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Coprecipitation of lead and cadmium using copper(II) mercaptobenzothiazole prior to flame atomic absorption spectrometric determination

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Abstract. A coprecipitation method using a combination of 2-mercaptobenzothiazole (MBT) as a chelating reagent and copper as the coprecipitate carrier is described for the determination of trace lead and cadmium by flame atomic absorption spectrometry. The coprecipitation conditions, such as the effect of pH, the amount of carrier element and reagent, standing time, sample volume and matrix effects were examined in detail. It was found that lead and cadmium are coprecipitated quantitatively ($\geq$95%) with Cu(II)-MBT at pH 9 and that the relative standard deviations ($n = 7$) were $\leq$1.6%. When using the enrichment factors of 150-fold for lead and cadmium, the detection limits (3s/b) obtained are 1.08 for lead and $0.04\,\mu g\,L^{-1}$ for cadmium. The method was validated with spiked sea water, stream water, well water, and vegetable samples.

Key words: Coprecipitation; 2-mercaptobenzothiazole; lead; cadmium; flame atomic absorption spectrometry.

Many metals are of concern because of their toxic properties and some metals are also essential for survival and health of animals and humans. In risk assessments concerning toxicity of essential metals, their essentiality should also be taken into account to avoid too low intakes [1]. Lead and cadmium are two of the most hazardous elements to human health. Both metals causes adverse health effects in humans and their widespread presence in the human environment comes from anthropogenic activities [2].

The principal source of environmental lead comes from motor vehicle emissions through the addition of lead-based antiknock compounds to petrol. Other sources include lead plumbing, glazed pottery, solder used in tin cans, old pewter, and lead-based paints. The principal problems of lead in water are associated with mining, and ore processing, industrial effluents, lead plumbing, and urban road or motorway run-off. Lead is readily absorbed through the gastrointestinal tract. Around 70–90% of the lead assimilated goes into the bones, then liver and kidneys [3, 4]. It leads to renal tumors. It interferes in the metabolism of calcium and vitamin D and affects hemoglobin formation and causes anemia. It is a neurotoxin and causes behavioral abnormalities, retarding intelligence and mental development [5].

Cadmium is one of the toxic heavy metal elements for animals and humans even at low concentrations. Exposure to lower amounts of cadmium may cause gastrointestinal irritation, vomiting, abdominal pain and diarrohea. Acute exposure may affect kidneys resulting in tubular proteinosis and sometimes fatality

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[6]. In the environment Cd is present in air due to incineration of household wastes, through emission from industry including mining, and from energy production based on coal combustion. Cadmium particles can be transported in air long distances and thus the ground and water could be contaminated far from the emission source. Cadmium remains in the soil and water strongly bound to other compounds [1].

Through the food chain systems of soil-plant-animal-human, cadmium and lead are transferred into animals and human beings, causing severe contamination. Consequently, the development of reliable methods for the removal and determination of cadmium and lead in environmental samples is of particular significance.

Among the spectral methods, flame atomic absorption spectrometry (FAAS) is simple, rapid, reliable, low cost and present in almost all analytical laboratories. However, this technique suffers from lack of sensitivity for the ultra-trace metal concentrations usually encountered in environmental samples. In the determination of cadmium and lead in numerous real samples by atomic absorption spectrometry, there is crucial need for a preconcentration step before their analysis due to their frequent low concentrations. Additionally, since high levels of concomitant components usually accompany analytes, a separation step is often required. For this purpose, many preconcentration methods have been proposed and used to separate and preconcentrate trace elements, according to nature of the samples, the concentration of the analytes and the measurement techniques [4, 7]. Solvent extraction [8], ion-exchange [9], cloud-point extraction [10], solid-phase extraction [11–13] and coprecipitation [14–16] are well-known procedures for the preconcentration and separation.

Coprecipitation is one of the most efficient separation/enrichment techniques for trace heavy metal ions. The main requirement for this technique is that the collector should be easily separated from the matrix solution. This can be done by filtering, centrifuging and washing of the precipitate. In addition, it is desirable that the collector should be a pure and readily available substance. The advantages of this technique are its simplicity and the fact that various analyte ions can be preconcentrated and separated simultaneously from the matrix. Inorganics which are magnesium [17], indium [14], aluminum [16], cerium [18], terbium [19] and iron [20] hyroxides and organic coprecipitants, generally dithiocarbamates of bismuth [21], copper [22, 23], nickel [24] and cobalt [25] have been widely used as efficient collectors of trace elements.

2-Mercaptobenzothiazole is insoluble in water but is soluble in aqueous alkali and common organic solvents, including ethanol, benzene and acetone. It reacts with a wide variety of soft metal ions to form yellow to yellow-orange insoluble complexes and has been used as a gravimetric reagent for Cd ($K_{sp} = 8.9 \times 10^{-9}$) and Pb ($K_{sp} = 6.1 \times 10^{-14}$) [26].

Some solid phase extraction studies have been realized using 2-mercaptobenzothiazole (MBT) recently. Absalan and Mehrdjardi determined silver ion from aqueous sample solutions using MBT immobilized on surfactant-coated alumina [27]. Ma et al. realized separation and determination of trace Hg(II) in environmental samples with aminopropylbenzoylazo-MBT bonded to silica gel [28].

In the present study, Cu(II)-mercaptobenzothiazole (Cu(II)-MBT) was used as a new coprecipitant in order to determine the trace Pb(II) and Cd(II) in water and vegetable samples by FAAS. To our literature knowledge, there is no study on the coprecipitation of trace metal ions by using 2-mercaptobenzothiazole. The experimental conditions for coprecipitation of the Pb(II) and Cd(II) onto Cu(II)-MBT, including pH, amount of carrier element, reagent amount, sample volume, standing time, and matrix ions, were optimized.

Experimental

Instrument

A Perkin Elmer 3110 model flame atomic absorption spectrometer equipped with an air-acetylene burner, Shelton, USA (www.perkinelmer.com) was used for the analysis under the conditions suggested by the manufacturer. The operating conditions were as follows: wavelength, 283.3 and 228.8 nm; bandwidth, 0.7 and 0.7 nm, lamp current, 15 and 8 mA; acetylene and air flow rates, 2 and 4 L min^{-1}, for Pb(II) and Cd(II), respectively. A centrifuge of MLTW 54 model to centrifuge and a Schleicher and Schuell filtration apparatus to filtrate the solutions were used. The membrane filter used was made of mixed cellulose ester (0.45 μm pore size and 47 mm diameter; Advantec MFS Inc., CA, USA). All pH measurements were made with a Jenko 672 model digital pH meter equipped with a combined pH electrode.

Reagents and solutions

All chemicals 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. Pb(II), Cd(II) and carrier element Cu(II) stock solutions (1000 mg L^{-1}) were prepared from the nitrate salts of metals in 1% HNO_3 (w/w). 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. MBT solution of 1% (w/v) was prepared by dissolving 1.00 g of MBT (Merck, Darmstadt, Germany) in 100 mL of ethyl alcohol. The acetic acid/acetate buffer for pH 6 and ammonia/ammonium chloride buffer for pH 8–10 were used.

Coprecipitation procedure

The coprecipitation method was optimized with aqueous model solutions prior to its application to real samples. 750 µg Cu as carrier element and then 1 mL of 1% (w/v) MBT solution were added to 35 mL of a solution containing 30 µg Pb and 2 µg Cd in a centrifuge tube. The pH of solution was adjusted to pH 9 with an ammonia/ammonium chloride buffer solution. After 10 min, the solution was centrifuged at 3000 rpm for 5 min. The supernatant was decanted and the precipitate was dissolved with 5 mL of 3 mol L^{-1} HNO_3 by heating on a hot plate. The solution was evaporated near to dryness in a beaker and the residue was dissolved in 2 or 5 mL with 1 mol L^{-1} HNO_3, using volumetric flasks needed. The Pb and Cd in this solution were determined by FAAS.

The copper and reagent amounts were increased with increasing of sample volume. When the amount of Cu(II)-MBT coprecipitant was increased, the amount of needed nitric acid to digest the coprecipitate was also increased. Over the sample volume of 35 mL, 5 mL of 6 mol L^{-1} HNO_3 was used to digest the precipitate. The solution was evaporated nearly to dryness and then the residue dissolved with 5 mL of distilled water.

Preparation of the vegetable and water samples for analysis

The onion, parsley and dill samples were collected from an urban vegetable garden in Kayseri. Firstly, the vegetable samples were washed throughly with tap water followed by distilled water, dried at 110 °C, and ground to pass a 200 mesh sieve. A portion of 0.5 g of the sample was taken in a 100 mL beaker. For dissolution, 10 mL of concentrated nitric acid was added to the sample. The beaker was heated on a hot plate at about 130 °C for 3 h. After cooling to room temperature, 3 mL of concentrated hydrogen peroxide (30% w/w) was added drop wise. The mixture was again evaporated to dryness and the residue dissolved with 0.5 mol L^{-1} HNO_3, and then filtered through a blue band filter paper. The filtrate was diluted to 35 mL with distilled water. For analysis the certified reference material (GBW07605 Tea sample), the dissolving procedure described for vegetable samples was applied, with exception the use of concentrated perchloric acid (4 mL) instead of concentrated hydrogen peroxide [29]. The subsequent procedures were the same those described in *Coprecipitation Procedure* section. The analyte ions in this solution were determined by FAAS.

The sea water sample from Aegean Sea, İzmir, Turkey, and well water samples from Kayseri were immediately filtered through a Millipore cellulose membrane filter (0.45 µm pore size), acidified to pH 2 with HNO_3, and stored in precleaned polyethylene bottles. Tap water sample was analysed without any pretreatment. For the analysis, the sample containing 250 mL of acidified waters were firstly neutralized and then pH of which was buffered to 9. The proposed coprecipitation procedure was applied to the samples.

Results and discussion

Effect of pH

The effect of model solution pH on the coprecipitation of Pb(II) and Cd(II) ions with Cu(II)-MBT was investigated using buffer solutions. 1 mg of Cu as carrier element and 1 mL of 1% (w/v) MBT solution were added to 35 mL of a solution containing 30 µg Pb and 2 µg Cd. The pH of model solutions was adjusted to pH value requested by using acetic acid/acetate (pH 6) buffer and ammonia/ammonium chloride (8–10) buffer. Then the coprecipitation procedure described in *Coprecipitation Procedure* section was applied. Quantitative recoveries ($\geq$95%) were found at the pH 8.5–9.5 for the both analytes. Above pH 9.5, the percent recovery values of Pb and Cd decrease, probably due to the formation of Pb and Cd hydroxides. Therefore, the working pH was chosen as 9 for the following experiments.

Effect of amount of carrier element

When the trace elements are present in an aqueous sample solution at concentrations below about 1 mg L^{-1}, it is generally difficult or impossible to precipitate and separate them quantitatively. Therefore, carrier precipitation is generally applied to ensure quantitative trace recoveries [30]. For this purpose, the influence of Cu(II) amount needed for coprecipitation of Pb(II) and Cd(II) was investigated with model solutions including Cu(II) changing from 0 to 1000 µg. The results obtained indicate that the recoveries are quantitative in the range 500–1000 µg Cu(II) for lead and 650–1000 µg Cu(II) for cadmium (Fig. 1). The experiments were repeated without copper, the recoveries for Pb(II) and Cd(II) were found as 11 and 8%, respectively. Therefore, Cu(II) is necessary for the quantitative recoveries of the analytes by the described

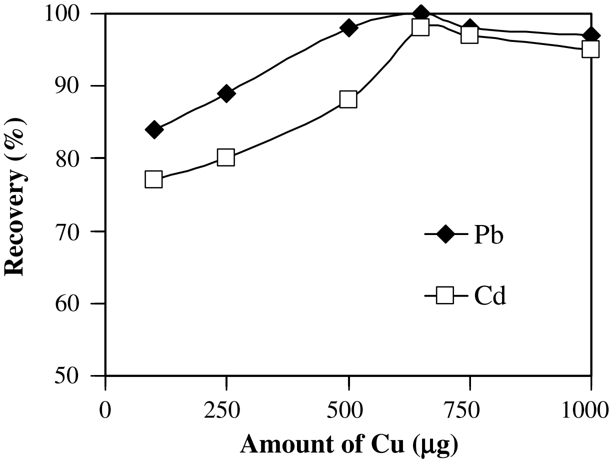

Fig. 1. The effect of copper amount on the recovery of analytes (amount of analytes: 30 µg of Pb and 2.0 µg of Cd)

coprecipitation method. The Cu(II) amount of 750 µg was taken as optimum in further experiments.

Effect of reagent amount

The effect of MBT amount on the coprecipitation of Pb(II) and Cd(II) was examined using the model solutions of 35 mL containing 750 µg Cu(II) at pH 9. The volume of MBT of 1% (w/v) added to the model solutions was increased from 0 to 3 mL. The quantitative recovery values for both Pb and Cd, were obtained for 750 µL–2.5 mL reagent volumes. The 1 mL of MBT was used in subsequent studies. Also, the experiments made without the MBT gave low recoveries such as 30% for Pb and 4% for Cd.

Effect of standing time for coprecipitation

The standing time, which is important for the quality of coprecipitation, was optimized working with the time period of 5–60 min. After 5 min, the quantitative recoveries for Pb and Cd were obtained. The requested time for formation of precipitate and the adsorption of Pb and Cd on the Cu(II)-MBT precipitant, was used as 10 min for all the optimization studies.

Effect of sample volume

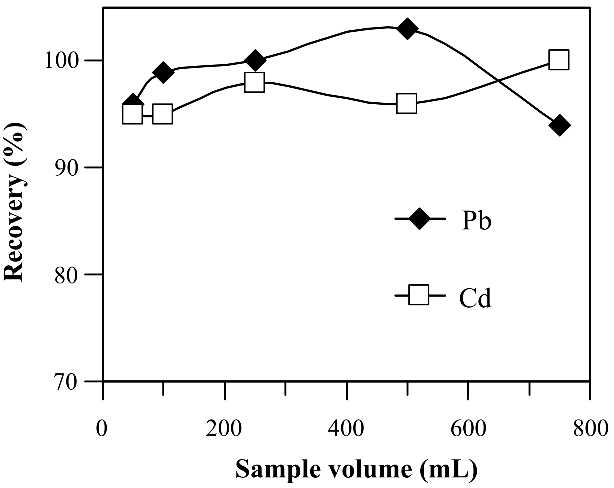

Fig. 2. Effect of sample volume on the recovery of Pb and Cd

The sample volume is one of the important parameters used to obtain a high concentration factor. For this reason, the ratio of sample to final volumes should be increased by lowering the final volume and/or increasing the sample volume. The maximum applicable sample volume was investigated using sample volumes from 50 to 750 mL and keeping the total amount of Pb (30 µg) and Cd (2 µg). The carrier element and reagent amount were increased with increasing sample volume. The results showed that the recoveries for Pb and Cd were quantitative in the range of 50–750 mL (Fig. 2). When the final solution volume was used as 5 mL, a preconcentration factor up to 150 for Pb and Cd can be obtained.

Effect of interfering ions

In order to detect potential interferences on the coprecipitation of Pb and Cd in water and vegetable samples, the various amounts of Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+} and Al^{3+} ions were added to the model solution containing fixed amounts of the analytes as their nitrate or chloride salts. The described coprecipitation procedure was applied for all the interfering ions separately. The results were listed in Table 1. As can be seen in Table 1, large amounts of the matrix components have no serious interfering effect on the recovery of the examined elements. These results show that the described copre-

Table 1. Effect of matrix ions on coprecipitation of Pb and Cd (pH 9; 30 µg of Pb and 2 µg of Cd; $n = 3$)

Ions	Added as	Concentrations studied (µg mL^{-1})	Concentrated tolerated (µg mL^{-1})	Recovery (%)	
				Pb	Cd
Na^+	NaCl	100, 500, 1000, 5000	5000	91 ± 2[a]	91 ± 1
K^+	KNO_3	150, 250, 500, 1000	1000	96 ± 2	102 ± 3
Ca^{2+}	$CaCl_2$	100, 150, 500	500	93 ± 3	89 ± 2
Mg^{2+}	$Mg(NO_3)_2$	50, 100, 500	500	99 ± 4	102 ± 2
Al^{3+}	$Al(NO_3)_3$	50, 100, 150, 250	250	98 ± 6	94 ± 1
Fe^{3+}	$Fe(NO_3)_3$	100, 250, 500	500	96 ± 1	98 ± 2
Cr^{3+}	$Cr(NO_3)_3$	25, 50, 100	100	99 ± 1	103 ± 1
Mn^{2+}	$Mn(NO_3)_2$	25, 50	50	93 ± 2	91 ± 1
Zn^{2+}	ZnO	25, 50, 100	100	94 ± 4	94 ± 2
Ni^{2+}	$Ni(NO_3)_2$	10, 25, 50	50	100 ± 2	93 ± 1

[a] $\bar{x} + s$ Mean value ± standard deviation.

cipitation method could be applied to samples containing the interfering ions at high levels.

Analytical performance

The analytical performance of the proposed method was evaluated under the optimum conditions mentiond above (pH 9, reagent: 1 mL of MBT of 1% (w/v), Cu amount: 750 µg, sample volume: 35 mL). For this purpose, the analyses were performed by applying the proposed method in seven replicates. The Pb and Cd concentrations in final solution were determined by FAAS. The mean recoveries were found to be 98 ± 2% for Pb and 98 ± 1% for Cd at 95% confidence level. The relative standard deviation values for recovery studies were 1.6 and 1.3%, for Pb and Cd, respectively.

The detection limit (DL) was also studied. The proposed coprecipitation method was applied to 35 mL of blank solution at the optimum conditions ($n = 10$). 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 (3s/b). DLs were found as 1.08 for Pb and 0.04 $\mu g\,L^{-1}$ for Cd using the preconcentration factor of 150.

Validation of the method and its application

In order to evaluate the accuracy of the proposed coprecipitation method, recovery experiments were carried out with spiked water and vegetable samples. The different amounts of analyte ions were spiked to 250 mL of the water samples and 35 mL of digestion solutions obtained from 0.5 g of vegetable sample. For 35 mL of vegetable solution, 1 mL of MBT of 1% (w/v) and 750 µg Cu were used. The pH of sample solution was adjusted to 9.0 and subjected to the recommended coprecipitation procedure for the preconcentration and determination of Pb and Cd. Five replicates analyses were performed for each sample. The recovery and the results of analysis of the water and vegetable samples are shown in Tables 2 and 3, respectively. A good agreement was obtained between the added and found analyte contents. The recovery values for the Pb and Cd were in the range of 87–105%, indicating that the accuracy of the procedure and its independence from matrix effects.

To evaluate the accuracy of the proposed procedure, lead was determined in the certified reference material (GBW07605 Tea sample). The lead content was found to be 4.2 ± 0.1 $\mu g\,g^{-1}$ with a satisfactorily recovery of 95.5% (the certified value: 4.4 ± 0.3 $\mu g\,g^{-1}$). Cadmium concentration in certified reference material could not determined.

Comparison with other coprecipitation methods

Table 4 shows the salient features of various coprecipitation procedures developed for cadmium and lead

Table 2. The recoveries of the analytes in the spiked sea, tap and well water samples (sample volume: 250 mL, $n = 5$)

Element	Sea water			Tap water			Well water		
	Added ($\mu g\,L^{-1}$)	Found[a] ($\mu g\,L^{-1}$)	*R* (%)	Added ($\mu g\,L^{-1}$)	Found[a] ($\mu g\,L^{-1}$)	*R* (%)	Added ($\mu g\,L^{-1}$)	Found[a] ($\mu g\,L^{-1}$)	*R* (%)
Pb	–	13 ± 1		–	<DL		–	<DL	
	40	54 ± 2	103	20	21 ± 1	105	40	39 ± 4	98
Cd	–	<DL		–	<DL		–	0.5 ± 0.1	
	4.0	3.8 ± 0.2	95	2.0	2.0 ± 0.4	100	2.0	2.5 ± 0.2	100

[a] $\bar{x} + s$ Mean value ± standard deviation.

Table 3. The determination of Pb and Cd in onion, parsley and dill samples (Cu amount: 750 µg, reagent amount: 1 mL of 1% (w/v) MBT, sample volume: 35 mL, $n = 5$)

Element	Onion			Parsley			Dill		
	Added ($\mu g\,g^{-1}$)	Found[a] ($\mu g\,g^{-1}$)	*R* (%)	Added ($\mu g\,g^{-1}$)	Found[a] ($\mu g\,g^{-1}$)	*R* (%)	Added ($\mu g\,g^{-1}$)	Found[a] ($\mu g\,g^{-1}$)	*R* (%)
Pb	–	0.8 ± 0.2		–	2.2 ± 0.5		–	1.0 ± 0.2	
	6.0	6.4 ± 0.2	93	4.0	6.4 ± 1.5	105	4.0	4.7 ± 0.4	93
Cd	–	<DL		–	0.11 ± 0.03		–	0.15 ± 0.03	
	1.2	1.04 ± 0.07	87	0.4	0.48 ± 0.06	93	0.4	0.54 ± 0.05	98

[a] $\bar{x} \pm s$ Mean value ± standard deviation.

Table 4. Preconcentration procedures using coprecipitation for the determination of cadmium and lead

Sample	Collector	Technique	DL ($\mu g\,L^{-1}$)		RSD (%)		Enrichment factor		pH		Reference
			Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	
Sea water, stream water, well water, onion, parsley and dill samples	Cu(II)-MBT	FAAS	0.04	1.08	1.3	1.6	150	150	9	9	This work
Wastewater, spring water, river water and seawater	Indium hydroxide	FAAS	0.6	8.6	1.6–3.5	2.8–4.2	50	75	9.5	9.5	[14]
Seawater and mineral water	Aluminum hydroxide	FAAS	6	16	2–3	2–3	125	125	7	7	[16]
Drinking water and sea water	Cerium (IV) hydroxide	FAAS	0.4	7	6.5–8.9	6.5–8.9	375	375	10.5	10.5	[18]
Contaminated river water	Terbium hydroxide	GFAAS	–	0.5	–	4.6	–	20	–	8.7–11.5 (9.0)	[19]
Tap water, river water and waste water	Cu-DDTC	FAAS	0.23	3.2	1.4–4.2	2.0–4.2	26	45	9.2	9.2	[23]
Sea water and dialysis concentrated	Co-DDTC	FAAS	4	64	4.0–6.0	4.0	225	225	1.0–8.0	1.0–10.0	[25]

determination in conjunction with AAS. The present method has lower DL and RSD % values than the other coprecipitation methods [14, 16, 18, 19, 23, 25]. The enrichment factor of the method is superior in comparison to all the other methods except the coprecipitation methods containing aluminum hydroxide [16] and Co-DDTC [25] collectors.

Conclusions

The coprecipitation method with Cu(II)-MBT can be applied to the determination of Pb and Cd in the water and the vegetable samples with acceptable accuracy and precision. This method is reliable, simple, economic, fairly rapid and precise. The time required for the coprecipitation method was about 30 min. The preconcentration factor was 150 for Pb and Cd. The recoveries of elements in the presence of the most common matrix elements containing the alkaline and alkaline earth metals and transition metals were fairly good.

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