ELSEVIER

A solid phase extraction procedure for Fe^{3+}, Cu^{2+} and Zn^{2+} ions on 2-phenyl-1H-benzo[d] imidazole loaded on Triton X-100-coated polyvinyl chloride

Mehrorang Ghaedi [a,*], Khodabakhsh Niknam [b], Ardeshir Shokrollahi [a], Ebrahim Niknam [b], Hamed Ghaedi [a], Mustafa Soylak [c]

[a] *Chemistry Department, Yasouj University, Yasouj 75914-353, Iran*
[b] *Chemistry Department, Persian Gulf University, Bushehr, Iran*
[c] *Chemistry Department, University of Erciyes, 38039 Kayseri, Turkey*

Abstract

A new and efficient solid phase extraction method is described for the preconcentration of trace heavy metal ions. The method is based on the adsorption of Fe^{3+}, Cu^{2+} and Zn^{2+} on 2-phenyl-1H-benzo[d] imidazole (PHBI) loaded on Triton X-100-coated polyvinyl chloride (PVC). The influences of the analytical parameters including pH and sample volume were investigated. Common coexisting ions did not interfere on the separation and determination of analytes under study. The adsorbed analytes were desorbed by using 5 mL of 4 mol L^{-1} nitric acid. The preconcentration factor is 90. The detection limits (3 sigma) were in the range of 0.95–1 μg L^{-1}. The sorbent exhibited excellent stability and its sorption capacity under optimum conditions has been found to be more than 2.7 mg of ions per gram of sorbent. The recoveries of analytes were generally higher than 95%. The relative standard deviations (R.S.D.s) were generally lower than 4%. The method has been successfully applied to some real samples.
© 2008 Elsevier B.V. All rights reserved.

Keywords: Surfactant-coated polyvinyl chloride; Trace metal; Atomic absorption spectrometry; Solid phase extraction

1. Introduction

The considerable emphasis has been carried out on the removal of toxic metal ions, lead to the development of a variety of analytical methodologies. Hence, there has been considerable growth in the analytical chemistry of various metal ions [1–4]. Accurate and precise analyses of traces of heavy metal ions by instrumental analysis techniques including inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and flame atomic absorption spectrometry (FAAS), etc. are an important part of the analytical chemistry [5–7], because of ecological and health problems associated with environmental contamination continues to rise. Direct instrumental analysis of these samples is difficult because of complex formation and signifi-

cant matrices, which invariably influence normal instrumental analysis [8]. In addition, some metals have low concentrations, which are near or below the limit of detection of the instrument. Preconcentration can solve the above two problems and leads to simplified heavy metal determination [9–14]. Solid phase extraction is a universal technique in this respect compared to the conventional liquid extraction [15–18]. Solid phase extraction is based on the utilization of a major constituent as bonded stationary phase immobilized with different ligand or functional group. The nature of the functional group determines the phase selectivity for metal ion while the regeneration of the phase depends on polymer matrix [15–19].

PVC-coated analytical reagent possesses some definite advantages [20]. It does not swell or strain, has good mechanical strength and undergoes heat treatment. Suitable applications of modified PVC for the separation and preconcentration of metal ions from large sample volume demand the process to be both thermodynamically and kinetically favorable. To achieve maximum efficiency it is necessary to optimize the operational

---

* Corresponding author. Tel.: +98 741 2223048; fax: +98 741 2223048.
E-mail address: m_ghaedi@mail.yu.ac.ir (M. Ghaedi).

variables. The time taken for the adsorption of the metal ion and the attainment of the equilibrium condition by the immobilized PVC is of considerable importance.

The purpose of this work is to investigate the feasibility of absorption of these ions including, copper, iron and zinc ions on Triton X-100-coated PVC modified with 2-phenyl-1*H*-benzo[*d*] imidazole (PHBI). For obtaining maximum signal for evaluation of these ion contents, the effective parameters, viz. pH of sample, amount of PHBI and solid phase, type and concentration of eluting agent must be optimized.

2. Experimental

2.1. Instruments

The measurements of metal ions were performed with a Shimadzu 680 atomic absorption spectrometer equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths using an air–acetylene flame. The instrumental parameters were those recommended by the manufacturer. A Metrohm 691 pH/Ion meter with a combined glass–calomel electrode was used for adjustment of test solution pH.

2.2. Reagent and solutions

Acids and bases were of the highest purity available from E. Merck, Darmstadt, Germany and were used as received. Doubly distilled deionized water was used throughout. Nitrate salts of lead, cadmium, mercury, cobalt, nickel, copper, zinc, magnesium, calcium, strontium, barium, silver, sodium and potassium (E. Merck, Darmstadt, Germany) were of the highest purity available and used without any further purification. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to prepare the desired pH solution. The ligand BHBI was synthesized according to literature [21] (Scheme 1).

2.3. Measurement of amount of PHBI loaded on Triton X-100-coated PVC

A 10 mL of 0.005 mol L^{-1} NaOH solution containing 20 mg of PHBI was added to 1 g of PVC and 50 mg of Triton X-100 in a 25-mL vial and shaken. Then a portion of the supernatant liquid was diluted to the appropriate volume and the absorbance of the solution was measured at maximum wavelength. Comparisons of the absorbance of supernatant solution with absorbance of PHBI solution before addition indicate the amount of PHBI adsorbed on Triton X-100-coated PVC.
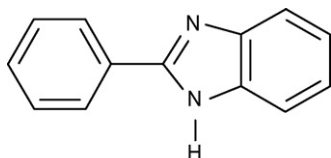
Scheme 1. The structure of ligand.

2.4. Preparation of PHBI-coated PVC

50 mg of Triton X-100 and 20 mg of PHBI were added to 40 mL of water solution containing 1 g PVC particles and its pH was adjusted to 10 by addition of dilute nitric acid. The pH was adjusted to 2 with 2 mol L^{-1} hydrochloric acid to form PHBI-impregnated ad-micelles on PVC particles while shaking the suspension with a stirrer. After mixing for 15 min, the supernatant solution was discarded and the remaining was packed into a column. The column was washed by passing 5 mL of 4 mol L^{-1} HNO$_3$, and then the column was neutralized with 0.01 mol L^{-1} aqueous ammonia. When kept in a refrigerator the sorbent is stable at least for 1 week. The concentration of Triton X-100 was fixed below the critical micellization concentration of Triton X-100.

2.5. Model studies

The performance of method was tested with model solution prior to its application to real samples. pH of the 200 mL of the model solution containing analytes was adjusted by addition of dilute nitric acid or sodium hydroxide to prepare the desired pH solution. The solutions were contacted for 80 min with solid phase. The adsorbed ions were then eluted with 5 mL of 4 mol L^{-1} nitric acid in acetone. The analyte ions in the eluent were determined by flame atomic absorption spectrometer.

2.6. Pretreatment and analysis of real samples

The orange juice was treated according to literature [22]. All the real samples were prepared according to our previous publications [23–25]. Then the procedure given in Section 2.5 was applied to each sample.

3. Results and discussion

3.1. Influences of pH

The PHBI chemical structure shows that it could behave as a basic substance. In acidic media active nitrogen sites could be protonated. This reveals that the mechanism of sorption of ions is pH dependent and pH could affect the stability of the complexes. One of the most important factors in a solid phase extraction procedure is the pH of the aqueous phase for the quantitative recoveries [26–33]. The reaction between analyte ions and the complexing agent can be influenced by changes of pH value. The influences of the pH on iron, copper, zinc and PHBI sorption onto Triton X-100-coated PVC was investigated over the range from 2.0 to 9.0 keeping other parameters constant. Fig. 1 shows that iron, zinc and copper were effectively adsorbed in pH of 6.0.

3.2. Effects of amounts of PHBI

The sorbent was employed in this work as a proper ligand for the extraction of trace of these ions from aqueous solu-
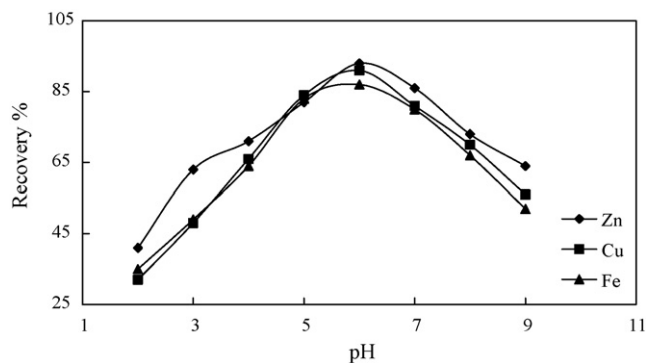
Fig. 1. Effect of pH on the recoveries of analyte ions (eluent: 5 mL of 4 mol L^{-1} nitric acid, $n = 3$).

Fig. 3. Effect of amount of PVC on the recoveries of analyte ions (pH 6, eluent: 5 mL of 4 mol L^{-1} nitric acid, $n = 3$).

tions. While cross-linked PVC shows only a little tendency (less than 10%), Triton X-100-coated (less than 40%) for the extraction of these ions, PHBI loaded on Triton X-100-coated PVC is capable of extracting these ions from the sample solutions quantitatively.

Due to the amount of PHBI, which is also an important factor in the preconcentration studies for the quantitative recoveries of analyte ions from the working media, the influences of the PHBI amounts on the retention of Fe^{3+}, Cu^{2+} and Zn^{2+} on Triton X-100-coated PVC was also examined in Fig. 2. Maximum recovery at 200 mL of 0.2 μg mL^{-1} for all analyte ions could be achieved using 20 mg PHBI. A series of different amounts of the solid sorbent (0.25–1.5 g) were used for sorption of ions from 200 mL of 0.2 μg mL^{-1} of these ions solutions. The percent adsorption of ions using different amount of the sorbent showed that the appropriate amount of the solid sorbent could be 1.0 g.

3.3. Effects of amounts of PVC

The influences of the amounts of PVC in solid phase were also investigated. The results are given in Fig. 3. The recoveries of analytes above 1.0 g of solid phase were below 95% with 6 mL of the eluent. In the proposed procedure, 1.0 g of PVC is recommended.
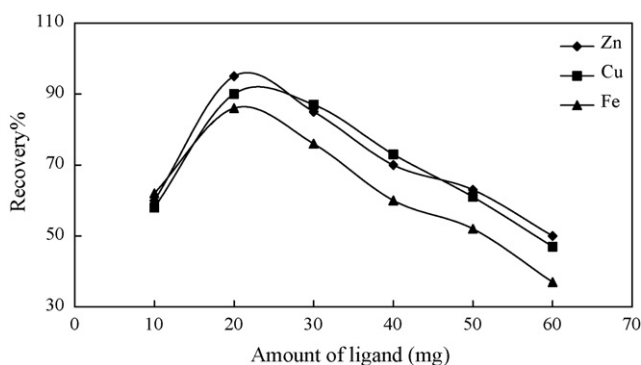
3.4. Effect of type of surfactant and amount of Triton X-100

The influence of Triton X-100 on the percentage of complexed ions adsolubilized was investigated by contacting 200 mL of a solution containing 40 μg of each ion with solid phase containing 50 mg of different surfactant including sodium dodecyl sulphate (SDS), Triton X-100, cetyl trimethylammonium bromide (CTAB) and dodecyl trimethylammonium bromide (DTAB) and various amounts of PVC and 20 mg PHBI at pH 6.0. In the absence of surfactant, ions were not retained quantitatively on solid phase extraction (SPE). Quantitative recoveries were obtained only with Triton X-100.

For examining the effect of Triton X-100, a set of similar experiment using solid phase compromise of 1 g PVC and different amount of Triton X-100 were conducted. The results are presented in Fig. 4. As can be seen by using Triton X-100, complete and reversible adsorption–desorption could be achieved. The retention of metal ions on hemi-micelles, which have a hydrophobic surface, was clearly dependent on analyte complex polarity. Therefore, addition of Triton X-100 is necessary. The formation of minute amounts of ad-micelles was essential to achieve complete adsolubilization of these ions as respective complex. At surfactant concentrations higher than about 50 mg g^{-1} PVC, a decrease in the percentage of ions retained was observed as a result of the formation of micelles.

Fig. 2. Effect of amount of PHBI on recoveries of analyte ions (pH 6, eluent: 5 mL of 4 mol L^{-1} nitric acid, $n = 3$).

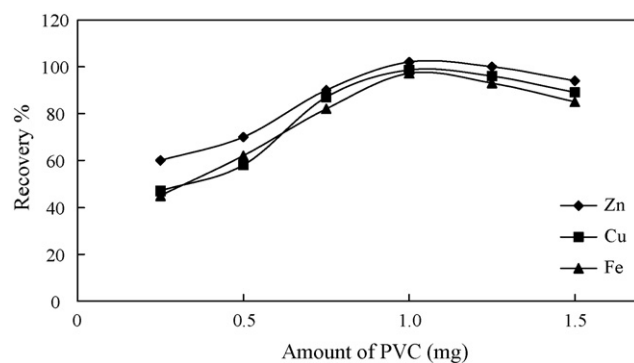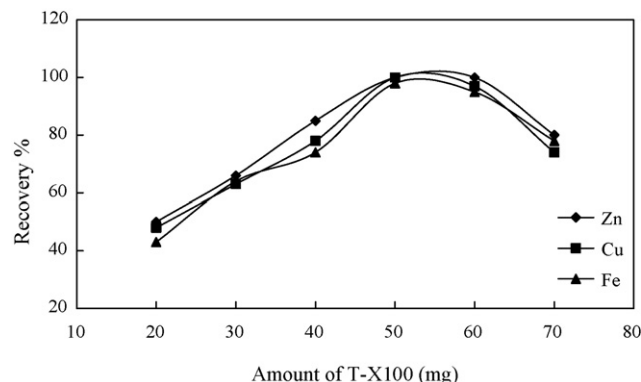Fig. 4. Influences of Triton X-100 concentration on recovery values (pH 6, eluent: 5 mL of 4 mol L^{-1} nitric acid, $n = 3$).

Table 1
Effect of type and concentration of eluting agent on recovery of analytes ($n = 3$, pH 6)

Eluent	Recovery (%)		
	Zn	Cu	Fe
H_3PO_4 (4 mol L^{-1})	40 ± 3	23 ± 4	28 ± 4
HCl (4 mol L^{-1})	90 ± 1	77 ± 2	63 ± 3
H_2SO_4 (4 mol L^{-1})	18 ± 4	21 ± 4	57 ± 2
CH_3COOH (4 mol L^{-1})	37 ± 3	26 ± 4	19 ± 4
HNO_3 (1 mol L^{-1})	53 ± 2	43 ± 3	48 ± 3
HNO_3 (2 mol L^{-1})	75 ± 2	68 ± 2	63 ± 2
HNO_3 (3 mol L^{-1})	90 ± 1	87 ± 2	83 ± 2
HNO_3 (4 mol L^{-1})	100 ± 1	98 ± 1	98 ± 1
HNO_3 (4 mol L^{-1}) 2 mL	50 ± 3	40 ± 3	45 ± 4
HNO_3 (4 mol L^{-1}) 4 mL	81 ± 3	70 ± 3	97 ± 3
HNO_3 (4 mol L^{-1}) 6 mL	100 ± 1	98 ± 1	97 ± 1
HNO_3 (4 mol L^{-1}) 8 mL	94 ± 2	83 ± 2	89 ± 2
HNO_3 (4 mol L^{-1}) 10 mL	96 ± 2	81 ± 2	95 ± 2

3.5. Eluent types and eluent volume

In order to choose the most effective eluent for desorbing the metal ions from the sorbent surface, a series of eluents (different acids) were used in order to find a selective eluent for desorbing enriched ions from sorbent surfaces. A total of 5 mL of 4.0 mol L^{-1} of the above-mentioned eluents were used for desorbing the adsorbed ions. The results (Table 1) showed that the recovery is best when nitric acid solution was used as the eluent. The influence of the concentration of nitric acid on the desorption of these ions was studied. For desorbing 40 μg of ions, already adsorbed on 1.0 g of adsorbent, different concentrations of the eluent (nitric acid) have been used. At concentrations more than 4 mol L^{-1} the extraction efficiency reached maximum.

3.6. Reusability of the synthetic adsorbent

The prepared synthetic sorbent was subjected to several loadings with metal solution and elution with suitable eluent by batch method. The shaking was continued up to 2 h and the desorbed metal ion was estimated following the procedure described in earlier section. The sorption and desorption were repeated several times on the same adsorbent and the metal ion eluted each time was estimated. The capacity of the synthetic adsorbent practically did not change after repeated use of even 10 times.

3.7. Preconcentration factor

The elution volume strongly affects the preconcentration factor, defined as the ratio of sample volume to elution volume. By applying the optimum conditions volumes up to 450 mL of 10 μg mL^{-1} of these ions can be completely adsorbed on the solid phase and could be easily desorbed and detected by AAS. This shows that a preconcentration factor of 90 and loading capacity of 2.7 mg g^{-1} of solid phase is achievable by the system.

3.8. Reproducibility of the process

In order to find the relative error in the determination of ions, the recommended procedure was repeated seven times under optimum conditions. The relative standard deviation (R.S.D.) was found to be 2.04% ($n = 7$). The prepared sorbent was subjected to several loadings with the sample solution and subsequent elution with eluent. The capacity of the adsorbent did not change after 10 cycles of sorption and desorption.

3.9. Effect of matrix ions

To assess the possible applications of the procedure, the effect of foreign ions which interfere with the determination of iron, copper, zinc and lead ions by the presented method or/and often accompany analyte ions in various real samples was examined with the optimized conditions at above. A fixed amount of analytes was taken with different amounts of foreign ions and recommended procedure was followed. The recoveries of analytes were higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of investigated analyte ions by the combination of Triton X-100-coated PVC solid phase extraction procedure and the flame atomic absorption spectrometric determination methods. The results are summarized in Table 2. As it is seen, large number of ions used have no considerable effect on the determination of analyte ions.

3.10. Figures of merit

The detection limit (LOD) of the present work was calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The limits of detection of the proposed method for the determination of investigated elements were studied under the optimal exper-

Table 2
Effects of the interferences ions on the recoveries of the examined metal ions ($n = 3$, pH 6)

Ion	Interference/analyte amount	Recovery (%)		
		Zn	Cu	Fe
Ba^{2+}, Mg^{2+}, Ca^{2+}	1000	100[a]	99	97
Na^+, K^+, Li^+	1000	100	97	96
Al^{3+}	1000	100	98	95
Ni^{2+}	450	97	94	92
Hg^{2+}	200	97	92	91
CH_3COO^-	900	98	91	90
Ti^{3+}	1000	100	98	99
Ag^+	150	95	94	91
Mn^{2+}	600	99	95	93
SO_4^{2-}	600	99	95	93
Pb^{2+}	450	98	91	90
Co^{2+}	500	98	96	95
Cd^{2+}	350	99	93	91
Cl^-	400	97	92	90

[a] All S.D.s are between 1% and 2.5%.

Table 3
Levels of analyte ions in soil, blood and vegetable samples ($n = 3$, pH 6)

	Added ($\mu g\,g^{-1}$)	Blood			Soil			lotus (tree)		
		Found ($\mu g\,g^{-1}$)	R.S.D. (%)	Recovery (%)	Found ($\mu g\,g^{-1}$)	R.S.D. (%)	Recovery (%)	Found ($\mu g\,g^{-1}$)	R.S.D. (%)	Recovery (%)
Fe	0.0	0.492	1.0	–	0.175	1.2	–	0.245	1.3	–
	0.2	0.697	0.8	102.5	0.384	1.0	104.5	0.450	0.9	102.5
Cu	0.0	0.168	1.3	–	0.209	1.1	–	0.265	1.4	–
	0.2	0.376	0.9	104.0	0.415	0.9	103.0	0.473	1.0	104.0
Zn	0.0	0.146	1.3	–	0.154	1.1	–	0.148	1.4	–
	0.2	0.351	0.9	102.5	0.358	0.9	102.0	0.355	1.0	103.5

imental conditions. The detection limits based on three times the standard deviations of the blank ($n = 5$, $XL = Xb + 3s$, where XL is the limit of detection and Xb is the blank value) for Fe^{3+}, Cu^{2+} and Zn^{2+} were found to be 0.95, 1.58 and 1.23 $\mu g\,L^{-1}$, respectively.

3.11. Applications

We have explored the feasibility of the methodology given in Section 2 using preconcentration with Triton X-100-coated PVC for the determination of Cu^{2+}, Zn^{2+} and Fe^{3+} 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 3 for blood, soil and lotus tree samples and in Table 4 for river water and orange juice. The recovery of spiked samples is satisfactorily reasonable and was confirmed using addition method, which indicates the capability of the system in the determination of Cu^{2+}, Zn^{2+} and Fe^{3+}. 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 presented procedure and its independence from the matrix effects.

Table 4
Recovery of trace elements from spiked environmental samples after application of presented procedure ($n = 3$, pH 6)

Ion	Added ($\mu g\,mL^{-1}$)	Found ($\mu g\,mL^{-1}$)	R.S.D. (%)	Recovery (%)
River water				
Fe	0	0.089	1.4	–
	0.2	0.295	0.9	103.0
Cu	0	0.079	1.3	–
	0.2	0.283	0.9	102.0
Zn	0	0.046	1.3	–
	0.2	0.249	0.9	101.5
Orange juice				
Cu	0	0.162	1.0	–
	0.2	0.368	0.8	103.0
Zn	0	0.294	1.0	–
	0.2	0.501	0.8	103.5
Fe	0.0	0.678	0.8	–
	0.2	0.883	0.6	102.5

4. Conclusions

The method is relatively rapid as compared with previously reported solid phase extraction procedures for the enrichment of metal ions at trace levels. The presented procedure was successfully applied to analyte ion contents of various environmental samples including natural waters. The recoveries of analytes from the model solutions including diver ions up to the high tolerance limit were almost quantitative (>95%). The detection limits of analyte ions investigated are superior to those of preconcentration techniques for analyses [34–42]. The good features of the proposed 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 in real samples.

References

[1] H.C. Sorkun, F. Bir, M. Akbulut, U. Divrikli, G. Erken, H. Demirhan, E. Duzcan, L. Elci, I. Celik, U. Yozgatlı, The effects of air pollution and smoking on placental cadmium, zinc concentration and metallothionein expression, Toxicology 238 (2007) 15–22.

[2] A. Sarı, M. Tuzen, D. Çıtak, M. Soylak, Equilibrium, kinetic and thermodynamic studies of adsorption of Pb(II) from aqueous solution onto Turkish kaolinite clay, J. Hazard. Mater. 149 (2007) 283–291.

[3] J.A. Puszynski, C.J. Buhan, J.J. Swiatkiewicz, Processing and ignition characteristics of aluminium–bismuth trioxide nanothermite system, J. Propul. Power 23 (2007) 698–706.

[4] S. Saracoglu, K.O. Saygı, O.D. Uluozlu, M. Tuzen, M. Soylak, Determination of trace element contents of baby foods from Turkey, Food Chem. 105 (2007) 280–285.

[5] M.M. Al-Taee, A.N. Al-Khateeb, F.H. Hussein, F.M. Abid, Evaluation of soluble non-essential trace metals in Shatt Al-Hilla, Iraq, Asian J. Chem. 19 (2007) 741–750.

[6] M. Maroulis, A. Economou, A. Voulgaropoulos, Determination of Cd and Pb in phosphorites and phosphate fertilizers by means of a portable voltammetric analyzer based on "virtual instrumentation", Electroanalysis 19 (2007) 2149–2154.

[7] S. Dejmanee, A. Chooyimpanit, Novel procedure for detection of some heavy metal ions in shrimp pond by liquid phase extraction with sodium acetate, Walailak J. Sci. Technol. 3 (2006) 219–236.

[8] L. Morales, M.I. Toral, M.J. Alvarez, A new Cu(II)-5-(4-sulphophenylazo)-8-aminoquinoline complex used for copper determination in presence of gold and silver in water and mineral samples, Talanta 74 (2007) 110–118.

[9] C.E. Dogan, G. Akcin, Solid phase extraction and determination of lead in water samples using silica gel homogeneously modified by thiosalicylic acid, Anal. Lett. 40 (2007) 2524–2543.

[10] L. Kékedy-Nagy, J. Szocs-Balázs, Determination of cadmium in environmental samples using the methane–air flame atomic absorption spectrometry, Studia Universitatis Babes-Bolyai, Chem. LII 2 (2007) 93–101.

[11] M. Soylak, U. Divrikli, M. Dogan, Column separation and enrichment of trace amounts of Cu, Ni and Fe on XAD-16 resin in industrial fertilisers after complexation with 4-(2-thiazolylazo) resorcinol, J. Trace Microprobe Tech. 15 (1997) 197–204.

[12] M. Ghaedi, M.R. Fathi, F. Marahel, F. Ahmadi, Simultaneous preconcentration and determination of copper, nickel, cobalt, and lead ions content by flame atomic absorption spectrometry, Fresen. Environ. Bull. 14 (2005) 1158–1166.

[13] A.R. Rod, S. Borhani, F. Shemirani, Cloud point preconcentration and flame atomic absorption spectrometry: application to the determination of manganese in milk and water samples, Eur. Food Res. Technol. 223 (2006) 649–653.

[14] A.A. Ismail, A selective optical sensor for antimony based on hexagonal mesoporous structures, J. Colloid Interf. Sci. 317 (2008) 288–297.

[15] P. Liu, Q.S. Pu, Z.X. Su, Synthesis of silica gel immobilized thiourea and its application to the on-line preconcentration and separation of silver, gold and palladium, Analyst 125 (1999) 147–150.

[16] M.S. Hosseini, R. Hassan-Abadi, Flotation separation and flame atomic absorption spectrometric determination of trace amount of lead in some environmental samples, Ann. Chim. 97 (2007) 1269–1278.

[17] M. Soylak, Determination of trace amounts of copper in metallic aluminium samples after separation and preconcentration on an activated carbon column, Fresen. Environ. Bull. 7 (1998) 383–387.

[18] H. Serencam, A. Gundogdu, Y. Uygur, B. Kemer, V.N. Bulut, C. Duran, M. Soylak, M. Tufekci, Removal of cadmium from aqueous solution by Nordmann fir (*Abies nordmanniana* (Stev.) Spach. Subsp. nordmanniana) leaves, Bioresource Technol. 99 (2008) 1992–2000.

[19] O. Dalman, V.N. Bulut, I. Degirmencioglu, M. Tufekci, Preconcentration of trace elements on amberlite XAD-4 resin functionalised with 1,2-bis(*o*-aminophenylthio) ethane and their determination by FAAS in environmental samples, Turk. J. Chem. 31 (2007) 631–646.

[20] M. Sarkar, M. Das, P.K. Datta, Solid-phase extraction for the decontamination of alkali metal, alkaline earth metal, and ammonium salts from heavy metal ions, J. Colloid Interf. Sci. 246 (2002) 263–269.

[21] K. Niknam, A. Fatehi-aviz, Synthesis of 2-substituted benzimidazoles and bis-benzimidazoles by microwave in the presence of alumina–methanesulfonic acid, J. Iran Chem. Soc. 4 (2007) 438–443.

[22] S.P. Fili, E Oliveira, V. Pedro, Oliveira, On-line digestion in a focused microwave-assisted oven for elements determination in orange juice by inductively coupled plasma optical emission spectrometry, J. Braz. Chem. Soc. 14 (2003) 435–441.

[23] M. Ghaedi, Selective and sensitized spectrophotometric determination of trace amounts of Ni(II) ion using α-benzyl dioxime in surfactant media, Spectrochim. Acta 66A (2007) 295–300.

[24] M. Ghaedi, F. Ahmadi, M. Soylak, Simultaneous preconcentration of copper, nickel, cobalt and lead ions prior to their flame atomic absorption spectrometric determination, Ann. Chim. 97 (2007) 277–285.

[25] M. Ghaedi, F. Ahmadi, A. Shokrollahi, Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry, J. Hazard. Mater. 142 (2007) 272.

[26] M. Ghaedi, M. Montazerozohori, M. Soylak, Solid phase extraction method for selective determination of Pb(II) in water samples using 4-(4-methoxybenzylidenimine) thiophenole, J. Hazard. Mater. 142 (2007) 368–373.

[27] S.K. Raju, M.S. Subramanian, A novel solid phase extraction method for separation of actinides and lanthanides from high acidic streams, Separ. Purif. Technol. 55 (2007) 16–22.

[28] H.B. Senturk, A. Gundogdu, V.N. Bulut, C. Duran, M. Soylak, L. Elci, M. Tufekci, Separation and enrichment of gold(III) from environmental samples prior to its flame atomic absorption spectrometric determination, J. Hazard. Mater. 149 (2007) 317–323.

[29] J. Muñoz, M. Gallego, M. Valcárcel, Speciation of copper by using a new fullerene derivative as a mixed-mode sorbent, J. Anal. At. Spectrom. 21 (2006) 1396–1402.

[30] U. Divrikli, A. Akdoğan, M. Soylak, L. Elçi, Solid phase extraction of Fe(III), Pb(II) and Cr(III) in environmental samples on amberlite XAD-7 and their flame atomic absorption spectrometric determinations, J. Hazard. Mater. 149 (2007) 331–337.

[31] M. Soylak, N.D. Erdogan, L. Elci, Membrane filtration of Fe(III), Cu(II) and Pb(II) ions as 1-(2-pyridylazo) 2-naphtol (PAN) for their preconcentration and atomic absorption determinations, J. Chin. Chem. Soc. 51 (2004) 703–706.

[32] K. Oshita, O. Noguchi, M. Oshima, S. Motomizu, Synthesis of cross-linked chitosan modified with the glycine moiety for the collection/concentration of bismuth in aquatic samples for ICP-MS determination, Anal. Sci. 23 (2007) 1203–1208.

[33] L.C.F.N. De Assumpcao, E.T. Da Silva, N.R.M.P. De Aquiar, A.W.S. Guarino, Characterizations of Brazilian commercial clays and application in the removal of Cu^{2+} from aqueous solutions, Tche Quimica 4 (2007) 5–10.

[34] S.J. Shahtaheri, M. Khadem, F. Golbabaei, A. Rahimi-Froushani, Solid phase extraction for monitoring of occupational exposure to Cr(III), Anal. Chem. Insights 2 (2007) 125–132.

[35] A. Baysal, N. Tokman, S. Akman, The use of solid-phase extraction and direct injection of a copolymer sorbent as slurry into the graphite furnace prior to determination of cadmium by ETAAS, Int. J. Environ. Anal. Chem. 88 (2008) 141–150.

[36] V.G. Cortés, Sequential injection analysis using second-order calibration for the development of analytical methods, Ph.D. Thesis, The Rovira i Virgili University, Tarragona, 2007.

[37] F.A. Aydın, M. Soylak, A novel multi-element coprecipitation technique for separation and enrichment of metal ions in environmental samples, Talanta 73 (2007) 134–141.

[38] M.R. Jamali, Y. Assadi, F. Shemirani, Homogeneous liquid–liquid extraction and determination of cobalt, copper, and nickel in water samples by flame atomic absorption spectrometry, Separ. Sci. Technol. 42 (2007) 3503–3515.

[39] M.S. Hosseini, M. Hosseini, A.H. Bandeh-Gharaei, Solvent impregnated resins containing quinizarin: preparation and application to batch-mode separation of Cd(II), Cu(II), Ni(II), and Zn(II) in aqueous media prior to the determination by flame atomic absorption spectrometry, Separ. Sci. Technol. 42 (2007) 3465–3480.

[40] A.R. Turker, New sorbents for solid-phase extraction for metal enrichment, Clean 35 (2007) 548–557.

[41] L. Elci, M. Soylak, B. Ozcan, Coprecipitation of Cu(II), Ni(II), Fe(III), Cd(II), Pb(II) and Co(II) in wastewater, sediment and metallic zinc samples with HMDTC-HMA for flame atomic absorption spectrometric determination, Anal. Lett. 36 (2003) 987–999.

[42] M. Soylak, Solid phase extraction of Cu(II), Pb(II), Fe(III), Co(II) and Cr(III) on Chelex 100 column prior to their flame atomic absorption spectrometric determinations, Anal. Lett. 37 (2004) 1203–1217.