

Gadolinium hydroxide coprecipitation system for the separation–preconcentration of some heavy metals

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Abstract

A simple and new procedure for the determination of trace amounts of lead(II), cobalt(II), manganese(II) and copper(II) is described, that combines atomic absorption spectrometry–gadolinium hydroxide coprecipitation. One milliliter of 1% gadolinium(III) solution was added to each sample; the pH was then adjusted to 11 in order to collect trace heavy metals on gadolinium(III) hydroxide. The precipitate was separated by centrifugation and dissolved in 1 mL of 1 mol L⁻¹ HNO₃. The influences of analytical parameters including amount of gadolinium(III), sample volume, etc. were investigated on the recoveries of analyte ions. The effects of concomitant ions were also examined. The recoveries of the analyte ions were greater than 95. The detection limits for the analyte elements based on 3 sigma ($n=20$) were in the range of 0.52–12.0 µg L⁻¹. The method was applied to the determination of analytes in real samples and good results were obtained (relative standard deviations <10%, recoveries >95%).

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1. Introduction

Metals are contaminants for the environment [1–3]. Industry, traffic and other human facilities are the main sources of the metals in the environment [3–6]. The accurate and precise determination of metals in the environmental samples including natural water, soil and sediment are important to obtain right results about them [7–9]. For that purpose, instrumental analytical techniques including atomic absorption spectrometry, electroanalytical techniques, spectrophotometry, mass spectrometry and inductively coupled plasma atomic emission spectrometry have been used by the researchers around the world [3,4,10,11]. The main limitations in these determinations are lower analyte levels than the limit of quantitation of the instrument and interfering effects of the main components of the samples [12,13]. In order to solve these two problems, separation–preconcentration techniques like solid phase extraction, membrane filtration, ion-exchange, conventional solvent extraction, cloud point extraction, etc. are used for trace metal

ions prior to their detection by the instrumental techniques [14–22].

Coprecipitation is also one of the efficient preconcentration techniques for the traces heavy metal ions [23,24]. It has several advantages: it is simple and fast, several analyte ions can be preconcentrated and separated from the matrix simultaneously and inorganic or organic coprecipitants can be used as efficient collectors of trace elements. Coprecipitation by hydroxide of various metal ions including cerium, scandium, magnesium, ytterbium, samarium, erbium, lanthanum, indium, dysprosium, zirconium and iron has been reported for the preconcentration–separation of trace elements from various media like natural water [23–28]. According to our literature survey until now, the gadolinium(III) hydroxide coprecipitation system for preconcentration and separation, as well as its use in analytical procedures has not been reported before.

In this work, a coprecipitation system for the preconcentration of lead(II), cobalt(II), manganese(II) and copper(II) ions by using gadolinium(III) hydroxide has been presented. The experimental conditions for coprecipitation of analyte ions including pH, gadolinium(III) concentration, sample volume, etc. were optimized.

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2. Experimental

2.1. Reagents and solutions

High purity reagents were used for all preparations of the standard and sample solution. Stock metal solutions, 1000 mg L⁻¹ (Sigma, St. Louis) were diluted daily for obtaining reference and working solutions. The standard solutions used for the calibration procedures were prepared before use by dilution of the stock solution with 1 mol L⁻¹ HNO₃. Stock solutions of diverse elements were prepared from the high purity compounds (99.9%, E. Merck, Darmstadt).

One percent solution of gadolinium(III) was prepared freshly by dissolving gadolinium(III) oxide (suprapure grade, Merck) in small amounts of nitric acid and diluting to 50 mL with double distilled water. Nitric acid (65%) used for preparing of diluted acid solution was supra pure grade from Merck.

2.2. Apparatus

A PerkinElmer Model 3110 atomic absorption spectrometer equipped with PerkinElmer 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 that was given in Table 1.

A pH meter, Sartorius PT-10 Model glass-electrode was employed for measuring pH values in the aqueous phase. ALC PK 120 model centrifuge was 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.

2.3. Model working

Prior to coprecipitation of the analyte ions from real samples, the procedure was optimized with test works. For that purpose, 1.0 mL of 1.0% gadolinium(III) solution was added to 10.0 mL of solution containing 10–20 μg of analyte ions. pH of these solution was adjusted to 11 by the addition of diluted NaOH. After 10 min, the solution was centrifuged at 3000 rpm for 10 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 1 mL of 1 mol L⁻¹ HNO₃. Final volume was completed to 2.0 or 5.0 mL with 1 mol L⁻¹ HNO₃. The concentration of the investigated analyte ions were determined by flame atomic absorption spectrometry.

Table 1
Analytical parameters for PerkinElmer 3110 AAS

Element	Wavelength (nm)	Slit width (nm)	Lamb current (mA)
Pb	283.3	0.7	15.0
Mn	279.5	0.2	20.0
Co	240.7	0.2	15.0
Cu	327.8	0.7	15.0

2.4. Analysis of real samples

Fifty milliliters of water is placed into a centrifugation tube. One milliliter of 1.0% gadolinium(III) solution was added to each sample and to form an gadolinium(III) hydroxide precipitate and coprecipitation. pH of these solution was adjusted to 11 by the addition of diluted NaOH. The tube is allowed to stand for several seconds. The precipitate is centrifuged at 3000 rpm for 10 min and the supernatant is discarded. A small precipitate adheres to the bottom tube. Then, 1 mL of 1 mol L⁻¹ HNO₃ is added to dissolve the precipitate. The solution was completed to 2.0 or 5.0 mL with 1 mol L⁻¹ HNO₃. The analyte ions in this solution were determined by flame atomic absorption spectrometer.

3. Results and discussion

3.1. Optimization stage

An attempt was initially made to examine the effect of gadolinium(III), due to the matrix of gadolinium(III), on the determination of analyte ions by flame atomic absorption spectrometer. Increasing concentrations of Gd(III) were added to aqueous solution containing analytes. These solutions were analyzed by FAAS without any pretreatment. The absorbance values for the analytes almost constant up to about 7800 mg L⁻¹ gadolinium(III). The concentration of gadolinium(III) in the final solution for the combination of coprecipitation method with flame AAS must to be excesses 500 mg L⁻¹.

Gadolinium(III) hydroxide was formed at basic pH values. The influences of pH of the aqueous solution on the recovery values of analytes were investigated at the pH range of 8–10. The results were depicted in Fig. 1. The recoveries of manganese(II) and cobalt ions were quantitative (95%) at the pH range of 8–10 and 10–12. Quantitative recoveries for lead(II) and copper(II) were obtained at the pH range of 11–12. All subsequent work was performed at pH 11 that was obtained by the addition of diluted NaOH.

The influences of gadolinium(III) amounts on the coprecipitation of analytes were also examined in the range of 0–1.7 mg. The results were given in Fig. 2. The recoveries of analyte ions were not quantitative (below 95%) without gadolinium(III).

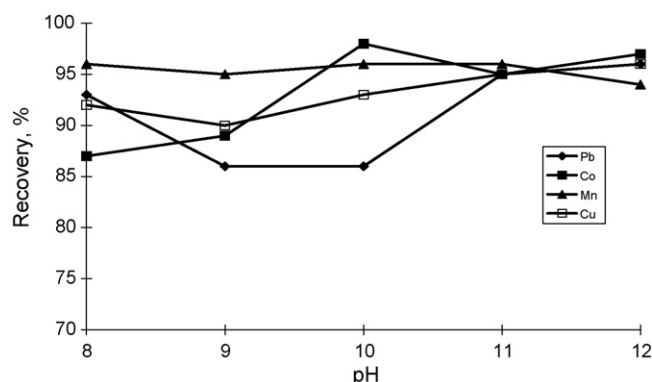


Fig. 1. Effects of pH on the recoveries of analyte ($N=3$).

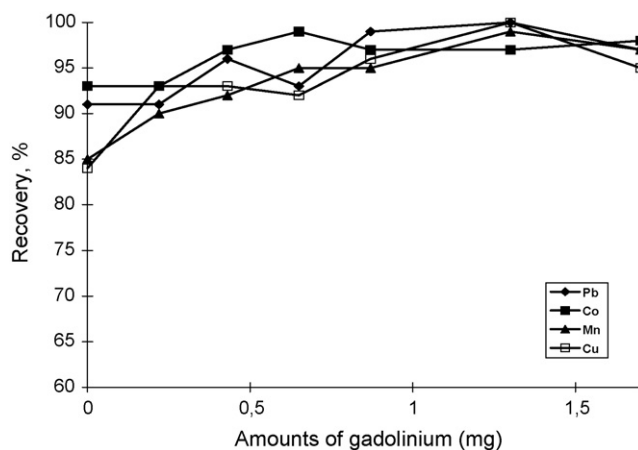


Fig. 2. Influences of amounts of gadolinium(III) on the recoveries ($N=3$).

Quantitative recovery values for all the analytes were obtained in the range of 0.25–1.7 mg of gadolinium(III). The optimum amount of gadolinium(III) was taken as 1.0 mg for all subsequent works.

The effect of the sample volume on the recoveries of lead(II), cobalt(II), manganese(II) and copper(II) ions were investigated in the sample volume range of 10–250 mL by using model solutions. The results are depicted in Fig. 3. While cobalt(II) was recovered quantitatively in the range of 10–100 mL, other analytes were quantitatively (95%) recovered in the sample volume range of 10–50 mL. The final volume of the coprecipitation work was 2.0–10.0 mL. Due to 2 mL of the final solution is quite small to measure the analytes by flame atomic absorption spectrometry, the determinations of analyte ions in the different three final solutions were prepared for each element, and then each ions were determined separately by flame atomic absorption spectrometry. A preconcentration factor of 50 for cobalt, 25 for manganese, copper and lead can be achieved when the final volume was 2.0 mL.

The influences of the standing time for gadolinium hydroxide precipitate on the recoveries of analytes were also studied. The results were given in Table 2. Analyte ions were quantita-

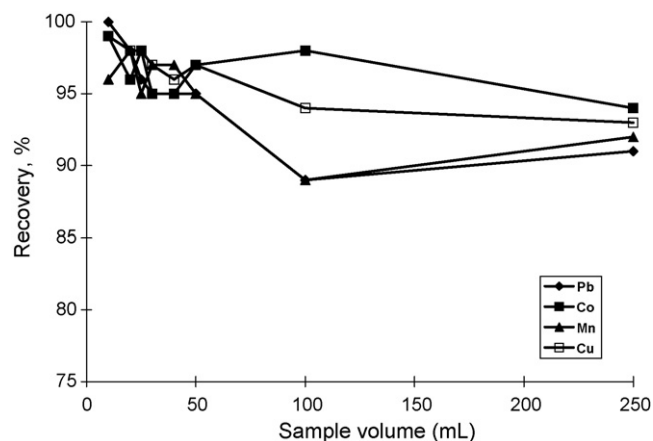


Fig. 3. Effects of sample volume ($N=3$).

Table 2
Effects of standing time for precipitate on the recoveries ($N=3$)

Standing time (min)	Recovery (%)			
	Pb	Co	Mn	Cu
5	95 ± 1	95 ± 2	95 ± 2	96 ± 1
10	99 ± 2	98 ± 1	95 ± 4	98 ± 1
20	94 ± 3	96 ± 3	93 ± 4	94 ± 0
30	94 ± 2	93 ± 2	92 ± 1	94 ± 1

tively recovered 5 and 10 min of standing times. After 10 min, the recovery values were not quantitative. For further works, 10 min was selected as standing time for gadolinium hydroxide precipitate.

The effect of concomitant ions on the coprecipitation efficiency of the analyte ions was examined. The coprecipitation procedure given in experimental was applied all the concomitant ions separately. The results were summarized in Table 3. The tolerated amounts of each concomitant ion were the concentration values tested that caused less than 5% the absorbance alteration. The ions normally present in water do not interfere under the experimental conditions used. Also, some of the transi-

Table 3
Tolerance levels of the concomitant ions on the recoveries of analyte ions ($N=3$)

Ion	Added salt	Concentration (mg L^{-1})	Recovery (%)			
			Pb	Co	Mn	Cu
Na ⁺	NaCl	10,000	97 ± 3	95 ± 2	95 ± 0	97 ± 0
K ⁺	KCl	500	99 ± 5	95 ± 2	96 ± 2	95 ± 0
Ca ²⁺	CaCl ₂	2,500	95 ± 0	96 ± 1	95 ± 0	95 ± 1
Mg ²⁺	MgCl ₂	250	100 ± 0	95 ± 1	100 ± 0	96 ± 2
SO ₄ ²⁻	Na ₂ SO ₄	500	100 ± 0	95 ± 3	97 ± 2	98 ± 2
Ni ²⁺	NiSO ₄	5	96 ± 4	95 ± 4	95 ± 2	99 ± 3
Al ³⁺	Al(NO ₃) ₃ 9H ₂ O	2	98 ± 3	95 ± 4	96 ± 2	95 ± 2
Fe ²⁺	Fe(NO ₃) ₃ 9H ₂ O	2	95 ± 2	93 ± 5	95 ± 0	96 ± 2
Pb ²⁺	Pb(NO ₃) ₂	10	–	98 ± 3	95 ± 3	97 ± 0
Cu ²⁺	Cu(NO ₃) ₂ 3H ₂ O	2	97 ± 3	95 ± 3	97 ± 1	–
Co ²⁺	Co(NO ₃) ₂ 6H ₂ O	5	100 ± 4	–	95 ± 0	99 ± 0
Mn ²⁺	MnSO ₄ H ₂ O	10	95 ± 4	95 ± 2	–	96 ± 2
Cr ³⁺	CrCl ₃ 6H ₂ O	10	97 ± 3	97 ± 3	98 ± 1	99 ± 0

Table 4
Limit of detection values for the analytes

Analytes	Limit of detection ($\mu\text{g L}^{-1}$)
Pb	12.0
Co	8.7
Mn	0.52
Cu	3.0

tion metals at mg L^{-1} levels were not interfered on the recoveries of the analyte ions.

3.2. Analytical performance

The relative standard deviations for atomic absorption spectrometric measurements for analyte ions are between 1 and 10% in the model solutions. The detection limits, defined as the concentration equivalent to three times the standard deviation ($n = 10$) of the reagent blank were given at Table 4.

3.3. Application of the proposed method

We have explored the feasibility of the methodology given in experimental using preconcentration for the determination of Pb(II), Mn(II), Co(II) and Cu(II) in different environmental matrices by standard addition method. Reliability was checked by spiking experiments and independent analysis. The results for this study are presented in Table 5 for three different water samples and in Table 6 for sodium chloride and potassium chloride samples. The recovery of analytes from spiked samples is satisfactory reasonable. A good agreement was obtained between the added and measured analyte amounts. The recovery values calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects.

Table 5
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 (%)
Pb	0	BDL ^a	–	BDL	–	BDL	–
	2.5	2.45	98 ± 0	2.55	102 ± 3	2.4	97 ± 3
	5.0	4.8	96 ± 1	4.9	98 ± 4	4.95	99 ± 2
	7.5	7.4	99 ± 1	7.1	95 ± 1	7.3	97 ± 2
Co	0	BDL	–	BDL	–	BDL	–
	1.25	1.2	97 ± 3	1.2	98 ± 3	1.3	102 ± 4
	2.5	2.4	98 ± 1	2.4	98 ± 1	2.4	97 ± 2
	3.75	3.7	98 ± 4	3.6	95 ± 0	3.6	96 ± 2
Mn	0	BDL	–	BDL	–	BDL	–
	1.25	1.2	99 ± 4	1.2	97 ± 1	1.2	95 ± 3
	2.5	2.5	100 ± 1	2.5	99 ± 1	2.4	97 ± 3
	3.75	3.7	98 ± 1	3.6	96 ± 1	3.7	98 ± 4
Cu	0	BDL	–	BDL	–	BDL	–
	1.25	1.2	95 ± 3	1.2	97 ± 2	1.2	98 ± 3
	2.5	2.4	95 ± 1	2.4	95 ± 1	2.4	98 ± 2
	3.75	3.6	97 ± 0	3.6	97 ± 1	3.7	99 ± 1

^a BDL: below the limit of detection.

Table 6
Application of the presented procedure for sodium chloride and potassium chloride samples ($N = 3$)

	Added (μg)	NaCl		KCl	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Pb	0	BDL ^a	–	BDL	–
	2.5	2.45	98 ± 3	2.5	100 ± 0
	5.0	4.9	98 ± 2	5.05	101 ± 2
	7.5	7.2	96 ± 1	7.1	95 ± 1
Co	0	BDL	–	BDL	–
	1.25	1.2	98 ± 0	1.2	96 ± 1
	2.5	2.45	98 ± 3	2.45	98 ± 3
	3.75	3.6	96 ± 2	3.7	99 ± 0
Mn	0	BDL	–	BDL	–
	1.25	1.3	102 ± 3	1.3	104 ± 1
	2.5	2.4	98 ± 2	2.6	103 ± 2
	3.75	3.7	100 ± 1	3.8	102 ± 1
Cu	0	BDL	–	BDL	–
	1.25	1.3	102 ± 2	1.3	103 ± 2
	2.5	2.4	97 ± 2	2.4	97 ± 0
	3.75	3.8	101 ± 1	3.8	101 ± 0

^a BDL: below the limit of detection.

4. Conclusion

Coprecipitation with gadolinium hydroxide offers a useful preconcentration technique in water analysis. The coprecipitated analyte ions can be sensitively determined by atomic absorption spectrometry without any influence of gadolinium hydroxide. The developed method is successfully employed for analysis of agricultural and geological materials after successful validation. Some advantages of the proposed method are: The use of gadolinium hydroxide as coprecipitant is new. Gadolinium hydroxide is non-toxic. The method is fast. The time

required for the coprecipitation and determination was about 30 min. The method is also economic. Only 2.0 g of Gd(III) is used in all the experiments in the presented coprecipitation work.

The detection limits of analyte ions investigated are superior to those of preconcentration techniques for analyses [26–34]. The good features of the proposed coprecipitation method showed that it is a convenient and simple one. Also the presented method is relatively rapid as compared with previously reported procedures for the enrichment of analytes of traces heavy metal ions in real samples.

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