



Coprecipitation of Ni²⁺, Cd²⁺ and Pb²⁺ for preconcentration in environmental samples prior to flame atomic absorption spectrometric determinations

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ABSTRACT

A coprecipitation procedure has been presented prior to flame atomic absorption spectrometric determination of nickel, cadmium and lead ions in environmental samples. Analyte ions were coprecipitated by using copper hydroxide precipitate. The influences of some analytical parameters like amounts of copper, sample volume, etc., on the recoveries of the analytes were investigated. The interference of other ions was negligible. Under the optimized conditions, the detection limits (3 sigma, $n = 15$) of lead(II), nickel(II) and cadmium(II) were 7.0, 3.0 and 2.0 µg/L, respectively. The proposed method has been successfully applied for the determination of traces of Ni, Cd and Pb in environmental samples like tap water.

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1. Introduction

Heavy metals are major pollutants in marine, lake and ground waters as well as in industrial and even treated effluents. Heavy metals are also major hazards to the soil–plant system [1–4]. They play negative roles in human life. For example, lead is a widely deposited environmental toxicant for neurological, renal, hepatic, and immune systems [5,6]. Nickel is widely used in modern industry. Its overexposure in human beings can provoke significant effects including lung, cardiovascular and kidney diseases [7–9]. The determinations of the heavy metals in environmental samples are important for human health. Flame atomic absorption spectrometry (FAAS) is one of the instrumental techniques for the determination of heavy metal ions at trace levels [10–13]. However, the direct determination of heavy metal ions by FAAS at trace levels in real samples remains a challenging problem because of their low concentration and matrix effects. Lower element concentrations than the quantitation limits of FAAS are another problem in flame atomic absorption spectrometric determinations [14–16]. In order to overcome these limitations, separation–preconcentration methods are used by the analytical chemists [17–19]. Several methods extensively used for preconcentration include liquid–liquid extraction, ion exchange, cloud point extraction,

membrane filtration, solid phase extraction and coprecipitation [20–25].

The coprecipitation technique for heavy metal ions is also widely applied for isolation and preconcentration of analytes from a liquid matrix and/or purified extracts. It has some advantages: simple, rapid and analytes could be preconcentrated and separated from the matrix simultaneously. Inorganic and organic coprecipitants have been used successfully in the coprecipitation of heavy metal ions at trace levels.

In the presented work, hydroxide was selected as an inorganic precipitant and copper(II) was selected as a carrier element. According to our literature survey, this combination was not used for the coprecipitation of metal ions. The analytical parameters including pH, amounts of copper, sample volume, etc., on the recoveries of nickel(II), cadmium(II) and lead(II) ions were investigated.

2. Experimental

2.1. Reagents

All the reagents used were of analytical grade. Deionized double distilled water was used throughout the experimental work. Laboratory glassware was kept overnight in a 10% v/v HNO₃ solution and then rinsed with deionized double distilled water. A solution of copper(II) (0.1%) was prepared by dissolving 0.1 g of Cu(NO₃)₂ (E-Merck, Germany) in deionized doubly distilled water in 100 mL standard flask. It was prepared daily. Diluted NaOH solutions (0.1M) were used at the pH adjustments.

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Stock standard solutions of analytes, 1000 mg/L, were prepared by dissolving appropriate amount of nitrate salts of analytes in 1% nitric acid. Stock metal ion solutions were diluted daily for obtaining reference and working solutions. The calibration curve was established using the standard solutions prepared in 1 mol/L HNO₃ by dilution from stock solutions.

2.2. Instruments

A Varian AA240 model flame atomic absorption spectrometer was used for determination of analytes. The operating parameters of instruments for nickel, cadmium and lead were set according to the manufacturer recommendation. For measuring pH values in the aqueous phase, WTW 330i model glass-electrode was employed. Ohaus EP214C model analytical balance was used for all mass measurements.

2.3. Model studies

1.0 mL of 0.1% (1 mg) copper(II) was added to 10 mL of solution containing 5–20 µg analyte ions. Then the pH of the solution was adjusted to related pH by the addition of 0.1 mol/L NaOH. After 10 min, the solution was centrifuged at 3500 rpm for 10 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 0.5 mL of concentrated HNO₃. The volume was completed to 5.0 mL by the addition of distilled water. The number of replicates for the test workings was three. The levels of analyte ions were determined by flame atomic absorption spectrometry.

2.4. Applications

0.1 g of salt sample was dissolved in 20 mL of distilled water. Then 1.0 mL of 0.1% copper(II) was added. In order to form a copper hydroxide precipitates, the pH of the solution was adjusted pH 9 by the addition 0.1 mol/L NaOH. The tube is slowly and carefully shaken for several seconds and allowed to stand for 10 min. The precipitate is centrifuged at 3500 rpm for 10 min and the supernatant is discarded. A small precipitate adheres to the bottom of the tube. Then, 0.5 mL of concentrated HNO₃ is added to dissolve the precipitate. The final volume was completed to 2.0–5.0 mL with distilled water. The analyte ions in this solution are determined with flame AAS.

For the analysis of water sample, 0.1% copper(II) was added to 200 mL of water sample analyzed. The pH of the solution was adjusted pH 9 by the addition 0.1 mol/L NaOH to obtain copper(II) hydroxide precipitates. Then the coprecipitation procedure given above was performed.

3. Results and discussion

3.1. Influences of pH

On the coprecipitation works, pH of the working solutions is one of the main factors to obtain quantitative recoveries of the analytes [26–30]. The influences of pH on the recoveries of cadmium, nickel and lead ions were investigated in the pH range of 8–12. pH of the model solutions was adjusted by the addition of 0.1 mol/L NaOH. The results are depicted in Fig. 1. Analyte ions were quantitatively recovered in the pH range of 9–12 except lead(II). Lead(II) was quantitatively recovered in the pH range of 9–11. All subsequent works were performed at pH 9.

3.2. Influences of amounts of copper(II) as carrier element

The influences of amounts of copper(II) as carrier element on the recoveries of analyte ions were also examined by using model solu-

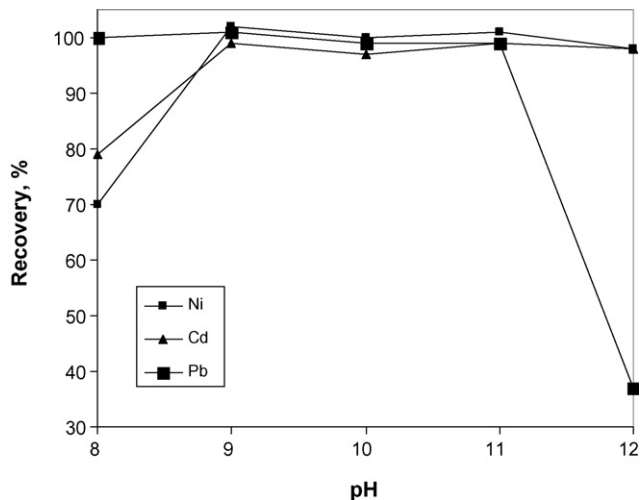


Fig. 1. Effects of pH on the coprecipitation efficiencies of analyte ions ($N=3$).

tions at pH 9. The results are given in Fig. 2. The recoveries of analyte ions were not quantitative without copper. Quantitative recoveries were obtained for cadmium(II), nickel(II) and lead(II) ions at the copper amounts range of 0.25–2.0 mg (Fig. 2). All further works were carried out by the addition of 0.1 mg of copper(II) as carrier element.

3.3. Effects of duration time for coprecipitation

The influences of duration time for the coprecipitation on the recoveries of analytes were also studied in the time range of 1–20 min. Quantitative recoveries for all the analytes were obtained all the ranges. The studies were performed at 10 min of duration time.

3.4. Influences of centrifugation time

The influences of centrifugation time on the recoveries of analyte ions were investigated at 3500 rpm. Quantitative recoveries for Cd(II), Pb(II) and Ni(II) ions were obtained in the range of 5–25 min. All further works were carried out at 15 min of centrifugation time.

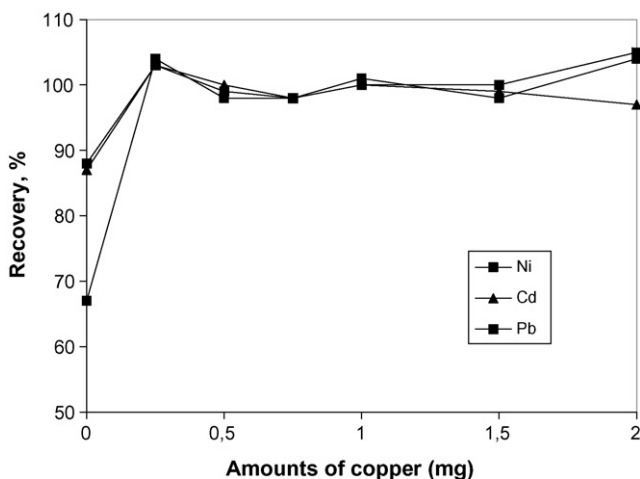


Fig. 2. Influences of copper(II) on the recoveries of analytes ($N=3$).

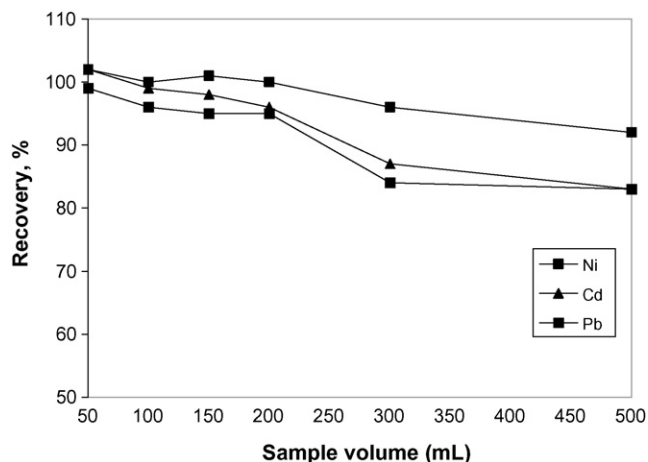


Fig. 3. Effects of sample volume on the recoveries (N=3).

3.5. Sample volume

The influences of the sample volume of aqueous solution on the recoveries of analytes were investigated in the sample volume range of 50–500 mL by using model solutions. The results are depicted in Fig. 3. Analytes were quantitatively (95%) recovered in the sample volume range of 50–200 mL. The final volume of the coprecipitation work was 2.0–10.0 mL. A preconcentration factor of 100 for the analytes can be achieved when the final volume was 2.0 mL.

3.6. Effect of matrix ions

The effects of potential diverse ions on the coprecipitation efficiency of analytes were examined by adding known concentrations of different ions. Then the coprecipitation procedure given in Section 2.3 was applied to all the diverse ions separately. The results were summarized in Table 1. The tolerated amounts of each diverse ion were the concentration values tested that caused less than 5% the absorbance alteration. The ions do not interfere under the experimental conditions used. Also, some of the transition metals at mg/L levels were not interfered on the recoveries of the analyte ions.

3.7. Detection limits

The detection limits for analyte ions were calculated after presented preconcentration procedure applied to the blank solutions.

Table 1
Effects of matrix ions on the recoveries

Ion	Added as	Recovery (%)			
		Concentration (mg/L)	Ni	Cd	Pb
Na ⁺	NaCl	5000	95 ± 2	101 ± 1	96 ± 3
K ⁺	KNO ₃	1250	101 ± 2	102 ± 2	98 ± 3
Mg ²⁺	MgCl ₂ ·6H ₂ O	500	98 ± 4	103 ± 1	102 ± 3
Ca ²⁺	Ca(NO ₃) ₂ ·4H ₂ O	500	96 ± 1	98 ± 1	98 ± 1
SO ₄ ²⁻	NaSO ₄	1250	97 ± 3	100 ± 1	96 ± 4
Fe ³⁺	Fe(NO ₃) ₃ ·9H ₂ O	7	96 ± 3	100 ± 3	102 ± 3
Ni ²⁺	Ni(NO ₃) ₂ ·6H ₂ O	7	–	100 ± 1	100 ± 4
Cd ²⁺	Cd(NO ₃) ₂ ·6H ₂ O	7	106 ± 4	–	98 ± 3
Co ²⁺	Co(NO ₃) ₂ ·6H ₂ O	7	105 ± 4	101 ± 3	99 ± 4
Pb ²⁺	Pb(NO ₃) ₂	10	101 ± 4	104 ± 4	–
Al ³⁺	AlCl ₃ ·6H ₂ O	7	95 ± 1	96 ± 4	95 ± 1
Cr ³⁺	Cr(NO ₃) ₃ ·9H ₂ O	7	106 ± 4	96 ± 1	105 ± 1

Table 2
Application of the presented procedure for water samples (N=3)

Added (μg)	Bottled mineral water		Tap water		Bottled drinking water	
	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Ni						
0	BDL ^a	–	BDL	–	BDL	–
5	4.7	94 ± 5	5.0	100 ± 1	5.0	100 ± 1
10	9.5	95 ± 1	9.8	98 ± 3	9.8	98 ± 4
15	14.1	94 ± 2	15.0	100 ± 1	14.4	96 ± 1
Cd						
0	BDL	–	BDL	–	BDL	–
5	4.7	95 ± 2	5.1	102 ± 3	5.0	100 ± 1
10	9.8	98 ± 1	9.5	95 ± 1	9.5	95 ± 2
15	14.2	95 ± 1	14.4	96 ± 3	14.2	95 ± 2
Pb						
0	BDL	–	BDL	–	BDL	–
10	10.0	100 ± 5	9.6	96 ± 1	10.5	105 ± 4
20	20.6	103 ± 4	19.0	95 ± 1	20.4	102 ± 3
30	28.5	95 ± 2	30.3	101 ± 4	30.3	101 ± 4

^a BDL: Below the limit of detection.

Table 3
Application of the presented procedure for salt samples (N=3)

Added (μg)	NaCl at analytical reagent grade		KCl at analytical reagent grade		Table salt	
	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Ni						
0	BDL ^a	–	BDL	–	BDL	–
5	5.0	100 ± 1	5.0	100 ± 1	5	100 ± 1
10	10.0	100 ± 1	9.6	96 ± 1	9.8	98 ± 3
15	14.4	96 ± 3	15.0	100 ± 3	14.4	96 ± 3
Cd						
0	BDL	–	BDL	–	BDL	–
5	4.9	98 ± 1	4.9	99 ± 1	4.9	99 ± 1
10	9.9	99 ± 1	9.8	98 ± 1	9.8	98 ± 1
15	14.4	96 ± 1	14.4	96 ± 2	14.4	96 ± 1
Pb						
0	BDL	–	BDL	–	BDL	–
10	9.7	97 ± 4	10.0	100 ± 1	9.7	97 ± 4
20	19.6	98 ± 2	20.0	100 ± 1	19.4	97 ± 1
30	28.8	96 ± 1	30.0	100 ± 1	30.3	101 ± 1

^a BDL: Below the limit of detection.

The detection limits, defined as the concentration equivalent to 3 times the standard deviation ($n = 15$) of the reagent blank, for lead, nickel and cadmium were 7.0, 3.0 and 2.0 μg/L, respectively.

3.8. Method validation

To the validation of present method was evaluated, the recoveries of analytes spiked into water samples and salt samples were also studied, satisfactory results were obtained as shown in Table 2 for waters samples and in Table 3 for salt samples. Good agreement was obtained between the added and analyte recovered content using

Table 4
Determination of Cd, Ni and Pb natural water samples after application of proposed coprecipitation procedure (N=3)

Sample	Concentration (μg/L)		
	Ni	Cd	Pb
Beypazari mineral water	8.3 ± 1.0	3.2 ± 0.8	9.5 ± 1.3
Fresa mineral water	7.7 ± 2.8	2.5 ± 0.3	BDL ^a
Talas tap water	BDL	BDL	BDL

^a BDL: Below the limit of detection.

Table 5
Comparative data from some recent studies on preconcentration-separation of heavy metal ions

Technique	Analytes	System	PF	Detection limit ($\mu\text{g/L}$)	Ref.
SPE	Cd, Cr, Cu, Pb, Zn	Sorbent (rice bran)	100	0.56–1.85	[6]
SPE	Cu, Fe, Mn, Ni	Chelate Che (chelating resin)	21.3–44.1	0.5–1.1	[37]
SPE	Fe(III), Pb(II), Ni(II)	<i>Aspergillus niger</i> loaded on silica gel	50	1.7–5.6	[35]
Coprecipitation	Cd(II), Cr(III), Pb(II), Mn(II)	Magnesium hydroxide	–	0.08–0.15	[27]
Coprecipitation	Mn(II), Co(II), Cr(III), Fe(III), Pb(II)	Erbium hydroxide	25	0.04–0.67	[30]
Coprecipitation	Ni(II), Cd(II), Pb(II)	Copper hydroxide	100	2.0–7.0	Presented work

SPE: solid phase extraction, PF: preconcentration factor.

the experimental procedure. The recovery values calculated for the standard additions for the investigated analyte ions were always higher than 95%, thus confirming the accuracy of the procedure and the absence of matrix effects.

3.9. Application

Based on the above findings, the presented procedure was applied to the determination of analytes in some water samples from Kayseri, Turkey. The results were summarized in Table 4. The concentrations given in Table 4 have been calculated on the assumption of 100% recovery of the analytes.

4. Conclusion

Coprecipitation with copper hydroxide offers a useful multi-element preconcentration technique in water analysis. The matrix effects with the method were reasonably tolerable. The recoveries were quantitative (95–106%). The preconcentration factor found for this work is superior to some coprecipitation methods and other preconcentration techniques [29–35]. The detection limits of analytes are superior to those of preconcentration techniques [29–33,35–40]. The method is relatively rapid as compared with previously reported procedures for the enrichment of analyte ions (Table 5). The presented method can be successfully applied to the preconcentration and determination of analyte ions in different real samples.

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