Determination of Lead and Cadmium in Water by Flame Atomic Absorption Spectrometry

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A rapid coprecipitation technique was studied for the determination of trace lead and cadmium in water with flame atomic absorption spectrometry (FAAS) after preconcentration of lead and cadmium by using zinc diethyldithiocarbamate (DDTC) as coprecipitant and known amount of zinc(W_{Zn0}) as an internal standard. Since lead, cadmium and zinc were well-distributed in the homogeneous precipitate, the concentration ratio of lead to zinc or cadmium to zinc kept unchanged in any part of the precipitate. The concentration of lead (C_{Pb1}), cadmium (C_{Cd1}) and zinc (C_{Zn1}) in the final sample solution can be measured by FAAS. The rapid coprecipitation technique does not require complete collection of the precipitate. The amount of lead (W_{Pb0}) and cadmium (W_{Cd0}) in the original sample solution can be calculated from the following formula: $W_{Pb0} = (C_{Pb1}/C_{Zn1}) \times W_{Zn0}$; $W_{Cd0} = (C_{Cd1}/C_{Zn1}) \times W_{Zn0}$. The optimum pH range for quantitative coprecipitation of lead and cadmium is from 8-10. The 13 diverse ions tested gave no significant interferences in the lead and cadmium determination. Under optimized conditions, lead ranging from 0 to 40 μg and cadmium ranging from 0 to 8 μg were quantitatively coprecipitated with Zn-DDTC from 100 mL sample solution (pH 8.5). The rapid coprecipitation technique coupled with FAAS was applied to the determination of lead and cadmium in water sample with satisfactory results (recoveries in the range of 95-110 %, relative standard deviations < 6.0 %).

Key Words: Rapid coprecipitation, Internal standard method, Lead, Cadmium, Flame atomic absorpton spectrometry.

INTRODUCTION

Lead and cadmium cause adverse health effects in human even at low concentrations and their intake must be controlled strictly. At present, both elements are widespread in human environment because of anthropogenic activities[1]. Through the food chain systems, lead and cadmium are transferred into animals and human beings, causing severe contamination. Lead is readily absorbed through the alimentary tract and gastrointestinal tract[2]. Most of the lead assimilated goes into the bones, then liver and kidneys. It leads to vascular disease, retarding intelligence, nephritis and bone injury[3,4]. Cadmium in human body mainly accumulates in kidney and liver. It results in injury to the bone, male urination system, reproductive system and digestive system. Teratogenicity and carcinogenicity of cadmium has been

approved by experiments on animals[5]. Consequently, the development of reliable methods for the determination of lead and cadmium in environmental samples is of particular significance.

Trace metals in water samples often determined by FAAS for its simple, rapid, reliable and low cost. However, this technique suffers from lack of sensitivity for the ultra-trace metal ions usually encountered in environmental samples. Among various preconcentration techniques, coprecipitation is one of the most important techniques for the separation and preconcentration of trace heavy metal ions[6]. A variety of coprecipitants such as zirconium hydroxide[7], bismuth nitrate[8], calcium carbonate[9], aluminum hydroxide[10], iron(III) diethyldithiocarbamate complex[11], copper(II) mercaptobenzothiazole[12] and 1-(2-pyridylazo)-2-naphthol nickel(II) chelate[13] have been reported. But this concentration technique sometimes troublesome and time-consuming because it requires complete filtration of mother liquor and complete collection of precipitate. Further more, in the process of filtration and separation of the precipitate, the precipitate loss must be strictly controlled. To overcome this shortcoming, a rapid coprecipitation technique has been proposed by Kagaya[14].

In this method, an accurately known amount of coprecipitant is added to the sample solution. The concentrations of both the coprecipitated trace metals and the coprecipitant in the final sample solution after the coprecipitation are measured. Since the coprecipitated trace metal and the coprecipitant were well-distributed in the homogeneous precipitation, the ratio of the coprecipitated trace metal to the coprecipitant in any part of the precipitation is completely same. The metal content in the original sample solution can be calculated from the amount of coprecipitant added to the initial sample solution, the amount of the coprecipitated trace metal and the coprecipitant in the final sample solution which was the dissolved part precipitate. Therefore, the precipitate can be easily separated from most of the mother liquor by decantation without any filtration and then be conveniently centri-fuged for its separation from the remaining mother liquor. This rapid coprecipitation technique was applied to the preconcentration of lead and iron using gallium phosphate and lanthanum phosphate as coprecipitant for flame atomic absorption spectrometric determination[14]. By using the rapid coprecipitation technique, the time required for the preconcentration is considerably shortened.

Zinc-diethyldithiocarbamate (Zn-DDTC) has been reported to be a useful coprecipitant for some metals and it has been utilized for the concentration of lead and cadmium prior to a FAAS determination, the added zinc has been precipitated almost completely[15]. In this work, zinc used as internal standard element, since the concentration of lead and cadmium in the original sample solution was calculated from the ratio of the lead or cadmium to the zinc in the final solution, the amount of zinc that existed in the original sample solution before sampling must be negligibly small. In this case, relatively more zinc was added to the original sample solution and subsensitive line at 307.6 nm was applied to the determination of zinc without further dilution. This method proposed here is simple, rapid and useful for the determination of lead and cadmium in water.

EXPERIMENTAL

A WFX-210 atomic absorption spectrometer with lead, cadmium or zinc hollow-cathode lamp (Ruili, China) was used for the measurement of the flame atomic absorbance of lead, cadmium or zinc. The operating conditions were as follows: wavelength, 283.3, 228.8 and 307.6 nm for Pb, Cd and Zn, respectively; band-width, 0.4 nm; lamp current, 8.0 mA; acetylene and air flow rates, 2.0 and 10.0 L min^{-1}; background correction, D_2 lamp method. For the separation of the precipitate from the remained mother liquor, a centrifuge of model 80-1 was utilized. The pH measurements were carried out with a model pHS-25 pH meter equipped with a model E-201 combined pH electrode.

All chemicals except nitric acid (guaranteed reagent grade) were of analytical reagent grade. Distilled-deionized water was used in all experiments. All the glassware and plastic vessels were treated by dilute (1:1) HNO$_3$ acid for 24 h and then rinsed with distilled water before the use. Lead(II), Cd(II) and carrier element Zn(II) stock solutions (1000 mg L^{-1}) were bought from Chinese National Research Center for Certified Reference Material. The working solutions of metals were obtained by diluting these stock solutions prior to use. The calibration curve was prepared using the standard solutions in 1 mol L^{-1} HNO$_3$ by dilution from stock solutions. Diethyldithiocarbamate solution 2 % (w/v) was prepared by dissolving 2.00 g of sodium diethylthiocarbamate (Shanghai, China) in 100 mL of distilled-deionized water. The HNO$_3$ water solutions (0.1 mol L^{-1}) and NaOH water solutions (0.1 mol L^{-1}) were utilized to adjust the pH of the precipitation reaction.

Recommended procedure: To seven 250 mL beakers,100 mL distilled-deionized water and 5.0 mL Zn(II) standard solution (1000 µg mL^{-1}) were added, respectively, then 0, 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 mL Pb(II) standard solution (10 µg mL^{-1}) and 0, 0.1, 0.2, 0.3, 0.4, 0.6 and 0.8 mL Cd(II) standard solution (10 µg mL^{-1}) were added respectively and then 20.0 mL DDTC (2 %) solutions were added, respectively. The pH values of the solutions was adjusted to about 8.5 with an HNO$_3$ and NaOH water solutions by using the pH meter. After the formation of the precipitate, let the precipitate left for 5 min. In every beaker, most of the mother liquor was decanted and then the remained solutions were centrifuged at 3000 rpm for 1 min. The supernatant was decanted and the precipitate was dissolved with heated 3 mol mL^{-1} HNO$_3$ and dilute with distilled-deionized water to 5 mL. The absorbance of Pb, Cd and Zn in the solutions were consecutively measured by FAAS at 283.3, 228.3 and 307.6 nm, respectively and thus obtained the calibration curves.

To the 100 mL sample solution in a 250 mL beaker, accurately 5.0 mL of the Zn(II) standard solution (1000 µg mL^{-1}) was added, followed by the addition of 20.0 mL of the DDTC (2 %) solution and the proposed coprecipitation and measure procedure was applied to the samples. The concentrations of lead (C_{Pb1} µg mL^{-1}), cadmium (C_{Cd1} µg mL^{-1}) and zinc (C_{Zn1} mg mL^{-1}) in the final solution were measured. The lead and the cadmium content in the original sample solution (W_{Pb0} µg and

W_{Cd0} µg) can be calculated respectively from the amount of zinc added to the initial sample solution (W_{Zn0} µg) by using the following equations: $W_{Pb0} = (C_{Pb1}/C_{Zn1}) \times W_{Zn0}$; $W_{Cd0} = (C_{Cd1}/C_{Zn1}) \times W_{Zn0}$.

RESULTS AND DISCUSSION

Optimum conditions for coprecipitation of lead and cadmium: The optimum conditions for the coprecipitation of lead and cadmium with Zn-DDTC were investigated. The pH of model solutions was adjusted to pH value using the dilute HNO_3 solutions (0.1 mol L^{-1}) and aqueous NaOH solutions (0.1 mol L^{-1}). Then the coprecipitation procedure described in recommended procedure section was applied. Quantitative recoveries (> 90 %) were found at the pH 8-10 for the both analytes (Fig. 1). Above pH 10 or below pH 8, the per cent recovery values of Pb and Cd decrease, Therefore, the working pH was chosen as 8.5 for the following experiments.
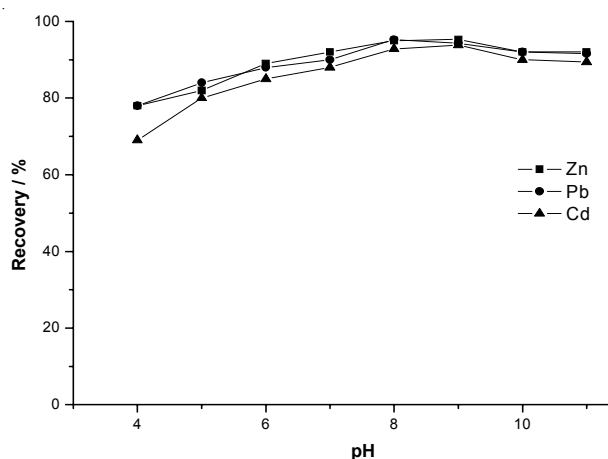

Fig. 1.   Effect of the pH on the recovery of analytes; Model sample volume, 100 mL; zinc, 5 mg; lead, 40 µg; cadmium, 8 µg; DDTC (2 %), 20.0 mL

The influence of carrier ion Zn(II) amount needed for coprecipitation of Pb(II) and Cd(II) was also investigated with model solutions including Zn(II) changed from 1 to 5 mg. The pH value of the solution was adjusted to about 8.5. The results obtained indicate that the recoveries of lead and cadmium are quantitative in the range 1-5 mg Zn(II) (Fig. 2). The Zn (II) amount of 5 mg was taken in further experiments.

The effect of DDTC amount on the coprecipitation of Pb(II) and Cd(II) was examined using the model solutions of 100 mL containing 2000 µg Zn(II) at pH 8.5. The volume of DDTC (2 %) added to the model solutions changed from 5 to 30 mL. The absorbency of the Pb and Cd in the model solutions was maximal and stable when the volume of DDTC (2 %) was in between 20 and 30 mL. The 20 mL of DDTC was used in subsequent studies.
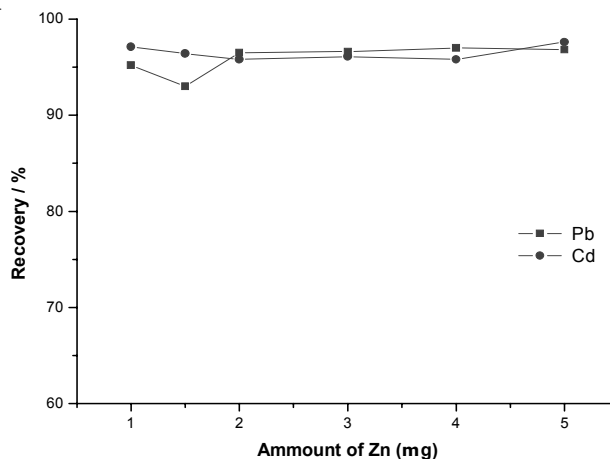
Fig. 2.   Effect of the carrier ion Zn(II) on the recovery of analytes; Model sample volume, 100 mL; pH, 8.5; lead, 40 µg; cadmium, 8 µg; DDTC (2 %), 20.0 mL

Evaluation of zinc as internal standard element for rapid coprecipitation technique: In this method, the amount of zinc in the original sample solution must be negligibly small and the added zinc must be precipitated almost completely because the content of lead and cadmium in the original sample solution is calculated based on the ratio of the added amount of zinc to the amount of zinc in part of the precipitate. In order to increase the amount of zinc added to the sample solution as carrier and internal standard element, subsensitive line 307.6 nm was applied to measure zinc in the final sample solution after the coprecipitation by FAAS without further dilution. Thus the content of zinc in the original water sample is relatively small and negligible. In the original water sample solutions used in present experiments, zinc was not detected by FAAS at 307.6 nm. Zinc can be used as the carrier and internal standard element for the rapid coprecipitation technique on the FAAS.

In order to prove that the ratio of the amount of lead or cadmium to the amount of the carrier element zinc in any part of the precipitate keep unchanged, the amount of lead, cadmium and zinc were measured in different part of the precipitate according to the recommended optimum conditions. The results showed that lead, cadmium and zinc were well-distribute in the whole precipitate and the concentration ratio of lead to zinc or cadmium to zinc in any part of the precipitate kept unchanged (Fig. 3).

Calibration curves: The amount of lead, cadmium and zinc added to the standard series solutions was determined according to the recommended procedure. The relation between the amount of lead added to the standard series solutions (W_{Pb0} µg) and the ratio of the concentration of lead (C_{Pb1} µg mL^{-1}) to the concentration of zinc (C_{Zn1} µg mL^{-1}) is shown in Fig. 4. The relation between the amount of cadmium added to the standard series solutions (W_{Cd0} µg) and the ratio of the concentration of cadmium (C_{Cd1} µg mL^{-1}) to the concentration of zinc (C_{Zn1} µg mL^{-1}) in the final solutions is shown in Fig. 5. The calibration curves of lead and cadmium displayed
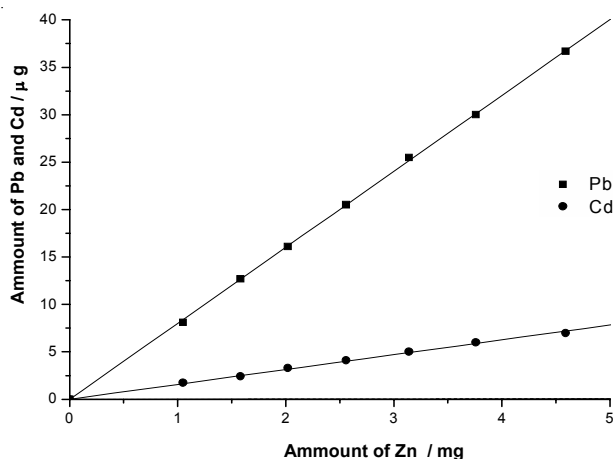
Fig. 3.   Relation between the amount of lead, cadmium and zinc in the precipitate
          Model sample volume, 100 mL; pH, 8.5; zinc, 5 mg; lead, 40 µg; cadmium,
          8 µg; DDTC (2 %), 20.0 mL

good linear relationship passing through the origin which range from 0-8 µg/mL
for lead and 0-1.6 µg/mL for cadmium. The linear correlation coefficient was 0.9988
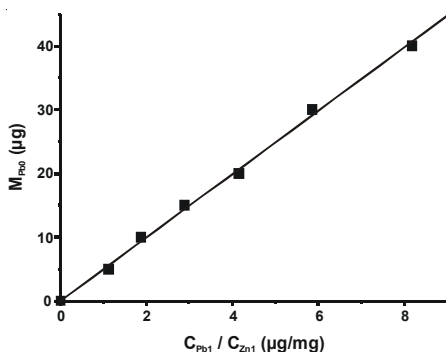for lead and 0.9982 for cadmium respectively.

Fig. 4.   Relation between W_{Pb0} and C_{Pb1}/C_{Zn1}
          in the final sample solution. Sample
          volume, 100 mL; pH, 8.5; zinc, 5 mg;
          DDTC (2 %), 20.0 mL
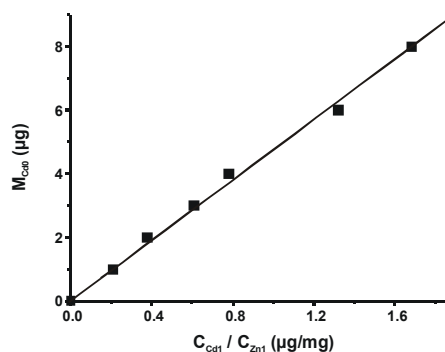

Fig. 5.   Relation between W_{Cd0} and C_{Cd1}/C_{Zn1}
          in the final sample solution. Sample
          volume, 100 mL; pH, 8.5; zinc, 5 mg;
          DDTC (2 %), 20.0 mL

Interferences: The influence of 13 diverse ions on the determination of 40 µg
of lead and 8 µg cadmium was examined using 100 mL sample solution according
to the recommended procedure. As shown in Table-1, large amounts of the matrix
components have no serious interfering effect on the recovery of the examined
elements. The recoveries of lead and cadmium were both in between 91.4 and 104
% in the presence of large amounts of sodium, potassium, magnesium, calcium,
chloride or nitrate.

TABLE-1
EFFECT OF MATRIX IONS ON THE DETERMINATION OF
Pb AND Cd (40 µg OF Pb AND 8 µg OF Cd; n = 3)

Ion	Added as	Amount added (mg)	Recovery (%)	
			Pb	Cd
Na^+	NaCl	500	95.2	96.5
K^+	KNO_3	200	98.3	95.0
Ca^{2+}	$CaCl_2$	100	104.0	95.7
Ba^{2+}	$BaCl_2$	1	99.5	98.7
Mg^{2+}	$Mg(NO_3)_2$	50	101.0	102.0
Li^+	$LiNO_3$	1	101.0	95.5
Al^{3+}	$Al(NO_3)_3$	1	95.1	98.2
Cu^{2+}	$Cu(SO_4)_2$	1	95.0	95.6
Fe^{2+}	$Fe(NO_3)_2$	1	97.6	95.8
Ni^{2+}	$Ni(NO_3)_2$	1	98.2	95.1
Mn^{2+}	$Mn(NO_3)_2$	1	93.6	91.4
Cr^{3+}	$Cr(NO_3)_3$	1	99.0	103.0
Co^{2+}	$Co(NO_3)_2$	1	96.4	99.0

Detect limit: The detection limits (DLs) of the proposed coprecipitation method for the determination of lead and cadmium were studied under optimal experimental conditions by applying the procedure for 100 mL blank solutions (n = 10). The detection limit was calculated as the ratio of the three standard deviations of the blank absorbance signals to the slope of the calibration curve (3 s/b). The detection limits (DLs) were found as 0.023 for Pb and 0.007 µg mL^{-1} for Cd, respectively.

Analysis of water samples: Tap water in our laboratory and well water from Houlin village were analyzed using the recommended procedure without any pre-treatment. The river water from Hucheng river was immediately filtered through a Millipore cellulose membrane filter (0.45 mm pore size, Millipore, USA), acidified to pH 2 with HNO_3 and stored in precleaned polyethylene bottles. The recoveries of lead and cadmium from some water samples spiked with lead and cadmium were examined. As shown in Table-2, recoveries in the range of 95-110 % were obtained from the water samples. The relative standard deviations for the results obtained from six replicate determinations were no more than 6.0 % for lead and cadmium in 100 mL of the sample solution. From these results, the proposed method seems to be applicable to analyses of these samples.

TABLE-2
RESULTS OF THE DETERMINATION OF LEAD AND CADMIUM IN
WATER SAMPLES (SAMPLE VOLUME: 100 mL, n=6)

Sample	Element	Average content (µg mL^{-1})	RSD % (n = 6)	Added (µg mL^{-1})	Found (µg mL^{-1})	Recovery (%)
River water	Pb	0.045	4.8	0.02	0.064	95
	Cd	0.012	3.2	0.01	0.022	100
Tap water	Pb	0.036	3.4	0.02	0.055	95
	Cd	0.014	5.4	0.01	0.025	110
Well water	Pb	0.032	6.0	0.02	0.053	105
	Cd	0.010	5.3	0.01	0.020	100

Conclusion

The rapid coprecipitation method with Zn-DDTC can be applied to the determination of lead and cadmium in water. This method is reliable, simple, economic, rapid and precise. The time required for the determination of lead and cadmium is much less than the time required by the method using a filtration technique for the separation of all the precipitate from the mother liquor and for the complete collection of the precipitate. In this method, the recoveries of the two elements in the presence of the most common matrix elements containing the alkaline and alkaline earth metals and transition metals were fairly good. The relative standard deviations for the results obtained from six replicate determinations are no more than 6.0 % in 100 mL of the sample solution.

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