

Determination of trace metals by atomic absorption spectrometry after coprecipitation with europium hydroxide

Mustafa Soylak*, Gokhan Onal

Erciyes University, Faculty of Art and Science, Department of Chemistry, 38039 Kayseri, Turkey

Received 2 February 2006; received in revised form 24 March 2006; accepted 24 March 2006

Available online 25 April 2006

Abstract

A procedure for the determination of trace amounts of chromium(III), iron(III), lead(II) and manganese(II) is described, that combines atomic absorption spectrometry—europium hydroxide coprecipitation. The influences of analytical parameters including amount of europium(III), amount of ammonia, 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 in the range of 95–104%. The detection limits (3 s) were in the range of 1.7–17.1 µg/L. The validation of the presented coprecipitation procedure was performed by the analysis of Bovine Liver 1577-b and BCR-144R Sewage Sludge (domestic origin) standard reference materials. The method was applied to the determination of analytes in real samples including natural waters and some food, soil and fertilizer samples, etc. and good results were obtained (relative standard deviations < 10%, recoveries > 95%).

© 2006 Elsevier B.V. All rights reserved.

Keywords: Flame atomic absorption spectrometry; Enrichment; Coprecipitation; Europium hydroxide

1. Introduction

In flame atomic absorption determinations of the heavy metal ions, unfavorable influences of matrix components of real samples and particularly low concentrations of heavy metal ions are two big problems [1–3]. In order to solve these important problems, separation/preconcentration procedures are widely used by the researchers around the world [4–8]. Coprecipitation is also one of the efficient preconcentration techniques for the traces heavy metal ions from aqueous media including natural waters [9,10]. The coprecipitation technique 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 magnesium, cerium, scandium, ytterbium, samarium, erbium, lanthanum, indium, zirconium and iron has been reported for the preconcentration–separation of trace elements

from various media like natural waters [10–18]. Hiraide et al. have been presented a coprecipitation work including coprecipitation of traces heavy metals in real samples by indium hydroxide [11]. A method for cadmium determination in spring water samples by graphite-furnace atomic absorption spectrometry (GFAAS) after coprecipitation with ytterbium hydroxide has been presented by Atsumi et al. [13]. We have been presented some coprecipitation works with hydroxides including samarium [15], erbium [16] hydroxides for traces heavy metal ions in our laboratories in environmental samples. Minami et al. have been proposed a preconcentration procedure based on the coprecipitation of copper, chromium and lead by terbium hydroxide [17].

We investigated a new coprecipitant for separation and concentrate of some trace heavy metals, and found europium(III) hydroxide is a selective collector for chromium(III), iron(III), lead(II) and manganese(II) ions. According to our knowledge, the europium(III) hydroxide system for coprecipitation and separation, as well as its use in analytical procedures has not been reported before. The experimental conditions for coprecipitation of analyte ions onto europium(III) hydroxide including pH, europium(III) concentration, sample volume, etc. were optimized.

* Corresponding author. Tel.: +90 352 4374933; fax: +90 352 4374933.
E-mail address: soylak@erciyes.edu.tr (M. Soylak).

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, 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 μ S/cm.

2.2. Reagents and solutions

High purity reagents were used for all preparations of the standard and sample solution. Stock metal solutions, 1000 mg/L (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 HNO₃. Stock solutions of diverse elements were prepared from the high purity compounds (99.9%, E. Merck, Darmstadt).

0.5% solution of Eu₂O₃ was prepared freshly by dissolving europium(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. The standard reference materials used in the experimental studies were Bovine Liver 1577-b and BCR-144R Sewage Sludge (domestic origin). 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. Model working

The coprecipitation method was tested firstly. 0.5 mg of europium(III) and 1.0 mL of concentrated NH₃, respectively, were added to 10 mL of solution containing 20 μ g chromium(III), 20 μ g lead(II), 10 μ g iron(III) and 10 μ g manganese(II) ions. After 10 min, the solution was centrifuged at 2750 rpm for 10 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 1 mL of 1 mol/L HNO₃. The final volume was completed to 2.0–10.0 mL with 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. Analysis of real samples

0.25 g of standard reference material (Bovine Liver 1577-b or BCR-144R Sewage Sludge (domestic origin)) and 1.0 g 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 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 20 mL with distilled water. Then 0.5 mg of europium(III) was added to each urine sample to form a europium hydroxide precipitates and to run coprecipitation, 1.0 mL of concentrated NH₃ is added. The tube is slowly and carefully shaken for several seconds and allowed to stand for 10 min. The precipitate is centrifuged at 2750 rpm for 10 min and the supernatant is discarded. A small precipitate adheres to the bottom of the tube. Then, 1 ml of 1 mol/L HNO₃ is added to dissolve the precipitate. The final volume was completed to 2.0–10.0 mL with distilled water. The analyte ions in this solution are determined with flame AAS.

3. Results and discussion

The influences of the various analytical parameters such as amount of europium(III) and ammonia, etc. on the coprecipitation efficiencies of analyte ions were examined by using model solutions. Initially, an attempt was made to examine the effect of europium(III), due to the matrix of europium(III), on the determination of analyte ions by flame atomic absorption spectrometer. Increasing concentrations of Eu(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 2000 mg/L Eu³⁺. The concentration of europium(III) in the final solution for the combination of coprecipitation method with flame AAS must to be excesses 300 mg/L.

3.1. Effects of ammonia concentrations

Europium(III) hydroxide was formed by the addition of ammonia to the aqueous solutions containing europium(III) for the coprecipitation of analyte ions. Because of this point, the effects of volume of the concentrated ammonia on the quantitative recovery efficiencies of analyte ions were studied. The recoveries of chromium(III), lead(II) and manganese(II) ions were quantitative (95%) and constant by the addition of 0.5 mL or higher volume of concentrated ammonia. Quantitative recoveries for iron(III) were obtained after 0.5 mL of ammonia. All subsequent work was performed by the addition of 0.5 mL of concentrated ammonia.

3.2. Effects of amounts of europium(III)

The influences of europium(III) amounts on the coprecipitation of chromium(III), iron(III), lead(II) and manganese(II) were also examined experimentally in the range of 0–3.0 mg. The results were given in Fig. 1. The recoveries of analyte ions were not quantitative (below 90%) without europium(III). Quantitative recovery values for all the analytes were obtained in the range of 0.5–3.0 mg of europium(III). The optimum

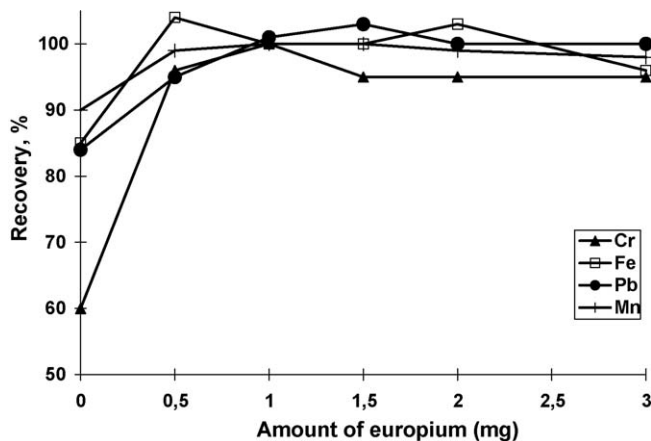


Fig. 1. Effect of amount of europium(III) on the coprecipitation efficiency of analyte ions ($N=3$).

amount of europium(III) was taken as 0.5 mg in further experiments.

3.3. Sample volume

The influences of the sample volume of aqueous solution on the recoveries of Cr(III), Fe(III), Pb(II) and Mn(II) were also investigated in the sample volume range of 10–1000 mL by using model solutions. The results are depicted in Fig. 2. While Cr(III) was recovered quantitatively in the range of 10–750 mL, iron(III) was quantitatively (95%) recovered in the sample volume range of 10–1000 mL. The recoveries for lead and manganese ions were quantitative till 500 mL of sample volume.

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 the analyte ions in the, different three final solutions were prepared for each element, then each ions were determined separately by flame atomic absorption spectrometry. A preconcentration factor of 500 for iron, 375 for chromium, 250 for manganese and lead can be achieved when the final volume was 2.0 mL.

Table 1
Tolerance levels of the concomitant ions on the recoveries of analyte ions ($N=3$)

Ion	Added as	Tolerable concentration (mg/L)	Recovery (%)			
			Fe	Pb	Mn	Cr
Na ⁺	NaCl	25000	102 ± 3	96 ± 2	99 ± 1	97 ± 1
NH ₄ ⁺	NH ₄ Cl	2500	100 ± 2	100 ± 2	93 ± 2	96 ± 3
K ⁺	KCl	1000	99 ± 2	100 ± 2	95 ± 2	98 ± 3
Ca ²⁺	CaCl ₂	1000	101 ± 3	100 ± 3	101 ± 1	98 ± 3
Mg ²⁺	MgCl ₂	1000	99 ± 2	99 ± 1	97 ± 3	97 ± 1
Cl ⁻	NaCl	25000	97 ± 3	95 ± 2	100 ± 2	97 ± 2
Ni ²⁺	NiSO ₄	50	100 ± 3	100 ± 3	101 ± 2	100 ± 3
Co ²⁺	CoSO ₄	50	98 ± 3	98 ± 3	100 ± 2	96 ± 1
Cu ²⁺	CuSO ₄	50	100 ± 3	100 ± 2	100 ± 1	102 ± 2
Al ³⁺	Al ₂ (SO ₄) ₃	50	95 ± 3	96 ± 2	93 ± 2	96 ± 3
Bi ³⁺	Bi(NO ₃) ₃	50	103 ± 3	100 ± 3	97 ± 2	100 ± 3
Zn ²⁺	Zn(NO ₃) ₂	50	103 ± 2	100 ± 3	96 ± 3	101 ± 4

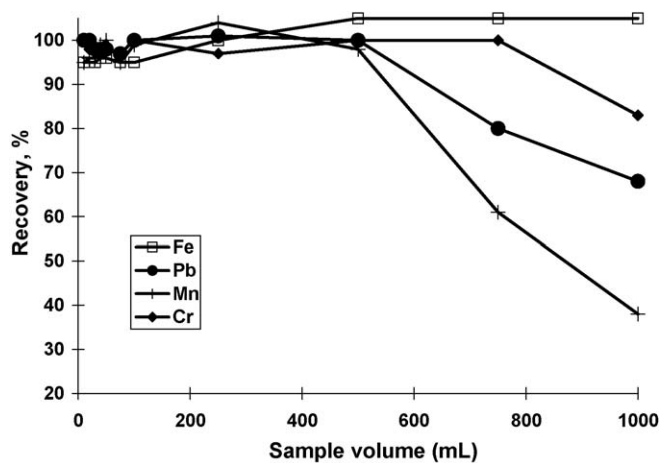


Fig. 2. Effects of sample volume on the recoveries of analytes ($N=3$).

3.4. Effect of concomitant ions

The effect of potential concomitant ions on the coprecipitation efficiency of the analyte ions was examined by adding known concentrations of each ion in a model solution containing analytes and then the coprecipitation procedure given in Section 2.3 was applied all the concomitant ions separately. The results were summarized in Table 1. 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 transition metals at mg/L levels were not interfered on the recoveries of the analyte ions. This results show that the proposed coprecipitation method could be applied to the highly saline samples and the samples that contains transition metals given in Table 1 at mg/L levels.

3.5. Analytical performance

In order to validate the accuracy of the presented coprecipitation procedure for trace metal ions, different amounts of analyte ions were spiked in natural water and urine samples. The results were given in Table 2. Good agreement was obtained between

Table 2
Analysis of natural waters and urine spiked analyte ions (sample volume 50 mL, $N=4$)

Analyte	Added (μg)	Tap water		Bottled drinking water		Spring water		Urine	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Fe	0	BDL	–	BDL	–	BDL	–	BDL	–
	5	4.8 ± 0.2	96	5.0 ± 0.1	100	4.9 ± 0.3	98	4.9 ± 0.5	98
	10	9.6 ± 0.3	96	10.5 ± 0.5	105	10.3 ± 0.6	103	9.8 ± 0.6	98
	15	15.0 ± 0.3	100	13.5 ± 0.6	90	14.7 ± 0.7	98	15.3 ± 0.8	102
Pb	0	BDL	–	BDL	–	BDL	–	BDL	–
	10	9.6 ± 0.1	96	9.2 ± 0.6	92	10.4 ± 0.6	104	10.0 ± 0.7	100
	20	19.6 ± 0.2	98	20.0 ± 0.4	100	20.8 ± 0.5	104	18.8 ± 1.0	94
	30	22.5 ± 0.4	75	30.6 ± 0.7	102	29.7 ± 0.9	99	30.0 ± 0.9	100
Mn	0	BDL	–	BDL	–	BDL	–	BDL	–
	5	5.2 ± 0.2	104	4.9 ± 0.3	98	4.9 ± 0.5	98	4.8 ± 0.2	96
	10	9.8 ± 0.2	98	9.5 ± 0.5	95	9.9 ± 0.5	99	9.7 ± 0.3	97
	15	14.7 ± 0.3	98	13.7 ± 0.4	91	14.9 ± 1.0	99	14.7 ± 0.5	98
Cr	0	BDL	–	BDL	–	BDL	–	BDL	–
	10	8.8 ± 0.2	88	10.0 ± 0.3	100	10.3 ± 0.7	103	9.7 ± 0.5	97
	20	19.4 ± 0.5	97	19.0 ± 0.4	95	20.0 ± 0.9	100	19.6 ± 0.6	98
	30	28.2 ± 0.5	94	29.4 ± 0.4	98	27.6 ± 1.0	92	30.6 ± 1.0	102

Table 3
Application of the present method to the standard reference materials ($N=3$)

Element	Bovine Liver 1577-b		BCR-144R Sewage Sludge (domestic origin)	
	Certified value ($\mu\text{g/g}$)	Observed value ($\mu\text{g/g}$)	Certified value ($\mu\text{g/g}$)	Observed value ($\mu\text{g/g}$)
Fe	184 ± 15	$190 \pm 25^*$	–	148.0 ± 112
Pb	0.129 ± 0.004	BDL	96.0 ± 1.5	89.0 ± 14.9
Mn	10.5 ± 1.7	10.1 ± 2.5	189 ± 6	200 ± 27
Cr	–	BDL	90 ± 6	85 ± 12

BDL, below the detection limit.

* $x \pm \text{t.s.}/\sqrt{2}$, $p=0.95$.

the added and found analyte content. The recovery values calculated for the standard additions were higher than 95% with some exceptions, thus confirming the accuracy of the procedure and the absence of matrix effects.

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 3 times the standard deviation ($n=10$) of the reagent blank, for chromium(III), iron(III),

lead(II) and manganese(II) were 2.1, 7.2, 17.1 and 1.7 $\mu\text{g/L}$, respectively.

3.6. Application of the proposed method

The developed coprecipitation method was applied to standard reference materials (Bovine Liver 1577-b and BCR-144R Sewage Sludge (domestic origin)) for the determination of analyte metals. The results are given in Table 3. The results

Table 4
Analyte levels in real samples after application coprecipitation procedure ($N=3$)

Sample	Concentration ($\mu\text{g/g}$)*			
	Fe	Pb	Mn	Cr
Bulgur (boiled wheat)	3.9 ± 1.3	BDL	BDL	BDL
Green lentil	6.0 ± 1.5	BDL	BDL	BDL
Vermicelli	4.3 ± 1.0	BDL	BDL	BDL
Potassium nitrate-based fertilizer	ND	0.8 ± 0.2	0.5 ± 0.1	0.5 ± 0.1
Ammonium nitrate-based fertilizer	ND	1.8 ± 0.5	1.5 ± 0.2	1.5 ± 0.3
Soil coded 1032	ND	2.2 ± 0.8	164 ± 7	1.6 ± 0.3
Soil coded 1033	ND	1.1 ± 0.5	284 ± 7	4.2 ± 1.4
Soil coded 1034	ND	0.7 ± 0.1	26.0 ± 5.5	1.8 ± 0.4

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

* $x \pm \text{t.s.}/\sqrt{2}$, $p=0.95$.

based on the average of three replicates for analytes which show that the results are in good agreement with the certified values.

The coprecipitation procedure was applied to the determination of chromium(III), iron(III), lead(II) and manganese(II) in some food samples, soil from three locations in Kayseri city and fertilizer samples. 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. The relative standard deviations values were lower than 10% with some exceptions.

4. Conclusion

Coprecipitation with europium hydroxide offers a useful multielement preconcentration technique in water analysis. The procedure has been successfully applied to chromium(III), iron(III), lead(II) and manganese(II) with acceptable accuracy and precision. The coprecipitated analyte ions can be sensitively determined by atomic absorption spectrometry without any influence of europium hydroxide. The developed method is successfully employed for analysis of agricultural and geological materials after successful validation. Some advantages of the proposed method are:

- (1) The use of europium hydroxide as coprecipitant is new. Europium hydroxide is non-toxic.
- (2) The method is fast. The time required for the coprecipitation and determination was about 30 min.
- (3) The method is also economic. Only 2.0 g of Eu(III) is used in all the experiments in the presented work.

Acknowledgments

The authors are grateful for the financial support of the Unit of the Scientific Research Project of Erciyes University (Project no: EÜBAP-FBT 04 47). The authors would like to thank the Scientific and Technical Research Council of Turkey (TUBITAK) for financial helps (Project no: 104T330).

References

- [1] M. Burguera, J.L. Burguera, D. Rivas, C. Rondón, P. Carrero, O.M. Alarcón, Y.P. de Peña, M.R. Brunetto, M. Galignani, O.P. Márquez, J. Márquez, On-line electrochemical preconcentration and flame atomic absorption spectrometric determination of manganese in urine samples, *Talanta* 68 (2005) 219–225.
- [2] E. Kendüzler, A.R. Türker, Bakirin Amberlyst 36'da Zenginleştirme Şartlarının Arastırılması ve Alevli Atomik Absorpsiyon Spektrometresi ile Tayini, *POS3*, p34 IX. Ulusal Spektroskopi Kongresi, Bilkent, 9–11 Haziran 2005. Ankara.
- [3] M.M. Hassanien, K.S. Abou-El-Sherbini, Synthesis and characterisation of morin-functionalised silica gel for the enrichment of some precious metal ions, *Talanta* 68 (2006) 1550–1559.
- [4] M.V. Tagle, M.F.G. Rosias, Study of the extraction of trace metals in modified C-18 with 1-(2-tiazolilazo)-2-naphthol (TAN) in water, *Afinidad* 62 (2005) 217–224.
- [5] M. Soylak, M. Dogan, Separation and enrichment of zinc, copper, iron, cadmium, cobalt, and nickel from urine with amberlite XAD-16 resin, *Trace Elem. Electroly.* 13 (1996) 130–132.
- [6] M. Soylak, A.U. Karatepe, L. Elci, M. Dogan, Column preconcentration/separation and atomic absorption spectrometric determinations of some heavy metals in table salt samples using amberlite XAD-1180, *Turk. J. Chem.* 27 (2003) 235–242.
- [7] G. Supriyanto, J. Simon, The chromatomembrane method used for sample preparations in the spectrophotometric determination of zinc and copper in pharmaceuticals, *Talanta* 68 (2005) 318–322.
- [8] K. Pyrzyńska, Recent developments in the determination of gold by atomic spectrometry techniques, *Spectrochim. Acta B* 60 (2005) 1316–1322.
- [9] L. Elci, U. Sahin, S. Oztas, Determination of trace amounts of some metals in samples with high salt content by atomic absorption spectrometry after cobalt-diethyldithio-carbamate coprecipitation, *Talanta* 44 (1997) 1017–1023.
- [10] O. Kujirai, K. Yamada, Application of cobalt ammine complexes for the simultaneous determination of traces of As, Fe, Ti, V and Zr in high-purity cobalt metal by lanthanum hydroxide coprecipitation and inductively coupled plasma-atomic emission spectrometry, *Fresenius J. Anal. Chem.* 354 (1996) 428–431.
- [11] M. Hiraide, Z.S. Chen, H. Kawaguchi, Coprecipitation of traces of heavy metals with indium hydroxide for graphite-furnace atomic absorption spectrometry, *Anal. Sci.* 7 (1991) 65–68.
- [12] L. Elci, S. Saracoglu, Applying magnesium hydroxide coprecipitation method for trace analysis to dialysis concentrate, *Talanta* 46 (1998) 1305–1310.
- [13] K. Atsumi, T. Minami, J. Ueda, Determination of cadmium in spring water by graphite-furnace atomic absorption spectrometry after coprecipitation with ytterbium hydroxide, *Anal. Sci.* 21 (2005) 647–649.
- [14] T. Akagi, H. Horaguci, Simultaneous multielement determination of trace metals using 10 ml of seawater spectrometry with gallium coprecipitation and microsampling technique, *Anal. Chem.* 62 (1990) 81–85.
- [15] S. Saracoglu, M. Soylak, L. Elci, Separation/preconcentration of trace heavy metals in urine, sediment and dialysis concentrates by coprecipitation with samarium hydroxide for atomic absorption spectrometry, *Talanta* 59 (2003) 287–293.
- [16] M. Soylak, S. Saracoglu, U. Divrikli, L. Elci, Coprecipitation of heavy metals with erbium hydroxide for their flame atomic absorption spectrometric determinations, *Talanta* 66 (2005) 1098–1102.
- [17] T. Minami, Y. Sohrin, J. Ueda, Determination of chromium, copper and lead in river water by graphite-furnace atomic absorption spectrometry after coprecipitation with terbium hydroxide, *Anal. Sci.* 21 (2005) 1519–1521.
- [18] G. Doner, A. Ege, Determination of copper, cadmium and lead in seawater and mineral water by flame atomic absorption spectrometry after coprecipitation with aluminum hydroxide, *Anal. Chim. Acta* 547 (2005) 14–17.