a) Treatment of Water Sample with HNO_3 : Prior to analysis, the water sample, 1000 ml, contained in a 1-l beaker, was acidified with HNO_3 , 10 ml, then the solution was boiled and cooled to room temperature. This operation was conducted in accordance with the description in the Water Supply Law of Japan.¹⁷

(b) Coprecipitation: This was conducted in accordance with the description by Sato and Saito^{6a} with partial modification as follows. The HNO_3 -treated water was warmed under stirring at 30 to 40°C in order to accelerate aggregation of the precipitate of $\text{Zr}(\text{OH})_4$. Then zirconium solution, 1.0 ml, was added to the solution, and the pH of the solution was adjusted by the dropwise addition of 4 N NaOH or (1+1) NH_4OH , under monitoring by means of a pH meter. After the pH had reached 9.0–9.5, the mixture was left at room temperature overnight in order to allow the precipitate to settle. The supernatant was removed by decantation and/or pipetting so that loss of the precipitate did not occur. The precipitate was then collected by filtration on a Toyo Roshi No. 5 A

Chart 1. The Standard Operating Procedure for Metal Analysis by Coprecipitation with $Zr(OH)_4$

TABLE I. Operating Conditions for Flame Atomic Absorption Spectrometry^a (Hitachi 170-50A)

	Cd	Cu	Mn	Pb
Wavelength (nm)	228.8	324.8	279.5	283.3
Lamp current (mA)	6	5	5	7.5
Slit width (mm)	1.1	2.2	1.1	1.1

a) Simultaneous background correction was conducted by the D_2 line method as necessary. acetylene, 0.3 kg/cm², air, 1.6 kg/cm².

filter paper (11-cm diameter). The residue was washed with water, 50 ml, in small portions, and dissolved in 6 N HCl, 8 ml. The filter paper was further washed with water to give a final volume of 50 ml. The solution was then examined for metal content by FAAS. Simultaneously, the same drinking water without addition of metal standard solutions, 1000 ml, was run as the control. The flow sheet is given in Chart 1.

(c) Conditions of FAAS: Table I shows a typical example of the FAAS operating conditions (Hitachi model 170-50 A). Adjustment of the operating conditions between different models of FAAS instruments was done by the use of the same standard metal

solutions distributed to all participating laboratories.

Examination of Chemical Interference between Zr and Cd, Cu, Mn, and Pb

This experiment was conducted by placing 40 ml of 1 N HCl in 50-ml flasks, then adding 2.0 ml of standard solution of Cd, Cu, Mn, or Pb (each metal, 25 μ g). Subsequently, zirconium solution 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, or 5.0 ml was added and the volume of each flask was made up to 50 ml with 1 N HCl. The resultant mixtures were designated as A 0-Cd to A 6-Cd, A 0-Cu to A 6-Cu, A 0-Mn to A 6-Mn, and A 0-Pb to A 6-Pb, respectively, of which A 0-Cd, A 0-Cu, A 0-Mn, and A 0-Pb were used as blanks for A 1-Cd to A 6-Cd, A 1-Cu to A 6-Cu, A 1-Mn to A 6-Mn, and A 1-Pb to A 6-Pb, respectively. On the other hand, zirconium solution, 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, or 5.0 ml, was added to 40 ml of 1 N HCl in 50-ml flasks and each mixture was made up to 50 ml with 1 N HCl. These mixtures were designated as B 0 to B 6, respectively, and were used as the controls. Then, all solutions were examined by FAA S; simultaneous calibration of the background absorption was done by using a deuterium lamp (D_2 -correction). Determination of each solution was repeated 3 times, and the mean value was calculated. Calculation of chemical interference was done by using the formula:

$$\text{Chemical interference(\%)} = [A 0D_2 - (A D_2 - B D_2)] / A 0D_2 \times 100$$

Where $A D_2$ and $B D_2$ represent the peak heights of metal solutions of A group, 1 to 6, and B group, 1 to 6, respectively, and $A 0D_2$ indicates the peak heights of the four solution series, A 0-Cd, A 0-Cu, A 0-Mn, and A 0-Pb, all of which were calibrated by the D_2 -correction method.

Examination of Spectrometric Interference between Zr and Cd, Cu, Mn, and Pb

For this purpose, the sensitivity of FAAS was adjusted so that the lower limits of quantitative determination of Cd, Cu, Mn, and Pb corresponded to the concentrations of 10, 20, 20, and 100 μ g/l, respectively. Then 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, or 5.0 ml of zirconium solution was added to a 1 N HCl solution of each metal at 10-times-higher concentration than those given above in order to obtain ca. 100 mm

peak height for each metal. Each mixture was made up to 50 ml with 1 N HCl to obtain 24 solutions designated as C0-Cd to C6-Cd, C0-Cu to C6-Cu, C0-Mn to C6-Mn, and C0-Pb to C6-Pb, respectively. The determination of peak height of each solution by FAAS was first conducted without D_2 -correction. Then the same solutions were again examined with D_2 -correction. Determination of each solution was repeated 3 times, and the average was calculated. Spectrometric interference was calculated as follows:

$$\text{Background value (\%)} = (C - C_{D_2}) / C_0 \times 100$$

Where C and C_{D_2} represent the peak height of each metal solution without D_2 -correction and that with D_2 -correction, respectively, and C_0 indicates the peak height of the control, which does not contain Zr, without D_2 -correction.

Results

Investigation of Optimum Conditions for Coprecipitation of Cd, Cu, Mn, and Pb with $Zr(OH)_4$

Figures 1-A, -B, -C, and -D demonstrate the relationship between recovery and pH in the coprecipitation of Cd, Cu, Mn, and Pb, respectively, with 4 N NaOH or (1+1) NH_4OH . The use of 4 N NaOH seemed preferable, since all metals coprecipitated quantitatively at higher pH than 9.0, while the optimum pH ranges for Cd and Cu with (1+1) NH_4OH were narrow, suggesting the formation of non-coprecipitable water-soluble metal-ammonia complexes. These results were consistent with those obtained in the previous coprecipitation studies with $Zr(OH)_4$ on deionized water and sea water.^{7,11-13,15} It should be stressed that, as shown by Sato and Saito,^{6a)} $Zr(OH)_4$ deposited from a neutral aqueous solution of Zr by the addition of alkali precipitates slowly, while adjustment to pH 1.0 with HCl or HNO_3 prior to the addition of alkali results in rapid coagulation of the precipitate. It is therefore reasonable to presume that the coagulative behavior of $Zr(OH)_4$ can be controlled by changing the ionic strength of the sample water. Recently, it was reported

Fig. 1. Relationship between pH and Recoveries of Cd, Cu, Mn, and Pb by Coprecipitation with $Zr(OH)_4$

(A), Cd; (B), Cu; (C), Mn; (D), Pb.

—○—; 4 N NaOH, —●—; (1+1) NH_4OH .

by Nakashima and Yagi¹⁴⁾ that the determination of $\mu\text{g/l}$ levels of Cu, Ni, and Co in water from rivers and lakes could be achieved successfully by adopting the coprecipitation method with $Zr(OH)_4$ followed by high temperature furnace AAS. They showed that in order to collect the precipitate of $Zr(OH)_4$ from mother liquor of low ionic strength, a combination method using a surfactant and bubbling of air to float the precipitate is convenient. However, the water sample used in the present study contained HNO_3 , 10 ml/l, and the salt formed by neutralization with 4 N NaOH or (1+1) NH_4OH increases the ionic strength, which would accelerate the coagulation of the precipitate.

Relationship between Added Zirconium and Recovery of Metals

In order to assess the proper amount of

TABLE II. Relationship between Amount of Added Zr and Recovery of Metals

Amount of Zr added to water, 1 l (mg) ^{a)}	Av. recovery (5 experiments) (%)			
	Cd ^{b)}	Cu ^{b)}	Mn ^{b)}	Pb ^{b)}
5.0	91.6	94.0	89.2	94.4
7.5	97.2	98.0	98.0	100.6
10.0	97.6	100.4	98.6	102.8
20.0	97.4	98.6	96.8	98.6
30.0	99.0	99.4	99.2	100.4
40.0	98.0	97.4	94.8	103.6
50.0	98.0	97.2	86.2	102.0

a) Concentration of zirconium solution was 10 mg Zr/ml.

b) Concentrations of Cd, Cu, Mn, and Pb were all 0.05 mg/l.

Zr to be added as the coprecipitant, a recovery test of the four metals with various amounts of Zr was conducted. As shown in Table II, no change of recovery was observed in the range from 0.75 to 5.0 ml, corresponding to 7.5 to 50 mg of Zr per liter of sample water. Therefore, the amount of zirconium solution to be used in the "General Operating Procedure" was limited to 1.0 ml.

Conditions for Dissolving the Precipitate of $\text{Zr}(\text{OH})_4$

Because the coagulated precipitate of $\text{Zr}(\text{OH})_4$ still retains a large amount of alkaline mother liquor, we investigated the conditions for washing and dissolving the precipitate with

water and a minimum amount of diluted HCl, respectively. The results indicated that the use of 50 ml of water for washing the precipitate on the filter paper resulted in a remarkable decline of Na concentration, as determined by means of a sodium concentration meter. In order to dissolve the washed precipitate, a small volume of 6 N HCl, 8 ml, was more advantageous than a large volume of hot 2 N HCl, 25 ml, the latter of which has been used by many workers.⁶⁻¹⁵⁾ Further washing of the filter paper with ca. 40 ml of water in small portions until the final volume of the combined filtrates reached 50 ml gave satisfactory results for all metals. Thus, the use of HNO_3 is not only favorable for the pretreatment of the sample water but also for the rapid coagulation of the precipitate of $\text{Zr}(\text{OH})_4$, and dissolution of the precipitate can be achieved more readily with 6 N HCl than with hot 2 N HCl.

Chemical Interference of Large Amounts of Zr on Peak Heights of Cd, Cu, Mn, and Pb in FAAS

The use of large amounts of Zr for coprecipitation of metals in water is central to this coprecipitation method. Therefore, it is necessary to assess the extents of interference between Zr and the four metals to be analyzed. Table

TABLE III. Chemical Interference between Zr and Cd, Cu, Mn, and Pb

Metal solution	Amount of Zr added (mg in 50 ml)	Extent of interference ^{a)}							
		Cd ^{b)}		Cu ^{b)}		Mn ^{b)}		Pb ^{b)}	
		Peak height (mm)	Interference (%)	Peak height (mm)	Interference (%)	Peak height (mm)	Interference (%)	Peak height (mm)	Interference (%)
A0	0	142	0.0	63	0.0	77	0.0	70	0.0
A1	5	141	-0.7	63	0.0	76	-1.3	70	0.0
A2	10	141	+0.7	63	0.0	76	-1.3	70	0.0
A3	20	142	0.0	64	+1.6	76	-1.3	72	+2.9
A4	30	143	+0.7	62	-1.6	75	-2.6	70	0.0
A5	40	143	+0.7	64	+1.6	76	-1.3	72	+2.9
A6	50	142	0.0	63	0.0	76	-1.3	71	+1.4

a) Determination of peak heights of all solutions including the control without addition of Zr was made with D_2 -correction.

b) Concentrations of Cd, Cu, Mn, and Pb were all 25 $\mu\text{g}/50$ ml.

TABLE IV. Spectrometric Interference of Zr with Cd and Pb

Metal solution	Amount of Zr added (mg in 50 ml)	Extent of interference ^{a)}			
		Cd		Pb	
		Difference of peak height ^{b)} (mm)	Interference (%)	Difference of peak height ^{b)} (mm)	Interference (%)
C0	0	0.0	0.0	0.0	0.0
C1	5	1.0	1.04	1.0	0.92
C2	10	1.0	1.04	1.5	1.38
C3	20	2.0	2.08	3.5	3.22
C4	30	3.0	3.12	6.5	5.98
C5	40	4.0	4.16	7.0	6.44
C6	50	5.0	5.20	8.5	7.82

a) Expressed as average difference between uncorrected and corrected peak heights of the same metal solutions with D₂ line.

b) The peak heights of solutions of Cd and Pb, 0.1 and 1.0 mg/l, under D₂-correction were 96 and 108 mm, respectively.

III summarizes the results. There was no significant change of peak height of the same metal solutions in the range of amount of added Zr from 0 to 50 mg in 50 ml. Therefore, we conclude that no chemical interference took place between Zr and the four metals, so Zr is available as a coprecipitant for metal analysis in combination with AAS.

Spectrometric Interference of Large Amounts of Zr on Peak Heights of Cd, Cu, Mn and Pb in FAAS

Spectrometric interference between Zr and the four metals was examined by subtracting the peak heights of metals without D₂-correction with those of the same metal solutions measured with D₂-correction. No spectrometric interference was observed for Cu and Mn, while Cd and Pb showed interference of less than 10% (Table IV). Because this kind of interference can be eliminated by D₂-correction, Zr is a suitable coprecipitant for preconcentration of metals to be analyzed by AAS.

Interlaboratory Recovery Test of Cd, Cu, Mn, and Pb by Coprecipitation with Zr(OH)₄

In order to confirm the reliability of analytical values of these four metals obtained by this coprecipitation method conducted in accordance with the "General Operating Procedure,"

TABLE V. Recoveries of Cd, Cu, Mn, and Pb in Drinking Water by the Coprecipitation Method with Zr(OH)₄ at pH 9.0 to 9.5 in Eight Laboratories

Laboratory ^{a)}	Average recovery (%)			
	Cd ^{b)}	Cu ^{b)}	Mn ^{b)}	Pb ^{b)}
A	98.8	98.2	101.7	101.1
B	98.6	100.2	103.1	101.3
C	100.2	100.2	87.7	103.3
D	98.8	96.8	104.4	100.0
E	99.4	99.8	96.5	102.5
F	97.8	98.8	106.2	100.3
G	94.0	97.4	98.5	97.7
H	100.2	99.2	102.3	109.4
Av. recovery (%)	98.5	98.8	100.0	102.0
±S.D.	±2.0	±1.3	±5.8	±3.4
C.V. (%)	2.0	1.2	5.8	3.3

a) Abbreviations of the laboratories that participated in this study are defined in the text.

b) Concentrations of Cd, Cu, Mn, and Pb were ca. 0.05, 0.05, 0.05, and 0.1 mg/l.

a series of recovery tests using a water sample containing fixed amounts of these metals and HNO₃ has been conducted by the workers of 8 laboratories designated as A to H. Table V summarizes the results. It is evident that average recoveries were satisfactory and highly consistent (S.D. and C.V. were less than ±5.8 and 5.8%, respectively), demonstrating that this procedure can be employed for the quantitative determination of these metals in drinking water.

TABLE VI. Effect of Coexisting Ions on Recoveries of Cd, Cu, Mn, and Pb from Water by Coprecipitation with $\text{Zr}(\text{OH})_4$

Ion	Amount added (mg/l)	Recovery (%)			
		Cd ^{a)}	Cu ^{a)}	Mn ^{a)}	Pb ^{a)}
Al ³⁺	100	91.0	87.2	92.7	86.6
	80	98.0	97.3	100.7	104.0
Ba ²⁺	100	98.5	99.7	100.4	96.0
Ca ²⁺	100	98.6	100.0	104.7	98.7
Cr ₂ O ₇ ²⁻	100	98.9	99.8	98.1	96.9
Mg ²⁺	100	97.6	99.0	100.8	95.4
Sr ²⁺	100	100.1	100.0	101.8	98.4
K ⁺	100	98.0	98.7	98.6	95.4
SO ₄ ²⁻	100	98.8	97.9	96.8	97.7
PO ₄ ³⁻	100	96.1	94.4	92.9	91.5
SiO ₃ ²⁻	100	96.3	96.1	96.3	95.5

a) Concentrations of Cd, Cu, Mn, and Pb were all 0.05 mg/l.

Influence of Coexisting Ions on Recoveries of Cd, Cu, Mn, and Pb

A water sample, 1000 ml, containing the four metals, each 50 $\mu\text{g/l}$, was supplemented with various cations and anions that are ordinary components of drinking water (each 100 mg/l), and subjected to coprecipitation with $\text{Zr}(\text{OH})_4$ followed by FAAS in accordance with the "General Operating Procedure." The results are shown in Table VI, indicating that some reduction in recoveries did occur. However, the additives at less than 50 mg/l did not affect the recoveries (not shown). Thus, the "General Operating Procedure" should be widely applicable to metal analysis of water samples con-

taining various inorganic ions at low concentrations.

Discussion

Our findings indicate that the coprecipitation method using $\text{Zr}(\text{OH})_4$ can be utilized as a reliable method for the quantitative determination of Cd, Cu, Mn, and Pb contained in water. No organic solvent extraction process is necessary, so that this coprecipitation method can be regarded as a safe procedure for laboratory personnel. Furthermore, because of the simplicity of operation of this method compared with the solvent extraction method, large numbers of water samples can be processed conveniently.

The results of determination of Cr were not included in the present paper owing to the low coprecipitability of Cr(VI) with $\text{Zr}(\text{OH})_4$ from deionized water, although Cr(III) was found to be recovered quantitatively from the same water by Mihara *et al.*¹¹⁾ Further, Fe and Zn were not examined, since these metals can be detected with sufficient sensitivity by FAAS without preconcentration.

Application of this coprecipitation method for the determination of metals in other water samples such as industrial waste water containing Cr(VI) and raw drinking water with high chemical oxygen demand is in progress in our laboratories.

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