Dysprosium(III) hydroxide coprecipitation system for the separation and preconcentration of heavy metal contents of table salts and natural waters[☆]

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Abstract

A procedure for the determination of trace amounts of Pb(II), Cu(II), Ni(II), Co(II), Cd(II) and Mn(II) is described, that combines atomic absorption spectrometry-dysprosium hydroxide coprecipitation. The influences of analytical parameters including amount of dysprosium(III), centrifugation time, 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 95.00–104.00%. The detection limits corresponding to three times the standard deviation of the blank for the analytes were in the range of 14.1–25.3 μg/L. The method was applied to the determination of lead, copper, nickel, cobalt, cadmium and manganese ions in natural waters and table salts good results were obtained (relative standard deviations <10%, recoveries >95%).
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Keywords: Table salt; Natural water; Flame atomic absorption spectrometry; Enrichment; Coprecipitation; Dysprosium hydroxide

1. Introduction

The main threats to human health from heavy metals are associated with exposure to lead, cadmium, nickel etc [1]. The positive or negative effects of these metals for human health have been studies and reviewed by the researchers and environmental foundation like World Health Organization [1–4]. The main sources of these elements in environment are natural or anthropogenic origin, mining, agricultural facilities, industrialization and traffic. Atmosphere, surface and ground waters, soil, foods and plants are affected by the trace elements due to these facilities. The determination of heavy metals at trace levels in the environmental samples is complicated, considering the low concentration of the metals and the high saline content of the matrices [5–7]. Because of these points, instrumental analysis methods including atomic absorption spectrometry and inductively coupled plasma mass spectrom-

etry always request previous steps of several preconcentration procedures including solid phase extraction, ion exchange, cloud point extraction have been performed as separation technique [8–12].

Coprecipitation has been also widely used for preconcentration–separation studies for heavy metals, due to its several advantages: simple, fast, high preconcentration factor, etc. Heavy metals are coprecipitated by inorganic or organic precipitants, environmentally and by a carrier element. As an inorganic precipitant, hydroxides are an important place in the enrichment-separation studies. Coprecipitation by hydroxide of various metal ions including magnesium [13,14], lanthanum [15], samarium [16], terbium [17], indium [18], europium [19], ytterbium [20,21], erbium [22] and gallium [23] as carrier element has been reported for the preconcentration–separation of trace elements from various media. According to our literature survey, until now, dysprosium hydroxide coprecipitation system is not used for the trace metal separation–preconcentration.

In the presented study, a coprecipitation system is proposed for the separation–preconcentration of Pb(II), Cu(II), Ni(II), Co(II), Cd(II) and Mn(II) ions. The system is based on coprecipitation of the analytes by dysprosium hydroxide. The influences

of the analytical parameters including pH of the solutions, amounts of dysprosium, sample volume, etc. is investigated. The proposed procedure was applied to the determinations of analytes contents of table salt and natural water samples.

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 μS/cm.

2.2. Reagents and solutions

All solutions were prepared with deionized water. Except if otherwise stated, analytical-grade acetone, acids, and other chemicals used in this study were obtained from Merck, Darmstadt, Germany. The calibration curve was established using standard solutions prepared in 1 M HNO_3 by dilution from 1000 mg/L stock solutions (E. Merck, Darmstadt, Germany). The calibration standards were not submitted to the preconcentration procedure.

A 0.1% solution of Dy_2O_3 was prepared freshly by dissolving dysprosium(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.

2.3. Preconcentration studies

A 1.0 mg of dysprosium(III) was added to 10 mL of solution containing 0.5–2.5 μg analyte ions. Then the pH of the solution was adjusted to related pH by the addition of diluted ammonia. After 10 min, the solution was centrifuged at 3000 rpm for 20 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 1 mL of 1 mol/L HNO_3. 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

A 2.0 g of table salt sample was dissolved in 20 mL of distilled water. Then 1.0 mg of dysprosium(III) was added. In order to form a dysprosium hydroxide precipitates, the pH of the solution was adjusted pH 11 by the addition diluted ammonia. The tube is slowly and carefully shaked for several seconds and allowed to stand for 10 min. The precipitate is centrifuged at 3000 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 HNO_3 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.

For the analysis of water sample, 1.0 mg of dysprosium(III) was added to 100 mL of water sample analyzed. The pH of the solution was adjusted pH 11 by the addition diluted ammonia to obtain dysprosium hydroxide precipitates. Then the procedure given above was performed.

3. Results and discussion

An attempt was initially made to examine the influences of dysprosium(III) on the determination of analyte ions by flame atomic absorption spectrometer because of the matrix of dysprosium(III). Increasing concentrations of Dy(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 Dy(III). The concentration of dysprosium(III) in the final solution for the combination of coprecipitation method with flame AAS must to be excesses 500 mg/L.

3.1. Effects of pH on the recoveries of the analytes by the presented coprecipitation method

pH is the one of the important factor on the quantitative recoveries of the analytes by hydroxide coprecipitation studies. Generally at the basic pH values, quantitative recoveries have been obtained for the analytes in the recent hydroxide coprecipitation works [16–19]. Because of these points, the influences of the pH of the model solutions on the quantitative recoveries of analytes on the dysprosium(III) hydroxide coprecipitation system were investigated in the pH range of 8–12. The results were depicted in Fig. 1. Dysprosium hydroxide precipitates were not formed in the acidic pH, therefore no recoveries were obtained at acidic pH's. Quantitative recovery values were obtained for Pb(II), Cu(II), Ni(II), Co(II), Cd(II) and Mn(II) in the pH range of 10–12. All subsequent works were performed at pH 11 for quantitative recoveries.
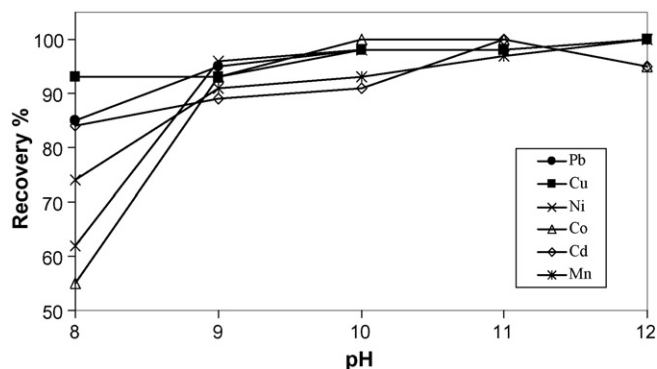

Fig. 1. Effects of pH on the recoveries of Pb(II), Cu(II), Ni(II), Co(II), Cd(II) and Mn(II) in dysprosium(III)hydroxide coprecipitation system ($N = 3$).
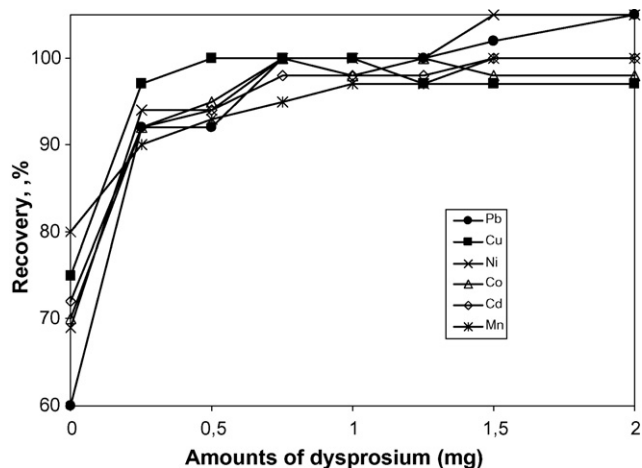
Fig. 2. Influences of amount of dysprosium(III) on the coprecipitation efficiency of analyte ions ($N = 3$).

Fig. 3. The effects of sample volume on the recoveries of the analytes ($N = 3$).

3.2. Effects of amounts of dysprosium(III)

The influences of amounts dysprosium(III) as carrier element on the coprecipitation of lead(II), copper(II), nickel(II), cobalt(II), cadmium(II) and manganese(II) ions were also investigated experimentally in the range of 0–2.0 mg of dysprosium(III) keeping other parameters constant. The results were given in Fig. 2. The recoveries of analyte ions were not below 80% without dysprosium(III). After addition dysprosium(III), the recovery values increased. Quantitative recovery values for all the analytes were obtained in the range of 1.0–2.0 mg of dysprosium(III). The optimum amount of dysprosium(III) was taken as 1.0 mg in further experiments.

3.3. Centrifugation time

The influences of the centrifugation time on the recoveries of the analyte ions were investigated in the range of 5–20 min at
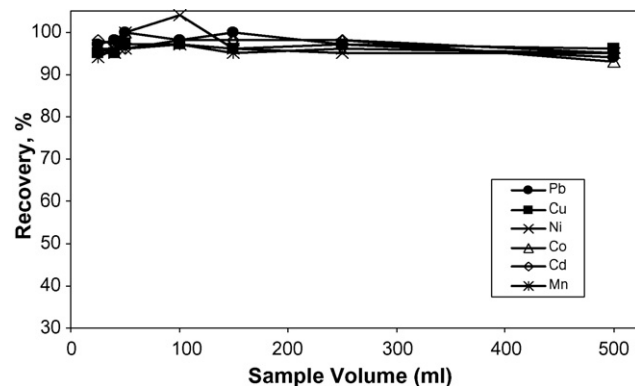
3000 rpm. Quantitative recoveries were obtained for all analytes in the range of 15–25 min. All further works were performed 20 min as centrifugation time.

3.4. Effects of sample volume

Studies were also repeated with solutions of large volume to explore the possibility of enriching solutions at low concentration with a high enrichment factor. The influences of the sample volume of aqueous solution on the recoveries of analyte ions were also investigated in the sample volume range of 10–500 mL by using model solutions. The results are depicted in Fig. 3. All the analyte ions could be quantitatively recovered at the all the range of the sample volume (10–500 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 the analyte ions, the samples were introduced to the nebulizer of the AAS by using microinjection method [24]. In this system, 100 μL of the samples were injected to a mini home-made Teflon funnel with an Eppendorf Pipette.

Table 1
The influences of the matrix ions on the recoveries of the analytes ($N = 3$)

Ion	Added	Concentration of matrix ion (mg/L)	Recovery (%)					
			Cd	Cu	Pb	Co	Mn	Ni
Na^+	NaCl	40,000	95 ± 1	93 ± 2	100 ± 0	95 ± 1	96 ± 1	96 ± 0
		50,000	93 ± 0	93 ± 2	95 ± 4	94 ± 1	96 ± 1	96 ± 0
Bi^{2+}	$Bi(NO_3)_3$	50	95 ± 1	95 ± 4	95 ± 4	93 ± 3	97 ± 1	99 ± 2
Zn^{2+}	$Zn(NO_3)_2$	50	95 ± 1	93 ± 2	97 ± 5	95 ± 0	97 ± 1	100 ± 0
K^+	KCl	1,000	97 ± 1	96 ± 3	96 ± 5	99 ± 2	100 ± 0	94 ± 0
Ca^{2+}	$CaCl_2$	1,000	96 ± 0	95 ± 2	93 ± 0	99 ± 1	99 ± 1	100 ± 0
Mg^{2+}	$MgCl_2 \cdot 6H_2O$	1,000	97 ± 1	99 ± 2	105 ± 4	101 ± 1	99 ± 1	99 ± 2
Al^{3+}	$AlCl_3 \cdot 6H_2O$	50	99 ± 1	98 ± 2	97 ± 4	99 ± 2	94 ± 2	99 ± 2
NH_4^+	NH_4Cl	500	94 ± 1	91 ± 2	98 ± 4	96 ± 4	96 ± 1	94 ± 0
Cl^-	NaCl	25,000	103 ± 1	101 ± 2	102 ± 3	101 ± 1	97 ± 1	101 ± 2
Cd^{2+}	$Cd(NO_3)_2$	20	–	99 ± 1	98 ± 3	101 ± 2	99 ± 1	98 ± 2
Cu^{2+}	$Cu(NO_3)_2 \cdot 3H_2O$	20	100 ± 4	–	100 ± 0	102 ± 2	95 ± 1	95 ± 2
Pb^{2+}	$Pb(NO_3)$	20	94 ± 1	96 ± 1	–	96 ± 0	97 ± 1	87 ± 2
Co^{2+}	$CoSO_4$	20	101 ± 1	98 ± 2	100 ± 6	–	92 ± 5	96 ± 3
Ni^{2+}	$NiSO_4$	20	97 ± 4	98 ± 3	98 ± 3	104 ± 4	100 ± 0	–
Mn^{2+}	$Mn(NO_3)_2 \cdot 4H_2O$	10	97 ± 1	94 ± 3	100 ± 0	98 ± 2	–	98 ± 3
Co^{2+}	$CoSO_4$	10	99 ± 1	94 ± 0	100 ± 9	–	97 ± 3	99 ± 2

Table 2
Analysis of a mineral water and two table salts spiked analyte ions ($N = 3$)

Analyte	Added (μg)	Yozgat Sorgun mineral water		Isıl table salt		Kochisar table salt	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Co	0	BDL	–	BDL	–	BDL	–
	1.25	1.33	106 ± 2	1.23	98 ± 6	1.21	97 ± 2
	2.50	2.58	103 ± 2	2.43	97 ± 1	2.38	95 ± 0.6
	3.75	3.71	99 ± 1	3.68	98 ± 3	4.90	98 ± 2
Cd	0	BDL	–	BDL	–	BDL	–
	0.63	0.6	95 ± 1	0.62	98 ± 4	0.64	102 ± 3
	1.26	1.23	98 ± 2	1.27	101 ± 3	1.24	98 ± 1
	1.89	1.74	92 ± 0	1.83	97 ± 4	1.87	99 ± 1
Pb	0	0.218	–	BDL	–	BDL	–
	2.5	2.82	112 ± 6	2.60	103 ± 5	3.0	120 ± 0
	5.0	5.2	104 ± 4	4.85	97 ± 3	5.0	100 ± 0
	7.5	7.58	101 ± 3	7.73	103 ± 5	7.95	106 ± 4
Ni	0	BDL	–	0.14	–	BDL	–
	1.25	1.54	123 ± 6	1.29	103 ± 2	1.24	99 ± 5
	2.50	2.50	100 ± 3	2.35	94 ± 2	2.43	97 ± 4
	3.75	3.98	106 ± 4	3.71	99 ± 3	3.75	100 ± 3
Mn	0	BDL	–	BDL	–	BDL	–
	1.25	1.18	94 ± 2	1.38	110 ± 2	1.29	103 ± 3
	2.50	2.50	100 ± 1	2.60	104 ± 4	2.48	99 ± 1
	3.75	3.49	93 ± 1	3.75	100 ± 3	4.05	108 ± 1
Cu	0	BDL	–	BDL	–	BDL	–
	1.25	1.23	98 ± 2	1.24	99 ± 2	1.25	100 ± 2
	2.50	2.48	99 ± 2	2.43	97 ± 1	2.43	97 ± 2
	3.75	3.65	97 ± 0	3.56	95 ± 1	3.56	95 ± 0

BDL: below the detection limit.

The Teflon funnel was connected to the nebulizer with capillary tubing. The peak height signals were recorded. A preconcentration factor of 250 for all the analyte ions can be achieved when the final volume was 2.0 mL.

3.5. Effect of concomitant ions

The one of the main problem in the atomic absorption spectrometric determination of the heavy metal ions is interference from the matrix. In the presented 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 [25–29]. 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. The ions normally present in water and table salt 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. The proposed preconcentration/separation method could be applied to the highly saline samples and the samples that contain some transition metals at the tolerable levels given in Table 1.

3.6. Figures of merit

In order to validate the accuracy of the presented coprecipitation procedure for trace metal ions, tests of addition/recovery in

the experiments for analyte determinations were performed on mineral water from Yozgat, Turkey and two table salt sample. The water sample was filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm. A 2.0 g of table salt sample was dissolved in 30 mL of distilled water. Then procedure given above was applied to the samples. The final volume was 10 mL. The results were listed in Table 2. Good agreement was obtained between 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 7% in the model solutions. The detection limits, defined as the concentration equivalent to 3 times the standard deviation ($n = 15$) of

Table 3
Analyte levels in Beypazari bottled mineral water after application coprecipitation procedure (sample volume: 100 mL, $N = 3$)

Element	Concentration (μg/L)
Cu	BDL
Pb	0.28 ± 0.02[a]
Cd	BDL
Co	BDL
Ni	0.19 ± 0.02
Mn	2.64 ± 0.08

BDL: below the detection limit.
[a] Mean ± S.D.

Table 4
Levels of analyte ions in some table salts after application of coprecipitation procedure ($N = 5$)

Salt sample	Concentration (μg/g)					
	Cu	Ni	Co	Mn	Pb	Cd
Nevşehir Kaya	0.28 ± 0.05^{a}	0.65 ± 0.05	0.26 ± 0.05	0.72 ± 0.07	0.70 ± 0.15	0.18 ± 0.01
Kastamonu Kaya	1.43 ± 0.18	0.50 ± 0.06	BDL	1.13 ± 0.13	1.10 ± 0.10	BDL
Kay Tuz	BDL	0.40 ± 0.04	0.25 ± 0.02	0.42 ± 0.04	0.45 ± 0.20	0.17 ± 0.01
Pan salt	0.52 ± 0.05	2.83 ± 0.30	1.07 ± 0.10	1.81 ± 0.05	3.36 ± 0.50	0.50 ± 0.08

BDL: below the detection limit.
[a] Mean $\pm$ S.D.

the reagent blank, for lead(II), copper(II), nickel(II), cobalt(II), cadmium(II) and manganese(II) ions were 21.1 μg/L, 22.0 μg/L, 24.0 μg/L, 22.2 μg/L, 14.1 μg/L and 25.3 μg/L, respectively.

3.7. Applications

The dysprosium(III) hydroxide coprecipitation procedure was applied to the determination of analyte ions in a bottled mineral water (Table 3) and some table salts from the different region of Turkey (Table 4). The concentrations given in Tables 3 and 4 have been calculated on the assumption of 100% recovery of the analytes. The relative standard deviations values were lower than 8.0% with some exceptions.

4. Conclusion

The dysprosium(III) hydroxide coprecipitation presented in this study is most promising for the analyte ions as the preconcentration factor is 250 based on the analytes. The preconcentration factor achieved with presented procedure is superior to some coprecipitation methods and other preconcentration techniques [14–20,30–32]. The detection limits of analytes are superior to those of coprecipitation techniques [15–21]. The method is relatively rapid as compared with previously reported procedures for the enrichment of analytes. The analyte ions can be sensitively determined by atomic absorption spectrometry without any influence of dysprosium hydroxide. Dysprosium hydroxide as coprecipitant is new, dysprosium hydroxide is non toxic. The method is economic. Only 2.0 g of Dy(III) is used in all the experiments.

References

[1] L. Jarup, Hazards of heavy metal contamination, Br. Med. Bull. 68 (2003) 167–182.

[2] K.A. Momani, Chemical assessment of bottled drinking waters by IC, GC, and ICP-MS, Instrum. Sci. Technol. 34 (2006) 587–605.

[3] M. Soylak, H. Colak, O. Turkoglu, Heavy metal content of some cereals, spices and pulses from middle anatolia region of Turkey, Fresenius Environ. Bull. 15 (2006) 345–348.

[4] R.E.S. Froes, C.C. Windmöller, J.B.B. da Silva, Emprego da modificação química permanente para a determinação de metais em matrizes diversas por espectrometria de absorção atômica em forno de grafite, Revista Anal. 23 (2006) 32–43.

[5] D. Afzali, A. Mostafavi, M.A. Taher, A. Moradian, Flame atomic absorption spectrometry determination of trace amounts of copper after separation and preconcentration onto TDMBAC-treated analcime pyrocatechol-immobilized, Talanta 71 (2007) 971–975.

[6] N. Pourreza, K. Ghanemi, Determination of copper by flame atomic absorption spectrometry after solid-phase extraction, Spectrosc. Lett. 39 (2006) 127–134.

[7] A. Mostafavi, D. Afzali, M.A. Taher, Atomic absorption spectrometric determination of trace amounts of copper and zinc after simultaneous solid-phase extraction and preconcentration onto modified natrolite zeolite, Anal. Sci. 22 (2006) 849–853.

[8] E. Kendüzler, A.R. Turker, Preconcentration of cobalt using Amberlyst 36 as a solid-phase extractor and its determination in various environmental samples by flame atomic absorption spectrometry, Int. J. Environ. Anal. Chem. 86 (2006) 843–853.

[9] W. Hu, B. Hu, Z. Jiang, On-line preconcentration and separation of Co, Ni and Cd via capillary microextraction on ordered mesoporous alumina coating and determination by ICP-MS, Anal. Chim. Acta 572 (2006) 55–62.

[10] J. Pan, S. Wang, R. Zhang, A novel Pb(II)-imprinted IPN for selective preconcentration of lead from water and sediments, Int. J. Environ. Anal. Chem. 86 (2006) 855–865.

[11] W.N.L. dos Santos, J.L.O. Costa, R.G.O. Araujo, D.S. de Jesus, A.C.S. Costa, An on-line pre-concentration system for determination of cadmium in drinking water using FAAS, J. Hazard. Mater. 137 (2006) 1357–1361.

[12] B. Mikula, B. Puzio, Determination of trace metals by ICP-OES in plant materials after preconcentration of 1,10-phenanthroline complexes on activated carbon, Talanta 71 (2007) 136–140.

[13] L. Elci, S. Saracoglu, Applying magnesium hydroxide coprecipitation method for trace analysis to dialysis concentrate, Talanta 46 (1998) 1305–1310.

[14] M. Tuzen, K.O. Saygı, M. Soylak, Separation and speciation of selenium in food and water samples by the combination of magnesium hydroxide coprecipitation-graphite furnace atomic absorption spectrometric determination, Talanta 71 (2007) 424–429.

[15] 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.

[16] 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.

[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] 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.

[19] M. Soylak, G. Onal, Determination of trace metals by atomic absorption spectrometry after coprecipitation with europium hydroxide, J. Hazard. Mater. 137 (2006) 1130–1134.

[20] 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.

[21] S. Kagaya, T. Sagisaka, S. Miwa, K. Morioka, K. Hasegawa, Rapid coprecipitation technique with hybrid hydroxide system using ytterbium(III), gallium(III), and magnesium(II) for simultaneous concentration of 13 elements in concentrated salt solution prior to their inductively coupled plasma atomic emission spectrometric determination, Bull. Chem. Soc. Jpn. 79 (2006) 717–724.

[22] 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.

[23] 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.

[24] H. Berndt, E. Jackwerth, Determination of Li, Na, K, Mg and Ca with a mechanised flame photometric micro-method. Mechanised micro-method (injection method) of flame photometry (atomic absorption–atomic emission) for the determination of serum electrolytes and trace elements (Fe, Cu, Zn), J. Clin. Chem. Clin. Biochem. 17 (1979) 71–76.

[25] F.A.C. Amorim, S.L.C. Ferreira, Determination of cadmium and lead in table salt by sequential multi-element flame atomic absorption spectrometry, Talanta 65 (2005) 960–964.

[26] 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.

[27] T. Balaji, P. Chiranjeevi, G.R.K. Naidu, Simultaneous determination of trace amounts of chromium, cobalt and lead in waste water and plant materials by extraction-atomic absorption spectrometry, Anal. Lett. 31 (1998) 1081–1094.

[28] I. Komjarova, R. Blust, Comparison of liquid–liquid extraction, solid-phase extraction and co-precipitation preconcentration methods for the determination of cadmium, copper, nickel, lead and zinc in seawater, Anal. Chim. Acta 576 (2006) 221–228.

[29] S.H. Babu, K.S. Kumar, K. Suvardhan, K. Kiran, D. Rekha, L. Krishnaiah, K. Janardhanam, P. Chiranjeevi, Preconcentration technique for the determination of trace elements in natural water samples by ICP-AES, Environ. Monit. Assess., doi:10.1007/s10661-006-9309-3.

[30] G. Venkatesh, A.K. Singh, 4-{[(2-Hydroxyphenyl)imino]methyl}-1,2-benzenediol (HIMB) anchored Amberlite XAD-16: preparation and applications as metal extractants, Talanta 71 (2007) 282–287.

[31] E. Pehlivan, T. Altun, Ion-exchange of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} ions from aqueous solution by Lewatit CNP 80, J. Hazard. Mater. 140 (2007) 299–307.

[32] K. Syamasundar, M.A. Chari, D. Shobha, Extractive spectrophotometric determination of cobalt(II) with 1-(benzimidazol-2-yl) ethanone thiosemicarbazone, Anal. Chem.: An Indian J. 2 (2006) 45–47.