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Short communication

Coprecipitation of heavy metals with erbium hydroxide for their flame atomic absorption spectrometric determinations in environmental samples

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Abstract

Trace amounts of copper, manganese, cobalt, chromium, iron and lead were quantitatively coprecipitated with erbium hydroxide on 0.05 M NaOH medium. The coprecipitant could be easily dissolved with 1 M nitric acid. The presence of up to 15 g/l of erbium ions did not interfere with the atomic absorption spectrometric determination of analyte ions. The recovery values for analyte ions were higher than 95%. The concentration factor was 25-fold. Coprecipitation parameters including reagent amounts and matrix effects are discussed. The relative standard deviations of the determinations were below 9%. The time required for the coprecipitation was about 30 min. The proposed method was successfully applied for the determination of trace amounts of analyte ions in urine, soil and sediment, natural water samples.

Keywords: Coprecipitation; Erbium hydroxide; Preconcentration; Environmental samples; Flame atomic absorption spectrometry

1. Introduction

Heavy metals in environment are generally a source of pollution. Every countries and communities has their regulations on the levels of traces metal ions on the environment. The levels of heavy metals should be lower than the levels of the regulations of the relevant country. Because of those points, the accurate determinations of metal ions at trace concentrations are an important field of the analytical chemistry. One of the important instrumental techniques for the determination of traces heavy metals is flame atomic absorption spectrometry, due to its low costs and easy usage. Enrichment-separation procedures for the traces metal ions in environmental samples including natural waters are necessity prior to their flame atomic absorption spectrometric (FAAS) determinations, due to their lower levels than the detection limits of FAAS and the interferic effects of the matrix constituents of the samples [1,2]. The main enrichment and separation techniques used for traces heavy metals are adsorption [3–6], solvent extraction [7,8], cloud point extraction [9], membrane filtration [10,11].

Among the preconcentration–separation techniques, coprecipitation is one of the efficient techniques for the traces heavy metal ions [12–14]. The coprecipitation technique has some advantages: simple, fast method and several analyte ions can be preconcentrated and separated from the matrix simultaneously. In the coprecipitation of heavy metal ions at trace levels for separation–preconcentration, inorganic and organic coprecipitants have been used successfully [12–14]. There is a different importance for the usage of the metal hydroxides on coprecipitation of the heavy metal ions, due to good trace recovery and sufficient separation factors for alkali and alkaline earth metals. Some advantages of the in-

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organic hydroxide coprecipitation as enrichment technique is pure inorganic reagents can be easily obtained and also the procedure is easily handled. In the works with hydroxides, generally a milligram quantity of carrier element was used. A number of metal ions such as lanthanum [15], tin [16], yttrium [17], iron [18], scandium [19], hafnium [20], zirconium [21], indium [22], and beryllium [23], etc. as carrier element on the metal hydroxides coprecipitation have been widely used for the preconcentration–separation of trace heavy metal ions.

Some studies have been performed by our working group on the coprecipitation by using various metal hydroxides including magnesium [24], cerium [25] and samarium [26] hydroxides for the separation–preconcentration of heavy metal ions at trace levels in various samples including natural waters, dialysis concentrates, sediments, etc. with successfully results. According to our literature scanning, there is no work on the coprecipitation of traces metal ions by using erbium hydroxide.

The aim of the present study to establish a coprecipitation method by using erbium hydroxide for the separation/preconcentration of copper(II), manganese(II), cobalt(II), chromium(II), iron(III) and lead(II) ions in various samples prior to flame atomic absorption spectrometric determinations of them. The experimental conditions including erbium(III) concentration, sample volume, etc., for coprecipitation of analyte ions onto erbium hydroxide were investigated.

2. Experimental

2.1. 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. 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.

2.2. Reagents and solutions

Analytical reagent-grade chemicals were employed for the preparation of all solutions. All aqueous solutions were prepared from doubled-quartz-distilled water. Stock solutions of the investigative ions, 1000 mg/l (E. Merck, Darmstadt) were diluted daily for obtaining reference and working solutions. The calibration curve was established using the standard solutions prepared in 1 M HNO_3 by dilution from stock solutions. The calibration standards were not submitted to the coprecipitation procedure.

Sodium hydroxide (supra pure grade, E. Merck, Darmstadt) was used for the preparation of 6 M NaOH solutions. An amount of 2 g/l Er^{3+} was prepared freshly by dissolving erbium (III) nitrate (suprapure grade, E. Merck, Darmstadt) in small amounts of nitric acid and diluting to 50 ml with double distilled water. Nitric, sulfuric and hydrochloric acids used for preparing of diluted acid solution was supra pure grade from E. Merck. Urine and water samples were collected in prewashed (with detergent, doubly distilled water, diluted nitric acid and doubly distilled water, respectively) polyethylene bottles.

2.3. Test studies for analytes

Prior to coprecipitation of the analyte ions from real samples, the procedure was optimized with test works. For that purpose, 0.5 ml of 2 g/l erbium solutions were added to 10.0 ml of solution containing 5–20 μg of analyte ions. Then, a certain amount of 6 M NaOH solution was added to adjust NaOH concentration to 0.05 M. 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 1 ml of 1 M HNO_3. Final volume was completed to 2.0 or 5.0 ml with 1 M HNO_3. The concentration of the investigated analyte ions were determined by flame atomic absorption spectrometry.

2.4. Analysis of real samples

The presented coprecipitation procedure was applied to various environmental samples for the determination of their copper, manganese, cobalt, chromium, iron and lead contents prior to their AAS determinations.

0.1 g of standard reference material (GBW 07309) or soil sample was digested with aqua regia (12 ml of concentrated hydrochloric acid and 4 ml of concentrated nitric acid) at room temperature then it was heated to 95 °C. After the evaluation of NO_2 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 distilled water was added and the sample was mixed. The resulting mixture was filtered through a blue band filter paper. The filtrate was diluted to 10 ml with distilled water. The subsequent procedures were the same those described in the model working section. The final solution was diluted to 2.0 or 5.0 ml. Analytes were determined by flame AAS.

Fifty milliliters of urine or water is placed into a centrifugation tube. 0.5 ml of 2 g/l Er^{3+} was added to each urine sample and to form an erbium hydroxide precipitate and coprecipitation. The concentration of hydroxide was adjusted to 0.05 M NaOH with 6 M NaOH solution. The tube is allowed to stand for several seconds. The precipitate is centrifuged at 2500 rpm for 20 min and the supernatant is discarded. A small precipitate adheres to the bottom tube. Then, 1 ml of 1 M HNO_3 is added to dissolve the precipitate. The solution was completed to 2.0 or 5.0 ml with 1 M HNO_3. The analyte ions in this solution were determined by FAAS.

3. Results and discussion

An attempt was performed to examine the effect of erbium concentration, due to the matrix of erbium, on the determination of the analyte elements by flame atomic absorption spectrometry. Increasing concentrations of erbium(III) was added to aqueous solution containing an appropriate amount of analytes. These solutions were analyzed by flame atomic absorption spectrometry without any pretreatment. The absorbance for the analyte elements remained almost constant up to about 15 g/l Er^{3+}.

The optimized conditions including reagent amounts, sample volume and matrix effects for the quantitative coprecipitation were established by using model solutions containing 5–20 μg of each analyte ions.

3.1. Effects of erbium(III) amount on the coprecipitation

In the coprecipitation studies for the traces heavy metal ions, the amounts of the carrier element was an important parameter. In the present work, erbium(III) was selected as carrier element and the influences of erbium(III) on the coprecipitation of analyte ions were investigated by using model solutions in 0.05 M of NaOH concentrations. The influence of Er^{3+} was investigated in the range of 0–1000 μg Er^{3+}. The results were depicted in Fig. 1. Without any erbium(III), only iron(III) and chromium(III) was quantitatively recovered, at this point the recoveries of the other metal ions investigated were in the range of 30–87%. After addition of erbium(III), the quantitative recoveries were obtained for analytes (Fig. 1). For all further work, 500 μg of Er^{3+} was added to the model solutions.

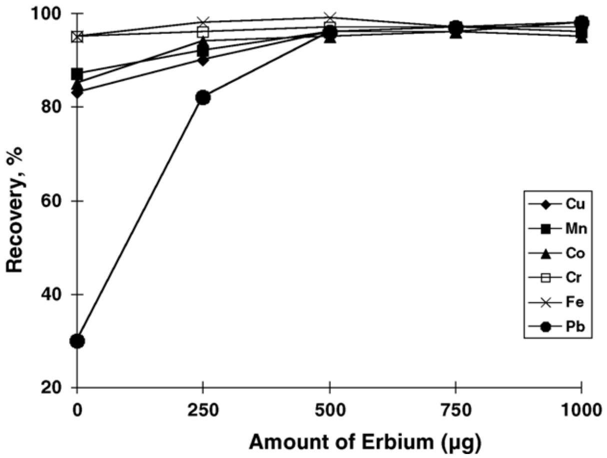

Fig. 1. Effect of erbium amount on coprecipitation (amounts of analytes: 10 μg of Co, Cu, Mn, Fe, 20 μg of Cr, Pb, *n* = 3).

3.2. Influences of NaOH concentration

Erbium hydroxide precipitate was occurred by the addition of different amount of 6 M NaOH to model solution containing 500 μg of Er^{3+} and 10 μg of Co, Cu, Mn, Fe and 20 μg of Cr, Pb ions for adjust the NaOH concentrations. Then test studies given in Section 2 were applied. The results obtained were given Fig. 2. The recovery values for copper, manganese, cobalt, chromium, iron and lead ions were not quantitative without NaOH. The recoveries increased with increasing amounts of sodium hydroxide and quantitative recovery values for analytes were obtained in the NaOH concentration range of 0.05–0.2 M. In all the further studies, the NaOH concentration of the aqueous solutions used was adjusted to 0.05 M.

3.3. Effects of the sample volume

The influences of the sample volume of the starting solutions were also investigated in the sample volume range of 10–150 ml to obtain high preconcentration factor. The analyte ions were quantitatively (95%) recovered in the sample volume range of 10–50 ml. After 50 ml of sample volume, the recoveries of all the investigated ions were not quantitative. Highest preconcentration factor was 25 when final volume was 2.0 ml.

3.4. Effect of matrix ions

As pointed in the Section 1, the one of the main problem in the atomic absorption spectrometric determination of the heavy metal ions is interference from the matrix. In our work, the influences of the some ions which are known as interferic ions in the AAS determination were investigated. The interference concentration choice was based on literature values found for separation and preconcentration studies [27–29]. The results for this study are given in Table 1. The tolerance limit of foreign ions was taken as that value which caused an error of not more than ±5% in the absorbance. Quantita-

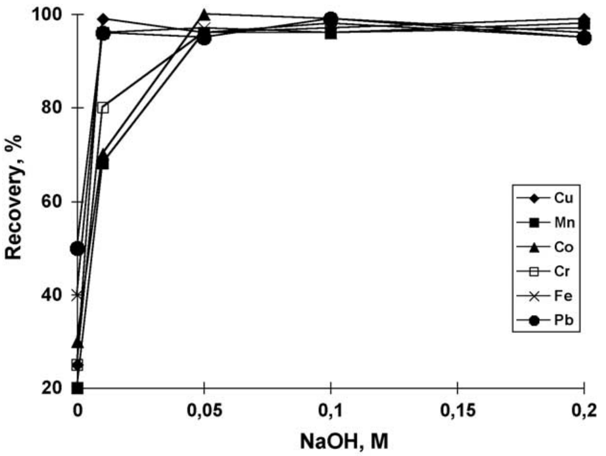

Fig. 2. Effect of NaOH concentration on coprecipitation of the analyte ions (*n* = 3).

Table 1
Tolerable levels of some ions on presented coprecipitation procedure ($n = 3$)

Ions	Added as	Tolerable concentration (mg/l)
Na^+	NaCl	25000
K^+	KCl	1000
Ca^{2+}	$CaCl_2$	1000
Mg^{2+}	$MgCl_2$	1000
$NH_4{}^+$	NH_4Cl	10000
$SO_4{}^{2-}$	Na_2SO_4	10000
Cl^-	NaCl	25000

Table 2
Levels of copper, cobalt, lead, chromium in stream sediment standard reference material (GBW7309) after application of erbium hydroxide coprecipitation procedure

Element	Certified value (μg/g)	Observed value (μg/g)
Copper	32.1	33 ± 1
Cobalt	14.4	14.0 ± 0.3
Lead	23.0	24.9 ± 0.5
Chromium	85.0	88 ± 3

Uncertainty at 95% confidence limit.

tive recoveries for 10 000 mg/l of $NH_4{}^+$, for 25 000 mg/l of Na^+ and Cl^-, for 1000 mg/l of Mg^{2+}, for 1000 mg/l of K^+, for 1000 mg/l of Ca^{2+} and for 10 000 mg/l of $SO_4{}^{2-}$ were obtained.

3.5. Analytical performance

The relative standard deviations for flame atomic absorption spectrometric determinations for analytes are between 1.0 and 9.0%. The detection limits, defined as the concentration equivalent to three times the standard deviation ($n = 11$) of the reagent blank, for copper, manganese, cobalt, chromium, iron and lead were 0.11, 0.04, 0.25, 0.87, 0.67 and 0.24 μg/l, respectively for 50 ml of sample volume and 2 ml of final volume.

In order to estimate the accuracy of the coprecipitation procedure, different amounts of the investigated metal ions were spiked in artificial seawater prepared according to literature [30]. The resulting solutions were submitted to the coprecipitation procedure given in Section 2. Good agreement was obtained between the added and found analyte content. The recovery values for the analyte ions were generally in the range of 94–103%. It shows that the presented method can be applied for the separation/preconcentration of analyte ions in the real samples which have high salt content.

3.6. Analysis of real samples

The developed preconcentration method was applied to a stream sediment standard reference material (GBW 07309) for the determination of copper, cobalt, lead and chromium ions. The results are given in Table 2. The results, based on the average of five replicates, are in good agreement with the certified values. If the concentration levels of the most common

Table 3
Analysis of tap water and urine samples

Element	Added (μg)	Tap water from Kayseri		Urine	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Cu	0	BDL	–	BDL	–
	5	4.9	98	4.9	98
	10	10.2	101	9.6	96
	20	20.2	101	20.3	102
Mn	0	BDL	–	BDL	–
	2.5	2.5	100	2.4	96
	5	4.9	98	5.0	100
	10	10.1	101	10.2	102
Co	0	BDL	–	BDL	–
	5	4.8	96	5.0	100
	10	9.7	97	10.1	101
	20	19.8	99	20.2	101
Cr	0	BDL	–	BDL	–
	10	9.5	95	10.0	100
	20	19.4	97	20.2	101
	40	39.0	98	40.9	102
Fe	0	BDL	–	BDL	–
	5	5.2	104	5.0	100
	10	10.4	104	10.2	102
	20	20.4	102	19.0	95
Pb	0	BDL	–	BDL	–
	10	10.0	100	9.8	98
	20	19.0	95	18.8	94
	40	40.0	100	38.0	95

BDL: below the detection limit.

Table 4
The levels of analyte ions in two soil samples after application of presented coprecipitation procedure ($n = 4$)

Element	Concentration (μg/g)	
	Soil 1	Soil 2
Copper	5.4 ± 0.5	28 ± 2
Manganese	1.5 ± 0.2	12.0 ± 0.8
Cobalt	BDL	BDL
Lead	BDL	BDL
Iron	104 ± 8	216 ± 8
Chromium	14 ± 1	45 ± 4

BDL: below the detection limit; uncertainty at 95% confidence limit.

matrix constituents in the reference stream sediment material and the accuracy of the presented method are considered together, it can be concluded that the proposed method is free from interferences of the various constituents.

Various amounts of analyte ions were spiked to drinking water from Kayseri and a urine sample. Then presented procedure applied. The results are given in Table 3. The levels of the analyte ions were found lower than detection limit of the procedure. The application of the presented procedure was performed with aqua regia digested two different soil samples from Kayseri, Turkey. The results were summarized in Table 4.

4. Conclusions

The proposed coprecipitation procedure is important and fortunate for analytical problem of the determination of metal traces in presence of alkali and alkaline earth salts for their preconcentration and separation. The combination of $Er(OH)_3$ coprecipitation preconcentration with flame AAS provides an effective, cheap, rapid and reliable technique for the determination of analyte ions in environmental samples. The preconcentration factor was 25 for 50 ml of sample volume and 2 ml of final volume.

The contamination risk for analytes from the carrier element is very low. The detection limits for the analyte ions are lower than the some other metal hydroxides coprecipitation procedures [21–24] for flame atomic absorption spectrometric determination of traces heavy metal ions.

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