Copper(II)-8-hydroxquinoline coprecipitation system for preconcentration and separation of cobalt(II) and manganese(II) in real samples

Mustafa Soylak [a,*], Betul Kaya [a], Mustafa Tuzen [b]

[a] *Erciyes University, Faculty of Art and Science, Department of Chemistry, 38039-Kayseri, Turkey*
[b] *Gaziosmanpasa University, Faculty of Science and Arts, Chemistry Department, 60250 Tokat, Turkey*

Abstract

A separation–preconcentration procedure based on the coprecipitation of cobalt(II) and manganese(II) ions with copper(II)-8-hydroxquinoline system has been developed. The analytical parameters including pH, amount of copper(II) as carrier element, amount of 8-hydroxquinoline, sample volume, etc., was investigated for the quantitative recoveries of Co(II) and Mn(II). No interferic effects were observed from the concomitant ions which are present in real samples. The detection limits for analyte ions by three sigma criteria were $0.86\,\mu g\,L^{-1}$ for cobalt and $0.98\,\mu g\,L^{-1}$ for manganese. The validation of the presented preconcentration procedure was performed by the analysis of NIST SRM 2711 Montana soil and GBW 07605 Tea certified reference materials. The procedure presented was applied to the analyte contents of real samples including natural waters and some food samples with successfully analytical results.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Coprecipitation; Cobalt; Manganese; 8-Hydroxquinoline; Environmental samples; Food; Natural water

1. Introduction

Heavy metal contaminations are serious public health problem due to negative effects of metal ions in human body [1–3]. Industrial facilities and traffic are the main sources in the heavy metal contaminations in the environment. The accurate and precise determination of traces metal ions in environmental samples is a potential studying area of analytical chemist [4–7]. Flame atomic absorption spectrometry is an important instrument at this area due to its simplicity and lower cost than other instruments. Two main limitations in flame atomic absorption spectrometric (FAAS) determinations of heavy metals ions are lower levels of analyte ions then the quantitation limits of FAAS and positive or negative influences of the concomitant ions on the signal of the analytes [8–11].

Preconcentration–separation methods including cloud point extraction, membrane filtration, solvent extraction, solid phase extraction, ion-exchange, solvent sublation, electrodeposition are widely used to solve these problems [12–22]. The separation/enrichment technique has been used to improve the sensitivity and selectivity of trace analyses by replacing the original sample matrix with a new non-interfering matrix. Coprecipitation is a preconcentration–separation technique of rapidly growing importance in trace heavy metal determination with flame furnace atomic absorption spectrometry [23–26]. It has some advantages including short analysis time, high preconcentration factors and low consumption of organic solvent. It has been applied to the preconcentration and separation of heavy metals in environmental samples including natural waters, food samples [27–35]. According to our literature survey, copper(II)-8-hydroxquinoline system is not used for the coprecipitation of heavy metal ions, until now.

In the presented work, a simple and sensitive enrichment technique for cobalt(II) and manganese(II) based on coprecipitation of these elements on copper(II)-8-hydroxquinoline. The analytical parameters including amount of copper(II) as carrier element, amount of 8-hydroxquinoline, sample volume, etc., were investigated.

Table 1
Instrumental conditions for the measurements of the analytes by FAAS

Analyte	Wavelength (nm)	Slit width (nm)	Lamp current (mA)
Co	240.7	0.2	30
Mn	279.5	0.2	20

2. Experimental

2.1. Apparatus

Perkin-Elmer Model 3110 and Perkin-Elmer AAnalyst 700 atomic absorption spectrometer were used in the studies. All measurements were carried out in an air/acetylene flame. Ten centimeter long slot-burner heads, hollow cathode lamps were used. The operating parameters for working elements were set as recommended by the manufacturer given in 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, Nuve NF 800 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 $1 \mu S \, cm^{-1}$.

Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used. Digestion conditions for microwave system for standard reference materials, black tea, rice, tobacco, honey, soil and coal samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min [36,37].

2.2. 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) HNO_3 solution and then rinsed with deionized double distilled water. 8-Hydroxquinoline solution (1.0%, w/v) was daily prepared in ethanol.

A stock solution of copper(II) ($1000 \, mg \, L^{-1}$) was prepared by dissolving 0.378 g of $Cu(NO_3)_2 \cdot 3H_2O$ (E-Merck, Germany) in deionised doubly distilled water in 100 mL. It was prepared daily. Stock standard solutions of analytes, $1000 \, mg \, L^{-1}$, 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 $1 \, mol \, L^{-1}$ HNO_3 by dilution from stock solutions.

Phosphate buffer solutions ($H_2PO_4^-/H_3PO_4$) 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 (CH_3COO^-/CH_3COOH) 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 ($H_2PO_4^-/HPO_4^{2-}$) 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, 6 and 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.

2.3. Model working

The copper-8-hydroxquinoline coprecipitation method was tested with model solutions prior to its application to real samples. Twenty five millilitres portion of an aqueous solution containing 5–20 μg of Co(II) and Mn(II) was placed in a centrifuge tube. The pH of solution was adjusted with an appropriate buffer solution. Then 1.0 mL of $1000 \, mg \, L^{-1}$ of copper(II) as a carrier element was added to this solution. The required volume of 8-hydroxquinoline 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 HNO_3. Then the final volume was completed to 2.0, 5.0 or 10.0 mL with deionized double distilled water. The analytes in the final solution were determined by flame atomic absorption spectrometry.

2.4. Application to real samples

Urine sample from a specimen living in Tokat City, three tap water from different location in Tokat City, river water from Green River-Tokat City and seawater from Black Sea-Samsun were collected in pre-washed (with detergent, doubly de-ionised distilled water, dilute HNO_3 and doubly de-ionised distilled water, respectively) polyethylene bottles. The urine and water samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. The pH of the samples was adjusted to 8.0 with buffer solution. Then the preconcentration–separation procedure given above was applied to all the samples. The levels of analyte ions in the final solutions were determined by flame atomic absorption spectrometry.

NIST SRM 2711 Montana soil (250 mg) certified reference material, soil sample from Tokat City (1.0 g) and coal from Tokat City (1.0 g) were digested with 6 mL HCl (37%), 2 mL of HNO_3 (65%) in microwave digestion system and diluted to 50.0 mL with deionized water. A blank digest was carried out in the same way. Then the preconcentration procedure given above was applied to the final solutions.

GBW 07605 Tea certified reference material (250 mg), black tea (1.0 g), rice (1.0 g), tobacco (1.0 g) and honey (1.0 g) samples were digested with 6 mL of concentrated HNO_3 (65%) and 2 mL of H_2O_2 (30%) in microwave system. After digestion of the samples, the volume of the digested sample was made up to 50.0 mL with distilled water. The blanks were prepared in the same way as the sample, but omitting the sample. The procedure given above was applied.

3. Results and discussion

3.1. Effects of pH on the coprecipitation

For the quantitative coprecipitation efficiency of analyte ions, pH of the working media is a main factor. The influences of pH
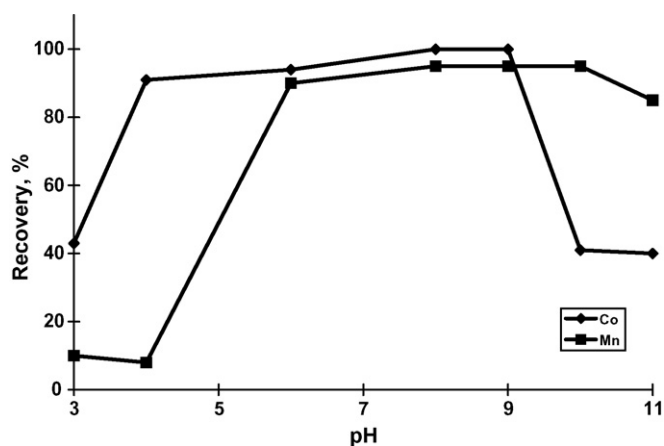
Fig. 1. Influences of pH on the recoveries of cobalt(II) and manganese(II) on the coprecipitation method ($N = 3$).

on the recoveries of analytes on copper-8-hydroxquinoline precipitate were studied in the pH range of 3–11 by using model solutions containing Co(II) and Mn(II). pH was adjusted by using related buffer solutions given at Experimental section. The results are depicted in Fig. 1. Quantitative recovery values were obtained for cobalt in the pH range of 4–10 and for manganese in the pH range of 8–9. pH 8 was selected as working pH for all further works.

3.2. Effects of amount of 8-hydroxquinoline

The effects of amount of 8-hydroxquinoline on the recoveries of Co(II) and Mn(II) ions were investigated. The results were given in Fig. 2. When the experiments were performed without 8-hydroxquinoline at pH 9, the recovery values for cobalt and manganese were 5% and 10%, respectively. The recoveries analyte ions increased with increasing amounts of 8-hydroxquinoline. This results show that for the quantitative and simultaneous recoveries of cobalt and manganese, 8-hydroxquinoline is necessary. All subsequent works 10 mg 1.0 mL of 1.0% (w/v) solution of 8-hydroxquinoline was used.
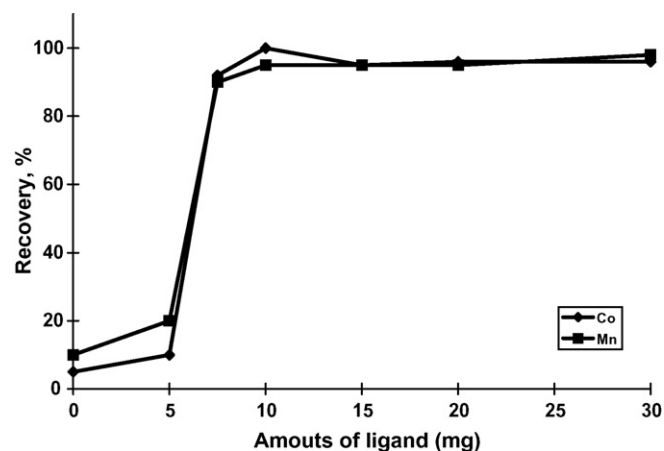
3.3. Effects of amounts of copper(II)

The influences of amounts of copper(II) as carrier element were also investigated for the coprecipitation system. Without copper, the recoveries for analyte ions were not quantitative. Quantitative recovery values were obtained for the all analyte ions in 0.5–2.0 mg of copper. All further works were performed with 1 mg (1 mL of 1000 mg L^{-1}) of copper(II) ions as carrier element.

3.4. Influences of sample volume on the recoveries

The influences of the sample volume on the coprecipitation efficiencies of the analytes were examined. Cobalt and manganese ions were quantitatively recovered in the sample volume range of 10–50 mL. The precipitate of copper(II)-8-hydroxquinoline that was including analytes was successfully dissolved 500 μL of concentrated nitric acid. The final volume was completed to 2.0, 5.0 or 10.0 mL by distilled water. The analytes were quantitatively recovered in these studies. 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 was 25.

3.5. Interference studies

One of the main problems of the atomic absorption spectrometry for determination of the heavy metal ions is the matrix interference. In our work, the influences of the some ions, which are known as interferic ions in the flame atomic absorption spectrometric determination were investigated. Various amounts of metal ions were added to a solution containing fixed amounts of cobalt and manganese ions and the present procedure was followed. The results for this study are given in Table 2. The tolerance limit was defined as the ion concentration causing a relative error smaller than ±5% related to the coprecipitation and determination of the examined elements. The results are desired in view of applications to real samples including various salts at high concentration levels.

Fig. 2. Effects of amounts of 8-hydroxquinoline on the recoveries of Co and Mn ($N = 3$).

Table 2
Influences of some foreign ions on the recoveries of analytes ($N = 3$)

Ion	Added as	Concentration (mg L^{-1})	Co	Mn
Na$^+$	NaCl	20000	96 ± 2	98 ± 3
K$^+$	KCl	5000	96 ± 2	95 ± 2
Ca^{2+}	CaCl$_2$	5000	98 ± 3	96 ± 3
Mg^{2+}	MgCl$_2$	5000	95 ± 2	97 ± 3
Cl$^-$	NaCl	30000	96 ± 3	96 ± 2
F$^-$	NaF	1000	98 ± 2	96 ± 2
NO$_3^-$	KNO$_3$	3000	95 ± 2	97 ± 3
HCO$_3^-$	NaHCO$_3$	1000	97 ± 3	96 ± 2
Al^{3+}	Al$_2$(SO$_4$)$_3$	50	96 ± 2	97 ± 2
Fe^{3+}	FeCl$_3$	50	95 ± 2	96 ± 3
Pb^{2+}	Pb(NO$_3$)$_2$	50	97 ± 4	95 ± 3
Zn^{2+}	ZnSO$_4$	50	95 ± 3	96 ± 3
Cr^{3+}	Cr(NO$_3$)$_3$	50	96 ± 2	97 ± 4
Cd^{2+}	Cd(NO$_3$)$_2$	50	95 ± 3	96 ± 3
Ni^{2+}	NiSO$_4$	50	95 ± 3	96 ± 3

Table 3
The results for tests of addition/recovery for Co and Mn determination in some real samples (sample volume: 25 mL, final volume: 5 mL ($N = 4$))

Element	Added (μg)	Tap water		Sea water		Urine	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Co	0	ND	–	ND	–	ND	–
	10	9.9 ± 0.2[a]	99	9.8 ± 0.3	98	9.5 ± 0.3	95
	20	19.6 ± 0.5	98	19.6 ± 0.7	98	19.4 ± 0.6	97
	40	38.5 ± 0.9	96	39.1 ± 0.8	98	38.2 ± 0.6	96
Mn	0	ND	–	ND	–	ND	–
	2.5	2.5 ± 0.1	100	2.4 ± 0.1	96	2.4 ± 0.2	96
	5	4.9 ± 0.2	98	4.9 ± 0.2	98	4.8 ± 0.2	96
	10	9.9 ± 0.5	99	9.7 ± 0.5	97	9.7 ± 0.4	97

[a] Standard deviation, N.D.: not detected.

3.6. Addition/recovery tests

Tests of addition/recovery in the experiments for analyte ions were performed in two natural samples and a urine 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 95–100%. These values were quantitative and it shows that the presented method can be applied for the separation–preconcentration of analyte ions in real samples.

3.7. Detection limits

The detection limits for analytes were calculated after presented preconcentration procedure applied to the blank solutions. The detection limits of the investigated elements based on three times the standard deviations of the blank ($k = 3$, $N = 11$) were $0.86 \,\mu g \, L^{-1}$ for cobalt(II) and $0.98 \,\mu g \, L^{-1}$ for manganese(II).

3.8. Application to real samples

The validation of presented procedure was studied by the analysis of NIST SRM 2711 Montana soil and GBW 07605 Tea certified reference materials. The results are given in Table 4. The results of our work and certified values for cobalt and manganese are in good agreement.

The coprecipitation procedure for analyte ions was applied to various environmental samples. The results are given in Table 5 and in Table 6. The results have been calculated on the assumption of 100% recovery of analyte ions.

Table 5
Cobalt and manganese levels of natural water and urine samples (final volume: 2 mL, $N = 4$)

	Concentration (μg L^{-1})[a]	
	Co	Mn
Urine	BDL	1.3 ± 0.1
Tap water 1	BDL	2.7 ± 0.2
Tap water 2	3.6 ± 0.2	4.5 ± 0.3
Tap water 3	4.7 ± 0.4	5.1 ± 0.2
River water	BDL	7.5 ± 0.5
Seawater	1.5 ± 0.1	5.9 ± 0.4

[a] Mean expressed as 95% tolerance limit, BDL: below the detection limit.

Table 6
Concentration of analyte ions in microwave digested solid samples after application presented coprecipitation procedure ($N = 5$, final volume: 2 mL)

	Concentration (μg g^{-1})	
	Co	Mn
Black tea	0.35 ± 0.02	940 ± 50
Rice	0.48 ± 0.04	3.3 ± 0.2
Tobacco	0.67 ± 0.05	75.1 ± 4.7
Honey	BDL	2.5 ± 0.2
Soil	3.2 ± 0.2	125 ± 10
Coal	15.6 ± 1.1	75.2 ± 6.3

Mean expressed as 95% tolerance limit, BDL: below the detection limit.

3.9. Comparison other coprecipitation studies

Table 7 compares the performance characteristics of the proposed coprecipitation method, with those of the previously reported coprecipitation methods for some metal ions in environ-

Table 4
The results for reference standard materials ($N = 4$)

Element	NIST SRM 2711 Montana soil (μg g^{-1})		GBW 07605 Tea (μg g^{-1})	
	Certified value	Our value	Certified value	Our value
Co	(10)[a]	9.5 ± 0.7[b]	0.18	0.20 ± 0.01
Mn	638	610 ± 42	1240	1205 ± 55

[a] The value in the parenthesis is not certified.
[b] Mean expressed as 95% tolerance limit.

Table 7
Comparative data from some recent studies on coprecipitation of heavy metal ions

Analytes	Coprecipitation system	Dissolving media	PF	DL ($\mu g\,L^{-1}$)	R.S.D. (%)	Ref.
Cu, Pb, Cd	Aluminum hydroxide	$4\,mol\,L^{-1}\,HNO_3$	125	3–16	2–3	[28]
Fe, Pb, Bi	Yttrium phosphate	$6\,mol\,L^{-1}\,HNO_3$	–	0.008–0.137 μg	1.2–4.1	[29]
Fe	Magnesium hydroxide	5% HCl	–	0.05–0.06 nmol	3–5	[30]
Cd, Pb, Ni	Copper(II) diethyldithiocarbamate	$0.5\,mol\,L^{-1}\,HCl$	22–45	0.23–3.2	<3	[31]
Pb	Manganese dioxide	HNO_3/H_2O_2	–	3.2	<5	[32]
Cu, Co, Pb, Cd, Ni	Cerium(IV) hydroxide	$0.5\,mol\,L^{-1}\,HNO_3$	375	0.18–7.0	<9	[33]
Cr	Pd/8-quinolinol/ tannic acid	–	–	0.020	–	[34]
Pb, Cu, Ni, Co, Cd, Mn	Dysprosium(III) hydroxide	$1\,mol\,L^{-1}\,HNO_3$	250	14.1–25.3	<10	[35]
Co, Mn	Copper(II) 8-hydroxquinoline	$1\,mol\,L^{-1}\,HNO_3$	25	0.86–0.98	<10	This study

PF: preconcentration factor, DL: detection limit.

mental samples. As it is obvious, the proposed coprecipitation method not only in the term of the preconcentration factor, but also in the terms of detection limit is superior to those previously reported [35–37].

4. Conclusion

The coprecipitation method presented is simple and sensitive for cobalt and manganese preconcentration in environmental samples. Under the optimum experimental conditions, quantitative recoveries were achieved for a preconcentration factor of 25. The presented method can be applied not only to analysed samples but also geological and biological samples.

Acknowledgements

References

[1] G.N. Shetty, Body Fluid Diagnostics in Microliter Samples, Ph.D. Thesis, Biomedical Engineering, Case Western Reserve University, 2006.

[2] J.S. Casas, J. Sordo, Lead: Chemistry, Analytical Aspects, Environmental Impact and Health Effects, Elsevier, Amsterdam, 2006.

[3] Z. Fan, Determination of antimony(III) and total antimony by single drop microextraction combined with electrothermal atomic absorption spectrometry, Anal. Chim. Acta 585 (2006) 300–304.

[4] E. Sesli, Trace metal contents of higher fungi from Zigana Highland in Turkey, Asian J. Chem. 19 (2007) 636–640.

[5] H. Cesur, M.E. Kartal, Determination of cadmium levels in agricultural areas of Carsamba and Bafra Plains, Environ. Monit. Assess., in press.

[6] D. Weng, GFAAS determination of trace amount cadmium in shark liver after microwave digestion, Spectrosc. Spectr. Anal. 26 (2006) 2147–2149.

[7] C. Sivani, G. Ramakrishna Naidu, J. Narasimhulu, D. Rekha, J.D. Kumar, P. Chiranjeevi, Determination of Co(II) in water and soil samples using spectrophotometry coupled with preconcentration on 4-amino methyl pyridine anchored silica gel column, J. Hazard. Mater., in press.

[8] V.N. Bulut, C. Duran, M. Tufekci, L. Elci, M. Soylak, Speciation of Cr(III) and Cr(VI) after Column solid phase extraction on Amberlite XAD-2010, J. Hazard. Mater., in press.

[9] E. Pehlivan, F. Gode, Batch sorption of divalent metal ions onto brown coal, Energy Sources Part A 28 (2006) 1493–1508.

[10] V.A. Lemos, E.S. Santos, M.S. Santos, R.T. Yamaki, Thiazolylazo dyes and their application in analytical methods, Microchim. Acta, in press.

[11] M. Ghaedi, Pyrimidine-2-thiol as selective and sensitive ligand for preconcentration and determination of Pb^{2+}, Chem. Anal. 51 (2006) 593–602.

[12] T. Yokoyama, K. Murata, S. Mukai, K. Uomoto, T. Itoh, M. Shibata, M. Zenki, Determination of aluminum in water samples by flame AAS after extraction of 8-quinolinol complex with nitrobenzene, Bunseki Kagaku 55 (2006) 757–763.

[13] C. Duran, H.B. Senturk, A. Gundogdu, V.N. Bulut, L. Elci, M. Soylak, M. Tufekci, Y. Uygur, Determination of some trace metals in environmental samples by flame AAS following solid phase extraction with Amberlite XAD-2000 resin after complexing with 8-hydroxyquinoline, Chin. J. Chem., in press.

[14] M.A. Aki, Y. Mori, K. Sawada, Solvent sublation and spectrometric determination of iron(II) and total iron using 3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)1,2,4-triazine and tetrabutylammonium bromide, Anal. Sci. 22 (2006) 1169–1174.

[15] D. Banerjee, B.C. Mondal, A.K. Das, Synthesis and analytical application of a new chelating resin containing 8-aminoquinoline group, J. Indian Chem. Soc. 81 (2004) 50–53.

[16] M. Tuzen, M. Soylak, Evaluation of some traces heavy metal levels of drinking waters from Tokat-Black Sea Region of Turkey, Polish J. Environ. Stud. 15 (2006) 915–919.

[17] D. Rekha, K. Suvardhan, J.D. Kumar, P. Subramanyam, P.R. Prasad, Y. Lingappa, P. Chiranjeevi, Solid phase extraction method for the determination of lead, nickel, copper and manganese by flame atomic absorption spectrometry using sodium bispiperdine-1,1′-carbotetrathioate (Na-BPCTT) in water, J. Hazard. Mater., in press.

[18] Y.K. Aktaş, H. Ibar, Determination of Cd, Mn, Sb, Ni And Fe in water samples after preconcentration on bentonite modified with trioctyl phosphine oxide, Fresen. Environ. Bull. 16 (2007) 8–10.

[19] B.F. Senkal, M. Ince, E. Yavuz, M. Yaman, The synthesis of new polymeric sorbent and its application in preconcentration of cadmium and lead in water samples, Talanta, in press.

[20] R.S. Praveen, G.R.K. Naidu, T.P. Rao, Dithiocarbamate functionalized or surface sorbed Merrifield resin beads as column materials for on line flow injection-flame atomic absorption spectrometry determination of lead, Anal. Chim. Acta, in press.

[21] J.Y. Song, M. Hou, L.X. Zhang, Determination of mercury at trace level in natural water samples by hydride generation atomic absorption spectrophotometry after cloud point extraction preconcentration, Chin. Chem. Lett. 17 (2006) 1217–1220.

[22] M. Ghaedi, A. Shokrollahi, Chromosorb, an alternative suitable support for trace copper ion enrichment using 2-mercaptobenzoxazole as modifier, Fres. Environ. Bull. 15 (2006) 1373–1381.

[23] K. Watanabe, M. Tojo, M. Itagaki, Flow injection analysis of Cr(VI) using coprecipitation of metal hydroxides, Bunseki Kagaku 55 (2006) 781–786.

[24] M. Vircavs, V. Rone, D. Vircava, Coprecipitation study of As(III), Cu(II) and Cd(II) from aqueous solution using 5-bromo and 2-methlthioquinoline-8-thiol, Fres. J. Anal. Chem. 350 (1994) 650–651.

[25] D. Atanassova, V. Stefanova, E. Russeva, Co-precipitative preconcentration with sodium diethyldithiocarbamate and ICP-AES determination of Se, Cu, Pb, Zn, Fe, Co, Ni, Mn, Cr and Cd in water, Talanta 47 (1998) 1237–1243.

[26] I. Atsuya, K. Itoh, I. Ariu, Preconcentration by coprecipitation of lead and selenium with Ni/pyrolidine-dithiocarbamate complex and their simultaneous determination by internal standard atomic absorption spectrometry with the solid sampling technique, Pure Appl. Chem. 63 (1991) 1221–1226.

[27] S. Arpadjan, L. Jordenova, I. Karadjuva, Reductive coprecipitation and extraction as separation methods for the determination of gold in copper concentrates by AAS and ICP-AES, Fres. J. Anal. Chem. 347 (1993) 480–482.

[28] 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.

[29] S. Kagaya, Y. Araki, N. Hirai, K. Hasegawa, Coprecipitation with yttrium phosphate as a separation technique for iron(III), lead, and bismuth from cobalt, nickel, and copper matrices, Talanta 67 (2005) 90–97.

[30] J. Wu, E.A. Boyle, Determination of iron in seawater by high resolution isotope dilution inductively coupled plasma mass spectrometry after $Mg(OH)_2$ coprecipitation, Anal. Chim. Acta 367 (1998) 183–191.

[31] H. Chen, J. Jin, Y. Wang, Flow injection on-line coprecipitation preconcentration system using copper(II) diethyldithiocarbamate as carrier for flame atomic absorption spectrometric determination of cadmium, lead and nickel in environmental samples, Anal. Chim. Acta 353 (1997) 181–188.

[32] M.S. Bispo, E.S. da Boa Morte, M.G.A. Korn, L.S.G. Teixeira, M. Korn, A.C.S. Costa, Determination of Pb in river water samples by inductively coupled plasma optical emission spectrometry after ultrasound-assisted co-precipitation with manganese dioxide, Spectrochim. Acta 60B (2005) 653–658.

[33] U. Divrikli, L. Elci, Determination of some trace metals in water and sediment samples by flame atomic absorption spectrometry after coprecipitation with cerium(IV) hydroxide, Anal. Chim. Acta 452 (2002) 231–235.

[34] Q. Zhang, H. Minami, S. Inoue, I. Atsuya, Preconcentration by coprecipitation of chromium in natural waters with Pd/8-quinolinol/tannic acid complex and its direct determination by solid sampling atomic absorption spectrometry, Anal. Chim. Acta 401 (1999) 277–282.

[35] D.S.K. Peker, O. Turkoglu, M. Soylak, Dysprosium(III) hydroxide coprecipitation ystem for the separation and preconcentration of heavy metal contents of table salts and natural waters, J. Hazard. Mater., in press.

[36] M. Tuzen, E. Melek, M. Soylak, Celtek, Clay as sorbent for separation-preconcentration of metal ions from environmental samples, J. Hazard. Mater. 136 (2006) 597–603.

[37] M. Tuzen, H. Sari, M. Soylak, Microwave and wet digestion procedures for atomic absorption spectrometric determination of trace metals contents of sediment samples, Anal. Lett. 37 (2004) 1925–1936.