

Copper(II)–rubeanic acid coprecipitation system for separation–preconcentration of trace metal ions in environmental samples for their flame atomic absorption spectrometric determinations

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Abstract

A simple and facile preconcentration procedure based on the coprecipitation of trace heavy metal ions with copper(II)–rubeanic acid complex has been developed. The analytical parameters including pH, amounts of rubeanic acid, sample volume, etc. was investigated for the quantitative recoveries of Pb(II), Fe(III), Cd(II), Au(III), Pd(II) and Ni(II). No interferic effects were observed from the concomitant ions. The detection limits for analyte ions by 3 sigma were in the range of 0.14 µg/l for iron–3.4 µg/l for lead. The proposed coprecipitation method was successfully applied to water samples from Palas Lake-Kayseri, soil and sediment samples from Kayseri and Yozgat-Turkey.

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1. Introduction

Heavy metals are very harmful to plants and animals [1,2]. These metals are not bio- or photodegradable and once they enter the environment, their potential toxicity depends to a large extent on the chemical form [3]. The environmental exposure to the heavy metals is a well-known risk factor for human health [4,5]. Human activity may result in increasing level of contamination in the environment. Analyses of biologically essential or toxic metal ions found in the environment are very important [6–8].

Flame atomic absorption spectrometry are among the most widely used method for the determination of the heavy metals at trace levels, but sensitivity and selectivity of FAAS are usually insufficient for the determination of heavy metals at very low concentrations in complex matrix environmental samples [9–11]. In the trace analysis, therefore, preconcentration–separation of trace elements from the matrix is

frequently necessary, in order to improve the detection limit and selectivity for their determination by FAAS. The main advantage of preconcentration procedures is the possibility of determining lower analyte concentrations and avoiding matrix effects by effective separation of the analyte from interfering matrix components [12–14].

Several methods have been proposed and used to separate and preconcentrate trace heavy metal ions according to the nature of the samples, the concentrations of the analytes and the measurement techniques. Cloud point extraction [15,16], electroanalytical techniques [17,18], ion exchange [19,20], solvent extraction [21,22], membrane filtration [23] and solid phase extraction [24–26] are used for that purpose. Among the preconcentration/separation methods, coprecipitation is one of the most effective multi-element preconcentration methods because of its simplicity, rapidity and ability to attain a high concentration factor [27–29]. In the coprecipitation procedures for trace heavy metal preconcentration studies, a carrier element and a coprecipitant are selected [30,31]. As a carrier element, metals like copper and zinc are popular, because of their limited negative effects for environment. Inorganic including hydroxides, phosphates and organic coprecipitants like dithiocarbamate, diethyl-

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dithiophosphate, dimethylaminobenzilidene-rhodanine, etc. are used for various researchers [28,29,32–35].

Rubeanic acid (dithiooxamide) is a reagent for spectrophotometric determination of traces metal ions [36–38]. Rubeanic acid has been used for preconcentration and determination of some metal ion from various media [39–42].

In the presented work, a coprecipitation procedure has been proposed for palladium(II), iron(III), cadmium(II), gold(III), lead(II) and nickel(II) prior to their flame atomic absorption spectrometric determinations. The procedure was applied to the various environmental samples including waters and sediments.

2. Experimental

2.1. Reagents and solutions

All the reagents used were of analytical reagent grade. Deionized double distilled water was used throughout. Laboratory glassware was kept overnight in a 10% (v/v) HNO₃ solution and then rinsed with deionized double distilled water. Rubeanic acid solution 0.5% (w/v) was daily prepared in ethanol.

A stock solution of copper(II) (1000 mg/l) was prepared by dissolving 0.378 g of Cu(NO₃)₂·3H₂O (E-Merck, Germany) in deionized doubly distilled water in 100 ml standard flask. It was prepared daily. Stock standard solutions of analytes, 1000 mg/l, was 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⁻¹ HNO₃ by dilution from stock solutions.

Phosphate buffer solutions (H₂PO₄⁻/H₃PO₄) were prepared by mixing of appropriate volumes of 1 mol l⁻¹ sodium dihydrogen phosphate and phosphoric acid solutions for pH 2, and 3. Acetate buffer solutions (CH₃COO⁻/CH₃COOH) were prepared by mixing of appropriate volumes of 1 mol l⁻¹ acetic acid and 1 mol l⁻¹ sodium acetate solutions for pH 4. Phosphate buffer solutions (H₂PO₄⁻/HPO₄²⁻) were prepared by mixing of appropriate volumes of 1 mol l⁻¹ sodium dihydrogen phosphate and 1 mol l⁻¹ sodium hydrogen phosphate for pH 5–7. Ammonium buffer solutions were prepared by mixing of appropriate amounts of 1 mol l⁻¹ ammonia and 1 mol l⁻¹ ammonium chloride solutions for pH 8–11.

2.2. Apparatus

A Perkin-Elmer Model 3110 atomic absorption spectrometer equipped with Perkin-Elmer single-element hollow cathode lamps and a 10-cm air-acetylene burner were used for the determination of the metal ions. All instrumental settings were those recommended in the manufacturer's manual book (Table 1). A pH meter, Nel pH-900 Model glass-electrode was employed for measuring pH values in the aqueous phase. Hettich Rotofix 32 model and Mistral 2000 model centrifuges were used to centrifuge of solutions. The water was purified in a Human model RO 180, resulting water with a conductivity of 1 μS cm⁻¹.

Table 1

Instrumental conditions for the measurements of the analytes by FAAS

Analyte	Wavelength (nm)	Slit width (nm)	Lamb current (mA)
Fe	248.3	0.2	30
Pb	283.3	0.7	15
Ni	232.0	0.2	30
Au	242.8	0.7	10
Cd	228.8	0.7	12
Pd	244.8	0.2	12

2.3. Model working

The copper-rubeanic acid coprecipitation method was tested with model solutions prior to its application to real samples. Twenty-five milliliters portion of an aqueous solution containing 5–20 μg of Pb(II), Fe(III), Cd(II), Au(III), Pd(II) and Ni(II) was placed in a centrifuge tube. The pH of solution was adjusted with an appropriate buffer solution. Then 1.0 ml of 1000 mg/l of copper(II) as a carrier element was added to this solution. The required volume of rubeanic acid solution was poured into the tube. After 10 min, the solution was centrifuged at 2500 rpm for 20 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 500 μl of concentrated HNO₃. Then the final volume was completed to 2.0, 5.0 or 10.0 ml with deionized double distilled water. The number of replicates for the test workings was three. The analytes in the final solution were determined by flame atomic absorption spectrometry.

2.4. Analysis of real samples

One gram of food, fertilizer and soil samples was digested with aqua regia (12 ml concentrated hydrochloric acid and 4 ml of concentrated nitric acid) at room temperature then it was heated to 95 °C. After the evolution of NO₂ fumes had ceased, the mixture was evaporated almost to dryness on a sand-bath and mixed with 8 ml of aqua regia. Then the mixture was again evaporated to dryness. After evaporation 8–9 ml of deionized double distilled was added and the sample was mixed. The resulting mixture was filtered through a blue band filter paper. The residue on the filter paper is washed with 4–5 ml of deionized double distilled. The filtrate was diluted to ≈20 ml with deionized double distilled water. Then the procedure given above was applied. The analyte ions in this solution are determined by flame AAS.

The water samples collected from Lake Palas, Kayseri-Turkey were collected in pre-washed (with detergent, doubly deionized distilled water, dilute HNO₃ and doubly deionized distilled water, respectively) polyethylene bottles. The samples were filtered through a Millipore cellulose membrane of pore size 0.45 μm. The samples were stored in 1 l polyethylene bottles and acidified to 1% with nitric acid and were subsequently stored at 4 °C in a refrigerator. Prior to trace metal analysis, the acidified sea water sample was neutralised and adjusted to pH 7.0. Then the procedure was applied to the water samples. The levels of the investigated analyte ions in the final solutions were determined by flame atomic absorption spectrometry.

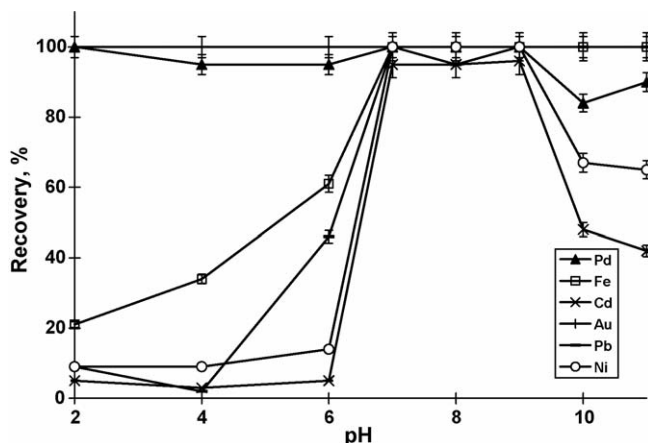


Fig. 1. Influences of pH on the recoveries of analyte ions ($N=3$).

3. Results and discussion

3.1. Effects of pH on the coprecipitation efficiency of analytes

pH is an important parameter to obtain quantitative coprecipitation efficiencies for heavy metal ions [29,31]. The influences of pH of the sample were investigated in the pH range of 2–11. For this purpose, 1.0 ml of 1000 mg/l of copper(II) as carrier element and 0.5 ml of 0.5% (w/v) rubeanic acid were added to test solutions containing analyte ions, then pH of this solution were adjusted by the addition of related buffer solution. The results for this study were given in Fig. 1. Gold(III) and palladium(III) were recovered quantitatively at the pH range of 2–11 and 2–9, respectively. Quantitative recoveries for Ni(II) and Cd(II) ions were obtained in the pH range of 7–9, while Pb(II) and Fe(III) were recovered at pH range of 7–11. The decrease on the recoveries for Pd, Ni and Cd after pH 9 may be related decomposition of copper–rubeanic acid complex. Due to the optimum condition for effective coprecipitation of analytes was found to be a neutral pH (pH 7), which is a great advantage in the preconcentration and separation of trace metal ions from natural water samples without any chemical pretreatment of the sample, pH 7 was selected as working pH for each analyte ions.

3.2. Influences of amounts of rubeanic acid

The effects of amounts of rubeanic acid on the recoveries of analyte ions were examined. The results were given in Fig. 2. When the experiments were performed without rubeanic acid at pH 7, lead, palladium and iron ions were quantitatively recovered. However, the recoveries of cadmium, gold and nickel were not quantitative in absence of rubeanic acid. The recoveries of cadmium, gold and nickel ions increased with increasing amounts of rubeanic acid. As can be seen in Fig. 2, cadmium(II), and nickel(II) ions could be recovered quantitatively in the range of 2.5–5.0 mg of rubeanic acid, while palladium could be recovered 0.5–5 ml of rubeanic acid. This results show that for the quantitative and simultaneous recoveries of all the investigated

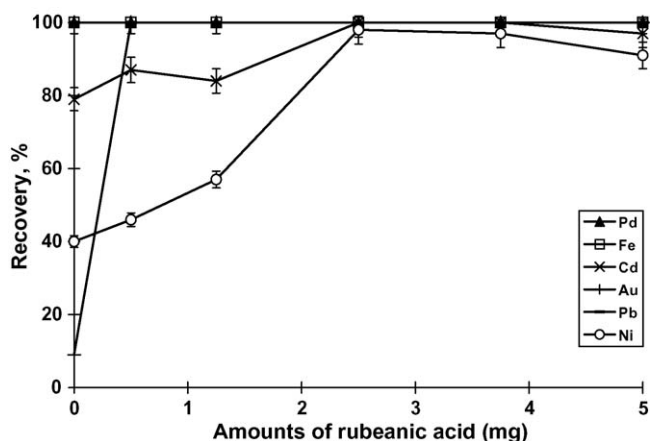


Fig. 2. Effects of amounts of rubeanic acid ($N=3$).

ions, rubeanic acid is necessary. All subsequent works 2.5 mg (0.5 ml of 0.5%, w/v) solution was used.

3.3. Amounts of copper as carrier element

The influences of amounts of copper(II) as carrier element were also investigated for this coprecipitation system. The results were depicted in Fig. 3. Without copper, the recoveries for analyte ions were below 60%. Increasing amounts of copper, the recoveries increased. Quantitative recovery values were obtained for the all analyte ions in 0.5–1.0 mg of copper. This results show that addition of copper(II) is necessary for the quantitative recoveries of the analytes by the presented coprecipitation work. The decrease in the recoveries for some metal ions especially for cadmium(II) may be related with decomposition of the copper–rubeanic acid complex with high amounts of copper ions. All further works were performed with 1 mg (1 ml of 1000 mg/l) of copper(II) ions as carrier element.

3.4. Effects of centrifuge time and rate

The effects of centrifuge rate were examined in the range of 1500–3500 rpm at the optimal analytical conditions with model

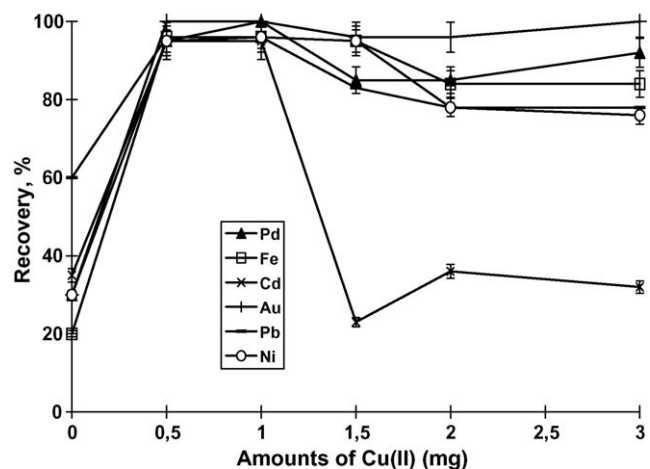


Fig. 3. Amounts of copper as a function of recovery ($N=3$).

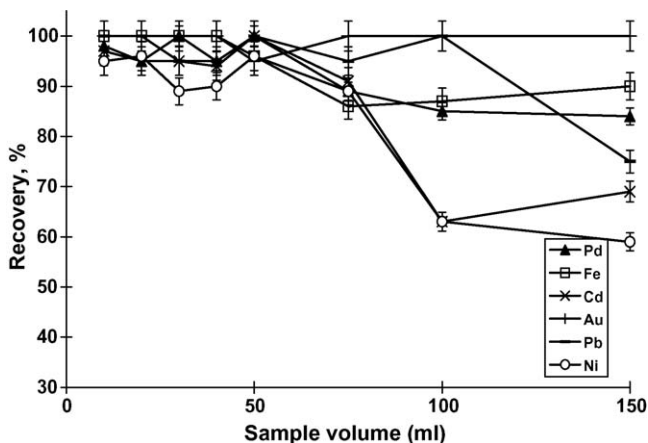


Fig. 4. Influences of the sample volume on the recoveries of analyte ions ($N=3$).

solutions. All the analytes were recovered quantitatively at the centrifuge rate of 1500–3500 rpm. Also the influences of centrifuge time were investigated. Quantitative recovery values for the analyte ions were obtained for 20 min at 2500 rpm. All the other works were performed at 2500 rpm for 20 min.

3.5. Influences of sample volume on the recoveries

To obtain high preconcentration factor, volume of the sample solution is an important parameter. Because of this point, the influences of the sample volume on the coprecipitation efficien-

Table 2

Influences of the foreign ions on the recoveries of the analytes ($N=3$)

Ion	Salt added	Concentration (mg/l)	Recovery (%)					
			Fe	Ni	Cd	Pb	Au	Pd
Na ⁺	NaCl	20000	96	95	95	96	95	81
K ⁺	KCl	1000	100	97	93	96	97	100
Ca ²⁺	CaCl ₂	1000	100	67	93	96	67	100
Mg ²⁺	MgCl ₂	1000	95	95	95	91	96	73
Cl ⁻	NaCl	20000	96	96	101	97	95	81
Al ³⁺	Al ₂ (SO ₄) ₃	25	100	102	100	104	100	82
Zn ²⁺	Zn(NO ₃) ₂	50	100	100	100	100	100	81
Co ²⁺	CoSO ₄	50	100	93	97	103	98	100
Cd ²⁺	CdSO ₄	50	96	100	–	100	102	86
Fe ³⁺	Fe(NO ₃) ₃	50	–	100	99	100	100	82
Pb ²⁺	Pb(NO ₃) ₂	50	100	100	100	–	101	82
Ni ²⁺	NiSO ₄	50	96	–	98	100	100	68

cies of the analytes were examined. The results were given in Fig. 4. Nickel, cadmium, iron and palladium ions were quantitatively recovered in the sample volume range of 10–50 ml. Quantitative recovery values were obtained for lead and gold ions in the sample volume range of 10–100 and 10–150 ml, respectively.

The precipitate of copper(II)–rubeanic acid that was including analytes was successfully dissolved 500 μ l of concentrated nitric acid. The final volume was completed to 2.0, 5.0 or 10.0 ml by deionized double distilled water. The analytes were quantitatively recovered in these studies.

Table 3

Analysis of two waters and 0.1 g KCl spiked analyte ions (sample volume 50 ml, $N=3$)

Analyte	Added (μ g)	Tap water		Bottled mineral water		KCl (analytical reagent grade)	
		Found (μ g)	Recovery (%)	Found (μ g)	Recovery (%)	Found (μ g)	Recovery (%)
Fe	0	BDL	–	BDL	–	BDL	–
	5	5.0 \pm 0.1	100	5.0 \pm 0.2	100	5.1 \pm 0.2	102
	10	8.8 \pm 0.2	87	10.2 \pm 0.3	102	10.0 \pm 0.4	100
	15	13.8 \pm 0.4	92	15 \pm 0.4	100	15.0 \pm 0.5	100
Ni	0	BDL	–	BDL	–	BDL	–
	5	4.8 \pm 0.1	96	5.0 \pm 0.2	100	4.8 \pm 0.2	96
	10	9.2 \pm 0.3	92	9.8 \pm 0.3	98	10.1 \pm 0.3	101
	15	12.0 \pm 0.3	84	13.1 \pm 0.4	87	15.0 \pm 0.3	100
Cd	0	BDL	–	BDL	–	BDL	–
	2.5	2.5 \pm 0.2	100	2.3 \pm 0.2	92	2.4 \pm 0.2	96
	5	4.7 \pm 0.1	94	4.3 \pm 0.3	86	4.7 \pm 0.4	94
	7.5	7.0 \pm 0.4	93	6.2 \pm 0.4	83	6.6 \pm 0.5	88
Pb	0	BDL	–	BDL	–	BDL	–
	10	10.0 \pm 0.2	100	10.1 \pm 0.2	101	9.8 \pm 0.2	98
	20	20.0 \pm 0.5	100	20.0 \pm 0.4	100	20.0 \pm 0.2	100
	30	30.3 \pm 0.6	101	29.7 \pm 0.6	99	30.0 \pm 0.3	100
Au	0	BDL	–	BDL	–	BDL	–
	5	5.0 \pm 0.1	100	2.0 \pm 0.2	40	5.0 \pm 0.1	100
	10	10.1 \pm 0.3	101	5.2 \pm 0.3	52	9.6 \pm 0.1	96
	15	14.8 \pm 0.2	99	8.1 \pm 0.2	54	15.6 \pm 0.4	104
Pd	0	BDL	–	BDL	–	BDL	–
	5	5.0 \pm 0.3	100	5.0 \pm 0.1	100	5.0 \pm 0.2	100
	10	9.5 \pm 0.2	95	7.5 \pm 0.2	75	10.2 \pm 0.3	102
	15	13.1 \pm 0.3	87	10.2 \pm 0.4	68	14.7 \pm 0.5	98

BDL: below the detection limit.

The preconcentration factor is calculated by the ratio of the highest sample volume for each analytes and the lowest final volume (2 ml). The preconcentration factor for Ni(II), Cd(II), Fe(III) and Pd was 25. For lead and gold ions, the preconcentration factor is 50 and 75, respectively.

3.6. Interference studies

In order to assess the possible analytical applications of the procedure presented, the effect of some foreign ions which may be interfere with the method or/and often accompany analyte ions in various real samples was examined with the optimized conditions at above. For these studies, a fixed amount of metal ions was taken with different amounts of foreign ions and recommended procedure given in Section 2 was followed. The recoveries of analyte ions were generally higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of analytes by the combination of the coprecipitation method presented and the flame atomic absorption spectrometric determination methods. The results are summarized in Table 2. As it is seen, large numbers of ions used have no considerable effect on the determination of analyte ions.

3.7. Addition/recovery tests

Tests of addition/recovery in the experiments for analyte ions were performed in two natural samples and a potassium chloride sample. The results are given in Table 3. A good agreement was obtained between the added and measured analyte amounts. The recovery values for the analyte ions were in the range of 96–104%. These values were quantitative and it shows that the presented method can be applied for the preconcentration of analyte ions in real samples.

3.8. Analytical performance

The relative standard deviations for atomic absorption spectrometric measurements for analyte ions are between 1 and 10%. The detection limits, defined as the concentration equivalent to three times the standard deviation ($n = 10$) of the reagent blank, for Pb(II), Fe(III), Cd(II), Au(III), Pd(II) and Ni(II) were 3.4, 0.14, 0.58, 1.3, 2.5 and 0.31 $\mu\text{g/l}$, respectively.

Table 4
Analyte levels in water samples from Palas Lake-Kayseri, Turkey

Element	Concentration ($\mu\text{g/l}$) ^a	
	District A	District B
Fe	25.2 \pm 3.2	30.4 \pm 4.2
Ni	11.2 \pm 1.6	10.0 \pm 1.4
Cd	BDL	BDL
Pb	BDL	BDL
Au	BDL	BDL
Pd	BDL	BDL

BDL: below the detection limit.

^a Mean \pm S.D., $N = 3$.

Table 5

Levels of analyte ions in the soil and sediment sample after application to presented coprecipitation procedure

Element	Concentration ($\mu\text{g/g}$) ^a		
	Soil from Yozgat	Soil from Kayseri	Sediment from Palas Lake
Fe	ND	ND	ND
Ni	2.7 \pm 0.6	2.3 \pm 0.2	3.2 \pm 0.5
Cd	BDL	BDL	BDL
Pb	10.0 \pm 1.1	6.7 \pm 0.4	3.5 \pm 0.6
Au	BDL	BDL	BDL
Pd	BDL	BDL	BDL

ND: not determined; BDL: below the detection limit.

^a Mean \pm S.D., $N = 3$.

3.9. Application to real samples

The coprecipitation procedure for analyte ions was applied to various environmental samples. The results are given in Table 4 for lake water samples and in Table 5 for soil and sediment samples. The results have been calculated on the assumption of 100% recovery of analyte ions.

4. Conclusion

Coprecipitation with rubeanic acid–copper(II) system offers a useful multielement preconcentration technique in environmental samples. The procedure has been successfully applied to analyte ions with acceptable accuracy and precision. The time required for the coprecipitation and determination was about 30 min. The coprecipitated analyte ions can be sensitively determined by atomic absorption spectrometry without any influence of copper and rubeanic acid.

The coprecipitation method presented in this study is most promising for the analyte ions as the preconcentration factor is 25–75 based on the analytes. The preconcentration factor achieved with presented procedure is superior to some preconcentration/separation procedures including cloud point extraction, solid phase extraction, electroanalytical techniques [3,9,11,15,16,22–24]. The detection limits of analytes are superior to those of preconcentration techniques for analyses [22–24,26,30]. The matrix effects with the method were reasonably tolerable. The good features of the proposed method showed that it is a convenient and low cost one. Also the method is relatively rapid as compared with previously reported procedures for the enrichment of analytes.

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