

Bi(III)4-methylpiperidinedithiocarbamate coprecipitation procedure for separation–pre-concentration of trace metal ions in water samples by flame atomic absorption spectrometric determination

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Received 27 February 2007; received in revised form 21 March 2007; accepted 22 March 2007

Available online 27 March 2007

Abstract

A pre-concentration method was developed for determination of trace amounts of cadmium, copper and lead in water samples by FAAS after coprecipitation by using potassium 4-methylpiperidinedithiocarbamate (K4-MPDC) as a chelating agent and Bi(III) as a carrier element. This procedure is based on filtration of the solution containing precipitate on a cellulose nitrate membrane filter following Cd(II), Cu(II) and Pb(II) coprecipitation with Bi(III)4-MPDC and then the precipitates together with membrane filter were dissolved in concentrated nitric acid. The metal contents of the final solution were determined by FAAS. Several parameters including pH of sample solution, amount of carrier element and reagent, standing time, sample volume for precipitation and the effects of diverse ions were examined. The accuracy of the method was tested with standard reference material (MBH, C31XB20 and CRM BCR-32) and Cd, Cu and Pb added samples. Determination of Cd, Cu and Pb was carried out in sea water, river water and tap water samples. The recoveries were >95%. The relative standard deviations of determination were less than 10%.

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Keywords: Dithiocarbamate; Coprecipitation; Pre-concentration; FAAS

1. Introduction

Since several heavy metals are generally present at trace concentration in environmental and metallurgical samples such as wastewater, sediment, soils, pure metal and alloy, sensitive and selective methods of the determination are needed for the samples including these complex matrices.

Flame atomic absorption spectrometry (FAAS) is one of the most reliable techniques to determine metal ions at trace concentrations. However, the detection limits of FAAS is usually insufficient for determining $\mu\text{g/L}$ concentration levels of metal ions. Therefore, FAAS is frequently combined with pre-concentration techniques to improve the detection limit and/or selectivity.

Many techniques have been proposed to pre-concentrate trace metals from matrices that adversely influence atomic absorption spectrometric detection. The various pre-concentration procedures include extraction [1–3], ion exchange supports [4], chelating resins [5,6] and coprecipitation [7–15]. The combination of coprecipitation and filtration offer a simple and rapid pre-concentration method mainly in water analysis.

Among the pre-concentration techniques used, the coprecipitation method is a useful means of enrichment and variety of coprecipitants have been proposed. Dithiocarbamates have been widely used as chelating agents for separation, pre-concentration and determination of trace metals with coprecipitation method [16–18]. Dithiocarbamate compounds have sulfur atoms as electron-donor in their structures. Uncharged chelates form when metal ions react with bifunctional ligands. The high molar absorptivities of metal dithiocarbamate complexes make them useful spectrometric reagents for trace metals analysis. Also, metal dithiocarbamates are more useful than ammonium or alkali metal salt of dithiocarbamic acids [19,20].

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Table 1
Operating conditions for FAAS

Metal	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Flame type	Fuel flow rate (L s ⁻¹)
Cd	228.8	0.5	10	Air/acetylene	1.2
Cu	324.8	0.5	5	Air/acetylene	1.2
Pb	217.1	0.5	10	Air/acetylene	1.2

In the presented work, a coprecipitation procedure has been proposed for the separation–pre-concentration of Cd(II), Cu(II) and Pb(II) ions prior to their flame atomic absorption spectrometric determinations. The procedure was based on coprecipitation of analytes by Bi(III)4-methylpiperidinedithiocarbamate (Bi(III)4-MPDC) and it was applied to the various water samples.

2. Experimental

2.1. Apparatus

A Unicam 929 model flame atomic absorption spectrophotometer was used for determination of Cd(II), Cu(II) and Pb(II), following the instrumental parameters recommended by the manufacturer were given in Table 1. pH measurements were performed with a Jenway 3040 model digital pH-meter.

2.2. Reagent and solution

The stock solutions containing 1000 mg/L of Cd(II), Cu(II), Pb(II) and Bi(III) were prepared by dissolving appropriate amount of Cd(NO₃)₂·5H₂O (Merck), Cu(NO₃)₂·3H₂O (Merck), Pb(NO₃)₂ (Merck) and Bi₅O(OH)₉(NO₃)₄ (Merck) in 1 mol/L HNO₃. Diluted standard solutions and model solutions were daily prepared from the stock standard solutions.

The potassium 4-methylpiperidinedithiocarbamate (K4-MPDC) was synthesised according to the method given in the literature [22]. A solution of K4-MPDC (2%, m/v) was daily prepared by dissolving solid K4-MPDC in deionized water.

Two certified reference materials were used to investigate accuracy of the method: phosphate rock standard reference material BCR-32 (Cd: 20.8 µg/g; Cu: 33.7 µg/g) and standard metal alloy MBH C31XB20 (Pb: 0.21%).

The membrane filter used was made of cellulose nitrate (Sartorius AG 37070 and 0.45 µm pore).

2.3. General procedure

An aqueous solution containing 4.0 mg Bi(III) and 2 mL of a 2% K4-MPDC solution was added while stirring to a sample solution (up to 1000 mL) containing 5.0 µg of Cd, 12.5 µg of Cu and 25.0 µg of Pb, and the pH was adjusted with acetate buffer. After the precipitate has settled, the mixture was filtered through a cellulose nitrate membrane filter under vacuum. The precipitate was washed with the deionized water. The precipitate together with the membrane was dissolved 1–2 mL of concentrate HNO₃ and the solution was evaporated almost to

dryness. The residue was dissolved in 1 mL concentrate HNO₃ and diluted up to 5 mL with deionized water. The analytes in the solution were determined by FAAS.

3. Results and discussion

3.1. Effect of pH on coprecipitation

The effect of the pH on coprecipitation with Bi(III)4-MPDC was studied with a solution containing 12.5 µg of Cu, 5.0 µg of Cd and 25.0 µg of Pb. The maximum recoveries were obtained over a pH range from 4.0 to 11.5 (Fig. 1). A pH of about 5 was used for coprecipitation of Cd(II), Cu(II) and Pb(II) and adjusted with acetate buffer for further experiments.

3.2. Effect of the amounts of Bi(III) as carrier element

Bi(III) is a suitable matrix for the determination of elements of interest by AAS. This reason was tested with a preliminary experiment. As a result, the atomic absorption of Cd(II), Cu(II) and Pb(II) was not affected even if 8.0 mg of Bi(III) was used for coprecipitation. Thus, 4.0 mg of Bi(III) was used in subsequent experiments.

The experiments were also repeated without Bi(III). In this case, the recovery yields were less than 50% (Fig. 2). As the concentration of trace elements is at the µg/mL level or even lower, they cannot form completely their own independent solid phases. Also K4-MPDC cannot precipitate in water [21]. Probably, the low recoveries are due to these two reasons. Therefore, for precipitation of trace elements from aqueous solution, a solid phase must be formed.

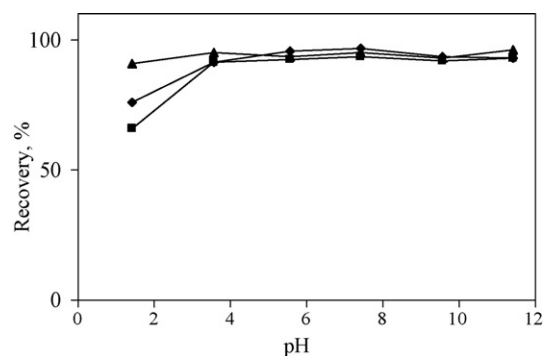


Fig. 1. Effect of pH on the recovery of copper, cadmium and lead from 250 mL of a sample solution containing 12.5 µg of Cu (▲) 5.0 µg of Cd (■) and 25.0 µg of Pb (◆) (amounts of carrier element and ligand: 4.0 mg Bi(III), 400.0 mg K4-MPDC, respectively. Final volume: 5 mL, N = 3).

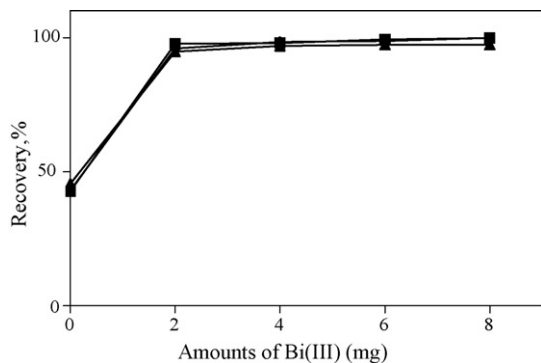


Fig. 2. Effect of the amounts of Bi(III) on the recovery of copper, cadmium and lead from 250 mL of a sample solution containing 12.5 µg of Cu (▲) 5.0 µg of Cd (■) and 25.0 µg of Pb (◆) (amounts of ligand: 400.0 mg K4-MPDC. pH: 5, final volume: 5 mL, $N=3$).

3.3. Effect of amounts of K4-MPDC

In this procedure, K4-MPDC performs two functions. Firstly, it forms the solid phase with Bi(III). Secondly, it reacts with the trace element ions to form the chelates in aqueous solution. Therefore, the effect of K4-MPDC amount on the coprecipitation was examined with the fixed amount of Bi(III) (4.0 mg), in the model solution. The amount of K4-MPDC was increased from 100.0 to 800.0 mg (Fig. 3). To obtain quantitative recovery, the optimal amount of K4-MPDC was found to be 400.0 mg for the examined metal ions.

3.4. Dissolution of the coprecipitant

For the dissolution of Bi(III)4-MPDC, several concentrated mineral acids such as nitric acid, sulfuric acid and hydrochloric acid were examined. As a result, it was found that Bi(III)4-MPDC dissolved easily in nitric acid.

3.5. Effect of matrix ions on coprecipitation

Various amounts of matrix ions were added to a solution containing fixed amounts of analytes following the procedure given here. The result were listed in Table 2. The tolerance limit

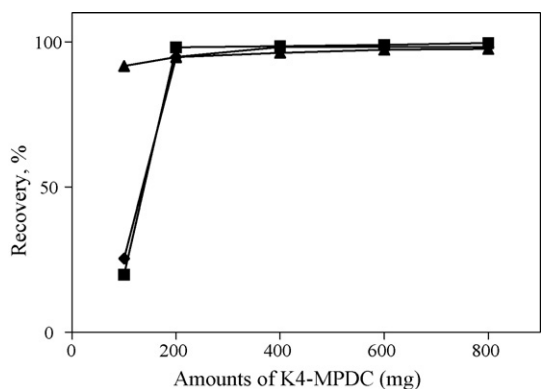


Fig. 3. Effect of the amounts of K4-MPDC on the recovery of copper, cadmium and lead from 250 mL of a sample solution containing 12.5 µg of Cu (▲) 5.0 µg of Cd (■) and 25.0 µg of Pb (◆) (amounts of carrier element: 4.0 mg Bi(III)). Final volume: 5 mL, pH 5, $N=3$).

Table 2

Tolerance limit^a for diverse salt and metal ions in Cu, Cd and Pb fixed solution

Tolerance limits ^a (g/L)			
Salts and metal ions	Cadmium	Copper	Lead
Sodium tartrate	>5	>5	>5
Sodium citrate	>5	>5	>5
Sodium acetate	>5	>5	5
Sodium oxalate	>2	>2	>2
Disodium EDTA	10	>10	10
NaI	>10	5	5
KCN	>10	5	10
Na ₂ SO ₄	>20	20	20
NaCl	>100	>100	100
NaF	>50	>50	>50
NaBr	50	>50	50
Ni(II)	0.2	0.1	0.1
Fe(II)	0.3	0.3	0.1
Cr(III)	2	0.5	0.5
Mn(II)	0.5	0.5	0.5
Mg(II)	10	1.5	10
Ca(II)	>15	15	15
Co(II)	>0.1	>0.1	0.1
Cd(II)	–	>0.1	0.1
Pb(II)	>0.1	0.1	–
Cu(II)	>0.1	–	0.1

^a Tolerance limit is the maximum amount in which there is less than 5% effect on the absorbance.

was defined as the ion concentration giving rise to a relative error less than $\pm 5\%$ related to the coprecipitation and determination of examined elements. The tolerance limits were higher than the concentration of diverse ions in sea water, river water and tap water samples.

3.6. Effect of the standing time for precipitate

The standing time for precipitate formation was also optimized as another important factor influencing the quality of coprecipitation. After 10 min, the quantitative recoveries for all elements were obtained. This period was long enough for the formation of precipitate and adsorption of traces on the precipitate.

3.7. Effect of sample volume

In the analysis of real sample using pre-concentration procedure, the sample volume was one of the important parameters used to reach high pre-concentration factor. Therefore, the recoveries of Cd(II), Cu(II) and Pb(II) from different sample volumes were examined from 250 to 1000 mL. The result showed that the recoveries were quantitative up to 1000 mL. In the analysis of a real sample, sample volume used was 1000 mL for obtained high pre-concentration factor. Thus, the concentration factor was found to be 200.

3.8. Method validation

The accuracy of the proposed method was investigated in water samples spiked with Cd(II), Cu(II) and Pb(II). For this

Table 3
Recovery studies for analytes from spiked water samples (sample volume 1000 mL, $N=3$)

Sample	Cd(II)			Cu(II)			Pb(II)		
	Added (μg)	Found (μg)	Recovery (%)	Added (μg)	Found (μg)	Recovery (%)	Added (μg)	Found (μg)	Recovery (%)
Tap water	5	4.94 \pm 0.17	98.8 \pm 3.3	10	11.15 \pm 0.57	92.5 \pm 4.7	20	20.09 \pm 0.62	100.4 \pm 3.1
Sea water									
Coastal region	5	4.78 \pm 0.21	95.7 \pm 4.1	10	12.11 \pm 0.54	91.9 \pm 4.1	20	19.34 \pm 0.50	96.4 \pm 1.9
Industrial region	5	5.25 \pm 0.05	104.9 \pm 0.9	10	11.82 \pm 0.54	103.5 \pm 4.7	20	19.88 \pm 0.83	99.5 \pm 3.9
Harbour region	5	5.05 \pm 0.17	101.0 \pm 3.2	10	11.83 \pm 0.40	102.9 \pm 3.5	20	19.69 \pm 0.75	98.5 \pm 3.6
River water									
The River Water	5	5.07 \pm 0.47	101.4 \pm 3.7	10	11.70 \pm 0.36	94.9 \pm 7.2	20	20.04 \pm 1.99	100.2 \pm 9.3
The Mert River	5	4.52 \pm 0.11	90.5 \pm 2.1	10	10.92 \pm 0.34	88.6 \pm 2.7	20	18.33 \pm 1.24	91.7 \pm 6.2

purpose, various amounts of analyte ions (Cd: 5 μg , Cu: 10 μg , Pb: 20 μg) were added to 1000 mL of water samples, and pre-concentration procedure was applied. The results were given in Table 3. As can be seen from Table 3, the recoveries were generally more than 95%. The analytes were quantitatively recovered in this study.

The standard reference materials (MBH C31XB20 and BCR-32) were also used for method validation. After dissolving reference material samples with concentrate mineral acids, their aqueous solutions were prepared. The proposed method given above was applied. The obtained results were as shown in Table 4. Good agreement was found between analytical values and certified reference values.

3.9. Analytical performance

The analytical performance of the method was illustrated by the results from flame atomic absorption spectrometric measurements. The precision of the method was evaluated as the relative standard deviations obtained after replicated analyzing samples. The relative standard deviations were less than 10% for standard reference material and samples.

The detection limits, defined as the concentration equivalent to three times the standard deviation ($N=10$) of the reagent blank, for Cd(II), Cu(II) and Pb(II) were 0.18, 0.50 and 0.20 $\mu\text{g/L}$, respectively.

3.10. Analysis of the real samples

The coprecipitation method presented here was applied to determination of Cd(II), Cu(II) and Pb(II) contents of the tap water, sea water and river water samples. Tap water samples were

Table 4
Results of determination of analyte ions in standard reference material (Cd and Cu: BCR-32; Pb: MBH C31XB20, $N=3$)

Element	Certified ($\mu\text{g/L}$)	Found ^a ($\mu\text{g/L}$)	Recovery ^a (%)
Cd	20.00	19.76 \pm 0.31	98.8 \pm 1.5
Cu	32.35	31.73 \pm 0.88	98.1 \pm 2.7
Pb	84.00	83.31 \pm 1.49	99.2 \pm 1.5

^a Mean of four determinations with 95% confidence level ($\bar{X} \pm ts/\sqrt{N}$).

taken from Ondokuz Mayıs University, sea water samples were collected from the coastal, industrial and harbour region (Black Sea), river water samples were obtained from The Mert River and The Kürtün River (Samsun-Turkey). The water samples were collected in pre-washed (detergent, deionized water, dilute HNO_3 and deionized water, respectively) polyethylene bottles. The samples were filtered through a Millipore cellulose nitrate membrane of pore size 0.45 μm . After adding acetate buffer to adjust pH, the samples were analyzed by general procedure. The results were given in Table 5.

The coprecipitation procedure with Bi(III)4-MPDC examined in this study provides a very simple, fairly rapidly, precise, accurate and reliable technique for the pre-concentration of Cu, Cd and Pb from aqueous solutions. Furthermore, high pre-concentration factors were obtained by the present method. The comparative data from coprecipitation studies in the literature were given in Table 6. The proposed method is superior to those reported in literature in term of high pre-concentration factor and good recovery. However, the method using iron(III) hydroxide [23] cannot avoid the coprecipitation of large amounts of alkaline earth metals, which may interfere with the cadmium determination. On the contrary, presented method can tolerate alkaline earth metals as seen from Table 2. Also that using cerium [11], samarium [12] and hafnium [13] hydroxide is expensive. The use of bismuth 4-MPDC also does not cause interference in the flame atomic absorption spectrometric determination of Cd, Cu and Pb.

Table 5
Determination of analyte ions in various water samples (sample volume 1000 mL, $N=3$)

Name of sample	Cd ($\mu\text{g/L}$)*	Cu ($\mu\text{g/L}$)*	Pb ($\mu\text{g/L}$)*
Tap water	BDL	2.01 \pm 0.38	BDL
Sea water			
Coastal region	BDL	3.18 \pm 0.54	BDL
Industrial region	BDL	1.42 \pm 0.19	BDL
Harbour region	BDL	1.49 \pm 0.19	BDL
River water			
The Kürtün River	BDL	2.32 \pm 0.33	BDL
The Mert River	BDL	2.33 \pm 0.26	BDL

BDL: below the detection limit. *Mean of three determinations with 95% confidence level ($\bar{X} \pm ts/\sqrt{N}$).

Table 6
Comparative data from some coprecipitation studies of heavy metal ions

Analytes	Matrix	Technique	System	Eluent	PF	Detection limit ($\mu\text{g L}^{-1}$)	Recovery (%)	Reference
Cu, Co, Pb, Cd, Fe, Mn, Ni	Water, sediment	FAAS	Cerium(IV) hydroxide	HNO ₃	150	0.18–1.56	92–100	[11]
Cu, Fe, Ni, Co, Pb, Cd, Mn, Cr	Urine, sediment, dialysis concentrates	FAAS	Samarium hydroxide	1 mol L ⁻¹ HNO ₃	10	1.1–0.99	95–100	[12]
Cr	Water	ETAAS	Hafnium hydroxide	HNO ₃	20	0.02	90–98	[13]
Cu, Fe, Pb, Mn, Zn, Cd, Cr, Ni	Water, dialysis concentrates	FAAS	Cobalt-DDTC	1 mol L ⁻¹ HNO ₃	225	4–64	≥95	[15]
Au	Water	ETAAS	Nickel-DDTC	Dilute HNO ₃	100	0.006	≥100	[17]
Bi, Sn, Pb, In, Ti, Cd, Cu, Co, Ni, Zn, Ti, Be, Zr	High purity tellurium	ICP-MS	Iron(III) hydroxide	Dilute HNO ₃	160	<0.1 $\mu\text{g g}^{-1}$	88–100	[23]
Cd, Cu, Pb	Water	FAAS	Bismuth-MPDC	Dilute HNO ₃	200	0.18–0.50	92–100	Present work

PF: pre-concentration factor, DDTC: diethyldithiocarbamate, APDC: ammonium pyrrolidone dithiocarbamate, PDC: pyrrolidinedithiocarbamate, and MPDC: 4-methylpyridinedithiocarbamate.

4. Conclusion

The pre-concentration method presented here has been successfully applied to AAS determinations of Cu, Cd and Pb in various water samples and various samples which are soluble in water.

Acknowledgement

The authors are grateful for the financial support of the Unit of the Scientific Research Projects of Ondokuz Mayıs University.

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