Flame atomic absorption spectrometric determination of trace amounts of heavy metal ions after solid phase extraction using modified sodium dodecyl sulfate coated on alumina

Mehrorang Ghaedi [a],*, Khodabakhsh Niknam [b], Ardeshir Shokrollahi [a], Ebrahim Niknam [a], Hamid Reza Rajabi [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 sensitive and selective solid phase extraction procedure for the determination of traces of Cu(II), Zn(II), Pb(II) and Fe(III) has been developed. An alumina-sodium dodecyl sulfate (SDS) coated on with meso-phenyl bis(indolyl) methane (MPBIM) was used for preconcentration and determination of Cu(II), Zn(II), Pb(II) and Fe(III) ions by flame atomic absorption spectrometry. The analyte ions were adsorbed quantitatively on adsorbent due to their complexation with MPBIM. Adsorbed metals were quantitatively eluted using 6 mL of 4 mol L^{-1} nitric acid. The effects of parameters such as pH, amount of alumina, amount of MBITP, flow rate, type and concentration of eluting agent were examined. The effects of interfering ions on the separation-preconcentration of analytes were also investigated. The relative standard deviation of the method was found to be less than 3.0%. The presented procedure was successfully applied for determination of analytes in real samples.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Surfactant coated on alumina; Atomic absorption spectrometry; Solid phase extraction; Trace metal enrichment; Environmental samples

1. Introduction

The roles of transition elements at trace level in human body are an important search subject of analytical chemists [1–3]. The line between the quantity being indispensable and harmful is very limited. The establishment of a level of metal ions at trace levels in food and water is difficult [4–7]. Heavy metal ions should be accurately evaluated in order to prevent the occurrence of harmful effects. The cycle of trace metal ions from environment to human is also an important part of environmental studies [8–11].

Flame atomic absorption spectrometric analysis of heavy metal ions in real samples is directly difficult, because of complex formation and significant matrices [12–15]. In addition, some metals have low concentrations, which are near or below the limit of detection of the instrument [16–19]. Separation-preconcentration step improves the analytical detection limit, increases the sensitivity by several orders of magnitude, enhances the accuracy of the results and facilitate the calibration. Various separation-preconcentration techniques like solvent extraction [20], electro-deposition [21], coprecipitation [22], cloud point extraction [23], membrane filtration [24] and solid phase extraction [25,26] are used for that purpose. Solid phase extraction is preferred by many researchers on account of the fast, simple and higher preconcentration factor, rapid phase separation, time and cost saving [27,28].

A number of supports have been widely used for the preconcentration and separation of trace metal ions from various matrices. The most prominent among the supports used are activated carbon, [29], SDS coated on alumina [30], modified chromosorb [31]. Among these adsorbents, alumina is an important place in the solid phase extraction studies of heavy metal ions [32–36]. A new modification mode for the alumina to use in solid phase extraction works was introduced by Hiraide et al. [37]. The organic reagent is incorporated in the cores of ad-micelles of sodium dodecyl sulfate attached to alumina surfaces.

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

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

Analyte	Wavelength (nm)	Slit width (nm)	Lamb current (mA)
Zn	213.9	0.2	5.0
Fe	248.3	0.5	5.0
Cu	324.8	0.5	3.0
Pb	283.3	1.0	5.2

New organic reagents are immobilized on surfactant coated on alumina for separation and enrichment of different metal ions [38–40], and recently polyaromatic hydrocarbon as well [41].

The purpose of this work is to investigate the feasibility of absorption of these ions including copper(II), iron(III), lead(II) and zinc(II) ions on SDS coated on alumina modified with MPBIM. The parameters including pH of sample, amount of ligand and solid phase, type of eluting agent and flow rate were 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, which are given in Table 1. 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

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Double deionized water was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute HNO_3 $(1+9)$ and were rinsed with distilled water prior to use. The element standard solutions used for calibration were produced by diluting a stock solution of $1000\,mg\,L^{-1}$ of the given element supplied by Merck. Stock solutions of diverse elements were prepared from high purity compounds.

The ligand meso-phenyl bis(indolyl) methane (MPBIM) (Scheme 1) was synthesized according to literature [42]. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to preparing the desired pH solution.

2.3. Preparation of MPBIM coated on alumina

About 50 mg of sodium dodecyl sulfate (SDS) and 20 mg of MPBIM were added to 40 mL of water solution containing 1 g alumina particles. The pH was adjusted to 7.0 with $2\,mol\,L^{-1}$ hydrochloric acid to form MBITP-impregnated ad-micelles on alumina particles while shaking the suspension with a stirrer. After mixing for 15 min, the supernatant solution was discar-
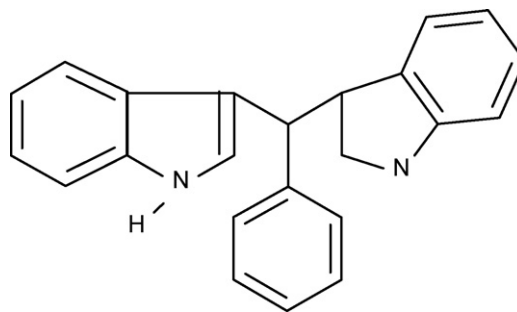
Scheme 1. Schematic diagram of MPBIM. Solid mp: 88–90 °C; ^{1}H NMR (200 MHz, $J=CDCl_3$): $\delta = 5.90$ (S, 1H, CH), 6.60 (d, 2H, $J=2.4\,Hz$), 7.05 (T, 2H, $J=8.2\,Hz$), 7.15 (t, 2 h, $j=8.2\,Hz$), 7.30 (m, 9H), 7.85 (brS, 2H, NH).

ded and the remaining was packed into a column. The column was washed by passing 5 mL of $2\,mol\,L^{-1}$ HNO_3, and then the column was neutralized with $0.01\,mol\,L^{-1}$ aqueous ammonia. On kept in a refrigerator the sorbent is stable at least for 1 week. The concentration of SDS was fixed below the critical micellization concentration (CMC) $(8 \times 10^{-3}\,M)$ of SDS (Scheme 1).

A 10 mL of $0.005\,mol\,L^{-1}$ NaOH solution containing 40 mg of MPBIM was added to 1 g of alumina and 50 mg of SDS 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 wavelengths (277 and 423 nm). The amount of MPBIM deposited on the SDS coated on alumina was estimated by spectrophotometric measurements from the residual amount of MPBIM in the solution. It was found that 96% of MPBIM was retained on the SDS coated on alumina.

2.4. Column preparation

A short glass column with an inner diameter of 50 mm and a length of 10 cm, equipped with porous frits, was filled up to a height of about 1.5 cm with a suspension of 1.09 g of SDS coated on alumina modified with MPBIM in water. SDS coated on alumina modified with MPBIM was preconditioned by the blank solution prior to each use. After each experiment, the column was rinsed with water and stored for the next experiment.

2.5. Test procedure

The pH of model solutions containing analytes was adjusted to pH 2–8 by dilute nitric acid or sodium hydroxide. The samples were passed through the column with the aid of a suction pump at a flow rate of $4\,mL\,min^{-1}$, to effect the deposition of analyte. The adsorbed ions were then eluted with 6 mL of $4\,mol\,L^{-1}$ nitric acid with a flow rate of $4\,mL\,min^{-1}$. The analyte concentrations in the eluent were determined by flame atomic absorption spectrometry.

2.6. Analysis of real samples

Water samples were collected from spring water Yasouj, Iran and Zohre River (Fahlian River), Iran; tap water and

wastewater are collected from Gachsaran, Iran. Before the analysis, the samples were filtered through a Millipore cellulose membrane filter of pore size 0.45 μm. The organic content of the water samples were oxidized in the presence of 1% H_2O_2 and addition of concentrated nitric acid. After acidification to 1% with concentrated nitric acid, they were stored in polyethylene bottles. For the preconcentration procedure, pH of the 800 mL of water samples was adjusted to 7 and the sample passed through the column at flow rate of 4 mL min^{-1}. The metals, which retained on modified SDS coated on alumina by complexation with MPBIM SDS coated on alumina, were eluted with 6 mL of 4 mol L^{-1} HNO$_3$. The effluent was sent to FAAS for evaluation of metal content.

Leaves of spinach were purchased from Gachsaran, Iran. Afterwards, they dried and were taken in small mesh. A 40 g leaves of spinach was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 °C. The residue was cooled, gain kept in furnace for 2 h at the same temperature, to decompose organic matter completely. The final residue was treated with 3 mL concentrated hydrochloric acid and 2–4 mL 70% perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at 7 made up to 250 mL by addition of diluted KOH solution. Then procedure in Section 2.6 was applied.

Twenty grams of homogenized soil sample or 20 mL of blood sample was weighed accurately and in a 200 mL beaker was digested with addition of 10 mL concentrated HNO$_3$ and 2 mL HClO$_4$ 70% was added and heated for 1 h, following the method recommended in our previous publication [27,28,43,44]. The content of beaker was filtered through a Whatman No. 40 filter paper into a 250 mL calibrated flask and its pH was adjusted to desired value and diluted to mark with de-ionized water. Then the procedure given in Section 2.6 was performed.

3. Results and discussion

In 1994, Hiraide el al. [43] proposed that water-insoluble organic ligand could be trapped into the aggregate of sodium dodecyl sulfate (SDS) on alumina particles. In the preliminary studies it was found that when 20 mg of MPBIM is mixed with SDS coated on alumina particles, the ligand is trapped homogenously on the hemi-micelles or ad-micelles formed by SDS on alumina surface in a manner similar to that demonstrated for the other organic ligands [43–48] and the color of alumina was changed from white to yellow.

3.1. Influences of pH

pH is the main investigated factor for the all extraction studies [49–55]. The effect of pH on the preconcentration of metal ions on SDS coated on alumina modified with MPBIM was studied by determination of individual elements. Fifty micrograms of each element were preconcentrated in the pH range of 2.0–8.0
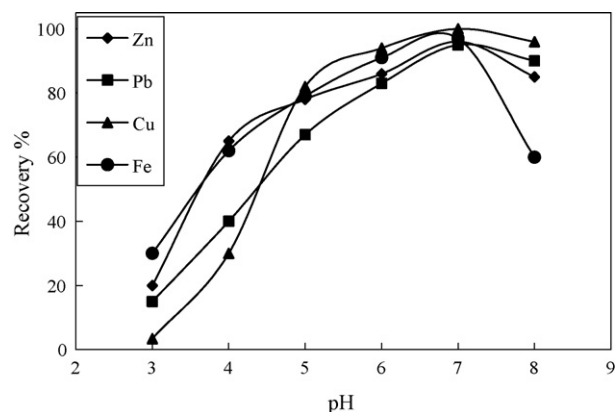

Fig. 1. Effect of pH on analyte ions recovery ($N = 3$).

by introducing 40 mg of MPBIM on the solid phase composites of 50 mg SDS and 1 g Al$_2$O$_3$. The results were shown in Fig. 1. The analyte ions could be retained quantitatively by the solid phase at the pH 7.0. So the pH 7.0 ± 0.1 has been selected for the determination of metals content.

3.2. Effects of amounts of MPBIM

To investigate the optimum amount of MPBIM on the quantitative extraction of understudy metals ions by the SDS coated on alumina, these ions extraction was conducted by varying the amount of MPBIM from 10 to 60 mg. The results are shown in Fig. 2 with increasing amount of MPBIM up to 40 mg an increase in recoveries can be achieved and further increase does not mentionable change in efficiency. Quantitative recoveries for the analytes were obtained after 40 mg of MPBIM. Subsequent studies for further experiments were carried out with 40 mg of MPBIM.

3.3. Amount of SDS

The influence of amounts of SDS on the recoveries of the analyte ions was investigated. The results obtained are presented in Table 2 and Fig. 3. In the absence of SDS, ions were not retained on SDS-alumina. Therefore, addition of SDS is
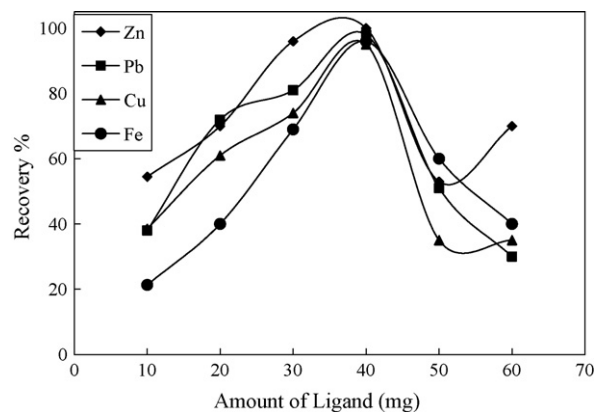

Fig. 2. Effect of amount of MPBIM on analyte ions recovery ($N = 3$).

Table 2
Effect of solid phase ingredient on ions recovery ($N = 3$)

Sample	Recovery (%)			
	Zn(II)	Pb(II)	Cu(II)	Fe(III)
Al_2O_3 (1 g), SDS (50 mg), without MPBIM	55 ± 2	36 ± 2	27 ± 2	24 ± 2
Al_2O_3 (1 g), MPBIM (40 mg), without SDS	30 ± 2	30 ± 2	28 ± 2	36 ± 2
Al_2O_3 (0.1 g), MPBIM (40 mg), SDS (5 mg)	50 ± 1	38 ± 2	37 ± 2	32 ± 2
Al_2O_3 (0.3 g), MPBIM (40 mg), SDS (15 mg)	91 ± 1	86 ± 1	82 ± 1	79 ± 1
Al_2O_3 (1 g), MPBIM (40 mg), SDS (50 mg)	100 ± 1	98 ± 1	97 ± 1	96 ± 1
Al_2O_3 (0.6 g), MPBIM (40 mg), SDS (50 mg)	90 ± 1	86 ± 1	79 ± 1	83 ± 1
Al_2O_3 (0.8 g), MPBIM (40 mg), SDS (50 mg)	93 ± 1	92 ± 1	93 ± 1	91 ± 1
Al_2O_3 (1.2 g), MPBIM (40 mg), SDS (50 mg)	92 ± 1	90 ± 1	89 ± 1	88 ± 1

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 $50 \, mg \, g^{-1}$ alumina, a decrease in the percentage of ions retained was observed as a result of the formation of micelles.

3.4. Effects of amounts of alumina

The influences of the amounts of alumina filled to the column were also investigated. The results display that up to 1.0 g of alumina efficiency of extractions increase and further addition has not significant effect on recoveries. The effect of the amount of alumina on the sorption of metal ions at pH 7.0 was examined in the range of 0.1–1.2 g. Quantitative recoveries (>95%) of lead(II), iron(III), copper(II) and zinc(II) ions were observed in the range of 0.9–1.0 g. The recoveries of analytes above 1.0 g of alumina were below 95% with 6 mL of the eluent. In the proposed procedure, 1.0 g of alumina is recommended.

3.5. Eluent type

A satisfactory eluent should effectively elute the sorbed analytes with small volume, which is needed for a high enrichment factor, and should not affect the accurate determination of the analytes and destroy life time and reusability of solid phase. For this reason, different solutions were attempted to be used

as the eluent. The respective results are presented in Table 3. As a result, 6.0 mL of $4.0 \, mol \, L^{-1}$ HNO_3 was sufficient for quantitative elution, and a good elution curve could be gained.

3.6. Effect of flow rate of sample and eluent solutions

The rate of the flow of model solutions through the column is one of the factors affecting the duration of the determination and directly related to the contact of the solution with the solid phase thereby providing information about the adsorption rate of the complexes on the solid phase. The model solutions of 250 mL were passed through the column with rates in the range of $1–6 \, mL \, min^{-1}$. It was observed that the recovery was not changed significantly up to $4.0 \, mL \, min^{-1}$ which was selected for further experiments. The flow rates of eluent solution were investigated in the range of $4.0 \, mL \, min^{-1}$. After $4.0 \, mL \, min^{-1}$ of eluent solution, the recovery values of the analytes were not quantitative. For the all experiments, $4 \, mL \, min^{-1}$ was selected as eluent flow rate.

3.7. Sample volume

Due to low concentration of heavy metals, preconcentrations have been done on large volume of real samples. Hence,
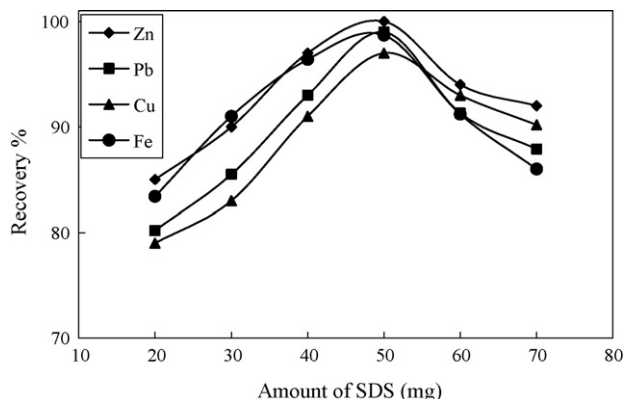

Fig. 3. Effect of SDS amount on analyte ions recovery ($N = 3$).

Table 3
Effect of type and concentration of eluting agent on recovery of analytes ($N = 3$)

Eluent	Recovery (%)			
	Zn(II)	Pb(II)	Cu(II)	Fe(III)
$4 \, mol \, L^{-1}$ H_3PO_4	20 ± 2	38 ± 2	10 ± 3	22 ± 3
$4 \, mol \, L^{-1}$ HCl	102 ± 1	85 ± 2	50 ± 2	54 ± 2
$4 \, mol \, L^{-1}$ H_2SO_4	4 ± 2	13 ± 2	2 ± 2	60 ± 2
$4 \, mol \, L^{-1}$ CH_3COOH	38 ± 2	5 ± 3	11 ± 3	60 ± 2
$1 \, mol \, L^{-1}$ HNO_3	32 ± 2	58 ± 2	27 ± 2	4 ± 2
$2 \, mol \, L^{-1}$ HNO_3	80 ± 2	62 ± 2	41 ± 2	52 ± 2
$3 \, mol \, L^{-1}$ HNO_3	96 ± 1	91 ± 1	86 ± 1	88 ± 1
$4 \, mol \, L^{-1}$ HNO_3	98 ± 1	98 ± 1	98 ± 1	96 ± 1
$5 \, mol \, L^{-1}$ HNO_3	83 ± 2	87 ± 2	80 ± 1	84 ± 1
$6 \, mol \, L^{-1}$ HNO_3	71 ± 2	67 ± 2	59 ± 2	68 ± 2
2 mL of $4 \, mol \, L^{-1}$ HNO_3	70 ± 2	66 ± 2	52 ± 2	60 ± 2
4 mL of $4 \, mol \, L^{-1}$ HNO_3	87 ± 2	82 ± 2	76 ± 2	82 ± 2
6 mL of $4 \, mol \, L^{-1}$ HNO_3	97 ± 1	98 ± 1	98 ± 1	96 ± 1
8 mL of $4 \, mol \, L^{-1}$ HNO_3	97 ± 1	98 ± 1	97 ± 1	95 ± 1

Table 4
Effects of the matrix ions on the recoveries of the examined metal ions ($N = 3$)

Interfering ions	Interfering ion/analyte fold ratio	Recovery (%)			
		Pb(II)	Cu(II)	Zn(II)	Fe(III)
Na$^+$	800	98 ± 2	97 ± 1	100 ± 1	93 ± 2
K$^+$	800	98 ± 1	96 ± 1	98 ± 2	95 ± 1
Li$^+$	800	97 ± 1	94 ± 2	99 ± 1	93 ± 2
Ba^{2+}	1000	98 ± 1	95 ± 1	101 ± 1	97 ± 2
Mg^{2+}	1000	97 ± 1	94 ± 2	98 ± 1	96 ± 1
Ca^{2+}	1000	97 ± 1	95 ± 1	99 ± 1	97 ± 1
Co^{2+}	500	96 ± 1	93 ± 2	98 ± 1	94 ± 2
Ni^{2+}	600	96 ± 1	94 ± 1	99 ± 1	97 ± 1
Mn^{2+}	600	95 ± 1	95 ± 1	98 ± 1	95 ± 1
Cd^{2+}	600	96 ± 1	94 ± 1	97 ± 1	96 ± 1
Hg^{2+}	150	96 ± 1	94 ± 1	97 ± 1	95 ± 1
Cl$^-$	300	97 ± 2	95 ± 2	97 ± 1	95 ± 1
Ti^{3+}	1000	98 ± 1	97 ± 2	98 ± 1	98 ± 3
Ag$^+$	750	97 ± 1	96 ± 1	99 ± 1	96 ± 2

Table 5
Specification of presented method at optimum conditions for each element

Parameters	Fe(III)	Cu(II)	Zn(II)	Pb(II)
Linear range (μg mL^{-1})	0.01–0.85	0.01–0.87	0.01–0.92	0.02–0.8
Detection limit (ng mL^{-1})	0.68	0.77	0.69	0.75
Loading capacity (mg g^{-1})	6.3	6.6	6.3	6.4
R.S.D. (%)	2.1	2.2	2.7	1.9
Recovery (%)	97.5	95.7	98.5	95.7

6.0 mL, therefore the preconcentration factors were 292 for the analytes.

3.8. Matrix effects

The influences of possible matrix ions in the environmental samples and some transition metals were also examined. The results were summarized in Table 4. The tolerated amounts of each ion were the concentration values tested that caused error less than 5% of the recovery alteration. The ions normally present in water do not interfere under the experimental conditions used. Also, some of the transition metals at mg L^{-1} levels were not interfered on the recoveries of the analyte ions. The matrix metal ions were not retained on the SDS coated on alumina because of their very low stability constants of complexes.

3.9. Analytical features

Adsorption capacity is an important factor to evaluate the sorbent, because it determines how much modified SDS coated on alumina is required to a given solution. The adsorption capacity of the modified SDS coated on alumina was studied and respective adsorption capacity calculated for Cu(II), Zn(II), Fe(III) and Pb(II) were presented in Table 5.

The precision studies were carried out at 0.2 μg mL^{-1} level of metal ions by carrying out five separate determinations using the above-mentioned procedure. The sample volume was maintained at 250 mL. The relative standard deviation of the method
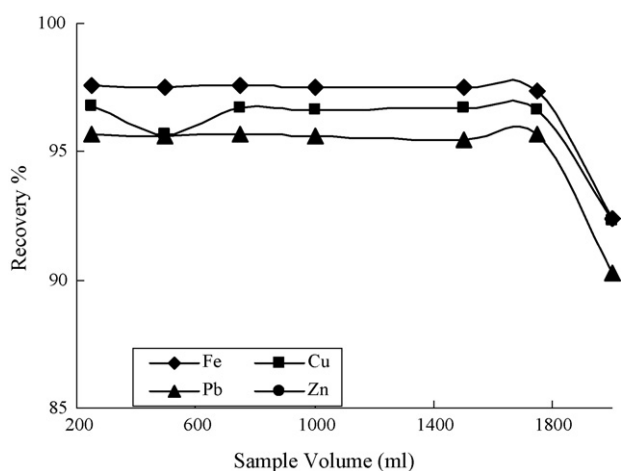

Fig. 4. Effect of sample volume on analytes recovery ($N = 3$).

the maximum sample volume was optimized by the investigation of the recovery of trace metals in various sample volumes in the range of 250–2000 mL. The results were given in Fig. 4. The recoveries of the analyte ions were quantitative until 1750 mL. In this study, the final solution volume was

Table 6
Levels of analyte ions in soil, blood and spinach samples ($N = 3$)

Ion	Added (μg g^{-1})	Blood sample			Soil sample			Spinach sample			
		Found (μg g^{-1})	R.S.D. (%)	Recovery (%)	Added (μg g^{-1})	Found (μg g^{-1})	R.S.D. (%)	Recovery (%)	Added (μg g^{-1})	Found (μg g^{-1})	R.S.D. (%)
Fe(III)	0.0	0.490	1.6	–	0.0	0.184	1.4	–	0.0	0.341	1.6
	0.1	0.594	1.0	104.0	0.1	0.286	1.0	102.0	0.1	0.445	1.1
Cu(II)	0.0	0.151	1.4	–	0.0	0.189	1.4	–	0.0	0.282	1.5
	0.1	0.254	1.0	103.0	0.1	0.292	1.0	103.0	0.1	0.386	1.0
Pb(II)	0.0	0.102	1.5	–	0.0	0.142	1.4	–	0.0	0.158	1.4
	0.1	0.200	1.1	98.0	0.1	0.245	0.9	103.0	0.1	0.260	1.0
Zn(II)	0.0	0.156	1.5	–	0.0	0.143	1.2	–	0.0	0.153	1.4
	0.1	0.260	1.0	104.0	0.1	0.248	0.9	105.0	0.1	0.256	1.0

Table 7
Recovery of trace elements from spiked environmental samples after application of presented procedure

Ion	Added (μg L^{-1})	Found (μg L^{-1})	R.S.D. (%)	Recovery (%)
River water				
Zn(II)	0	49.7	1.4	–
	75	127.2	0.9	103.3
Pb(II)	0	52.3	1.3	–
	75	128.9	1.0	103.2
Cu(II)	0	46.3	1.2	–
	75	124.1	0.9	103.7
Fe(III)	0	89.9	1.2	–
	75	167.3	0.8	103.2
Waste water				
Zn(II)	0	98.4	1.2	–
	100	202.1	0.8	103.7
Pb(II)	0	68.2	0.8	–
	100	170.3	0.9	102.1
Cu(II)	0	98.8	1.1	–
	100	201.7	0.8	102.9
Fe(III)	0	105.8	1.1	–
	100	208.3	0.9	102.5

was found to be less than 3.0%. The specifications of method are presented in Table 5.

The limit of detection LOD of the proposed method for the determination of ions was studied under the optimal experimental conditions. The detection limits were expressed as the amount of analyte in ng mL^{-1} giving a signal to noise ratio of 3. The LOD obtained from $C = K_b S_b \, m^{-1}$ for a numerical factor of $K_b = 3$ (Table 5).

3.10. Applications

The reliability of the presented method was checked by spiking experiments and independent analysis. The results for this study are presented in Tables 6 and 7 for environmental (soil and natural water) and biological samples (blood and spinach). 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 ions. 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 procedure and its independence from the matrix effects.

4. Conclusions

In the presented study, a new simple and low cost and environmentally friendship solid phase extraction technique was developed based on the preconcentration of copper(II), iron(III), zinc(II) and lead(II) in environmental samples on SDS coated on alumina prior to the determination by FAAS. The determination of analyte ions yields quantitative recoveries. SDS coated on alumina can be used as high as greater

than 20 experiments without any loss in its sorption behavior. The system was successful in preconcentration of analytes from large sample volume (1750 mL). The high enrichment factor and good figures of merit for method could be achieved.

References

[1] K. Pyrzynska, Application of carbon sorbents for the concentration and separation of metal ions, Anal. Sci. 23 (2007) 631–637.
[2] M. Duran, Y. Kara, G.K. Akyildiz, A. Ozdemir, Antimony and heavy metals accumulation in some macroinvertebrates in the Yesilirmak River (N Turkey) near the Sb-mining area, Bull. Environ. Contam. Toxicol. 78 (2007) 395–399.
[3] K. Szentmihalyi, M. Then, Examination of microelements in medicinal plants of the carpathian basin, Acta Aliment. 36 (2007) 231–236.
[4] O. Akoto, J. Adiyiah, Chemical analysis of drinking water from some communities in the Brong Ahafo region, Int. J. Environ. Sci. Technol. 4 (2007) 211–214.
[5] A.R. Kumar, P. Riyazuddin, Non-chromatographic hydride generation atomic spectrometric techniques for the speciation analysis of arsenic, antimony, selenium, and tellurium in water samples-a review, Int. J. Environ. Anal. Chem. 87 (2007) 469–500.
[6] K. Pyrzynska, K. Kilian, On-line sorption-based systems for determination of cadmium with atomic spectrometry detectors, Water Res. 41 (2007) 2839–2851.
[7] F. Duman, Sapanca ve Abant Gölü Su, Sediment ve Sucul Bitki Örneklerinde Ağir Metal Konsantrasyonlarinin Karşilaştirmali Olarak İncelenmesi, Ph.D thesis. Ankara University (2005).
[8] M.K. Jamali, T.G. Kazi, H.I. Afridi, M.B. Arain, N. Jalbani, A.R. Memon, Speciation of heavy metals in untreated domestic wastewater sludge by time saving BCR sequential extraction method, J. Environ. Sci. Health 42A (2007) 649–659.
[9] H.I. Afridi, T.G. Kazi, M.B. Arain, M.K. Jamali, G.H. Kazi, N. Jalbani, Determination of cadmium and lead in biological samples by three ultrasonic-based samples treatment procedures followed by electrothermal atomic absorption spectrometry, J. AOAC Int. 90 (2007) 470–478.
[10] A. Ramesh, K.R. Mohan, K. Seshaiah, N.D. Jegakumar, Determination of trace elements by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after preconcentration on a support impregnated with piperidine dithiocarbamate, Anal. Lett. 34 (2001) 219–229.
[11] D.Y. Sarica, A.R. Türker, Method validation for the determination of lead in raw cow's milk by electrothermal atomic absorption spectrometry, Ann. Chim. 97 (2007) 983–993.
[12] A. Tumuklu, M.G. Yalcin, M. Sonmez, Detection of heavy metal concentrations in soil caused by Nigde city garbage dump, Pol. J. Environ. Stud. 16 (2007) 651–658.
[13] Q.M. Li, R.Z. Ouyang, G.F. Zhu, G.G. Liu, Preconcentration by using microcrystalline phenolphthalein for determining trace molybdenum(VI) in water by GFAAS, Chem. Res. Chin. Univ. 21 (2005) 622–625.
[14] M. Saqib, M. Jaffar, M.H. Shah, Comparative high volume and-scrubbiug-based estimation of aerosol lead, J. Chem. Soc. Pak. 29 (2007) 125–130.
[15] M. Soylak, L. Elci, M. Dogan, Solid phase extraction of trace metal ions with Amberlite XAD resins prior to atomic absorption spectrometric analysis, J. Trace Microprobe Tech. 19 (2001) 329–344.
[16] A.K. Das, R. Chakraborty, M.L. Cervera, M. de la Guardia, Analytical techniques for the determination of bismuth in solid environmental samples, Trends Anal. Chem. 25 (2006) 599–608.
[17] N. Rajesh, S. Manikandan, Spectrophotometric determination of lead after preconcentration of its diphenylthiocarbazone complex on an Amberlite XAD-1180 column, Spectrochimica Acta Part A (in press).
[18] K. Prasad, P. Gopikrishna, R. Kala, T.P. Rao, G.R.K. Naidu, Solid phase extraction vis-a-vis coprecipitation preconcentration of cadmium and lead from soils onto 5,7-dibromoquinoline-8-ol embedded benzophenone and determination by FAAS, Talanta 69 (2006) 938–945.

[19] 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.

[20] L.H.J. Lajunen, A. Kubin, Determination of trace amounts of molybdenum in plant tissue by solvent extraction-atomic-absorption and direct-current plasma emission spectrometry, Talanta 33 (1998) 265–270.

[21] Z. Čánský, P. Rychlovský, Z. Petrová, J.P. Matousek, A technique coupling the analyte electrodeposition followed by in-situ stripping with electrothermal atomic absorption spectrometry for analysis of samples with high NaCl contents, Spectrochim. Acta 62B (2007) 250–257.

[22] S. Saracoglu, M. Soylak, L. Elci, Enrichment and separation of traces of cadmium, chromium, lead and manganese ions in urine by using magnesium hydroxide coprecipitation method, Trace Elem. Electrolytes 18 (2001) 129–133.

[23] Y. Ebihara, T. Shimizu, K. Jinno, N. Uehara, Speciation of chromium (III) and chromium (VI) in river water by graphite furnace atomic absorption spectrometry after cloud point extraction with ammonium pyrrolidinedithiocarbamate, Bunseki Kagaku 56 (2007) 737–743.

[24] A.U. Karatepe, M. Soylak, L. Elçi, Separation/preconcentration of Cu(II), Fe(III), Pb(II), Co(II) and Cr(III) in aqueous samples on cellulose nitrate membrane filter and their determination by atomic absorption spectrometry, Anal. Lett. 35 (2002) 1561–1574.

[25] 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.

[26] M. Soylak, L. Elci, M. Dogan, Flame atomic absorption spectrometric determination of cadmium, cobalt, copper, lead and nickel in chemical grade potassium salts after an enrichment and separation procedure, J. Trace Microprobe Tech. 17 (1999) 149–156.

[27] P. Liang, Y. Qin, B. Hu, T. Peng, Z. Jiang, Nanometer-size titanium dioxide microcolumn on-line preconcentration of trace metals and their determination by inductively coupled plasma atomic emission spectrometry in water, Anal. Chim. Acta 440 (2001) 207–213.

[28] G. Absalan, A. Aghaei Goudi, Optimizing the immobilized dithizone on surfactant-coated alumina as a new sorbent for determination of silver, Sep. Purif. Technol. 38 (2004) 209–214.

[29] M. Ghaedi, F. Ahmadi, M. Soylak, Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry, Ann. Chim. 97 (2007) 277–285.

[30] M. Ghaedi, Pyrimidine-2-thiol as selective and sensitive ligand for preconcentration and determination of Pb^{2+}, Chem. Anal. 51 (2006) 593–603.

[31] M. Ghaedi, M.R. Fathi, A. Shokrollahi, F. Shajarat, Highly selective and sensitive preconcentration of mercury ion and determination by cold vapor atomic absorption spectroscopy, Anal. Lett. 39 (2006) 1171–1185.

[32] V. Smuleac, D.A. Butterfield, S.K. Sikdar, R.S. Varma, D. Bhattacharyya, Polythiol-functionalized alumina membranes for mercury capture, J. Membr. Sci. 251 (2005) 169–178.

[33] E.M. Soliman, M.B. Saleh, S.A. Ahmed, Alumina modified by dimethyl sulfoxide as a new selective solid phase extractor for separation and preconcentration of inorganic mercury(II), Talanta 69 (2006) 55–60.

[34] A.R. Bowers, C.P. Huang, Adsorption characteristics of polyacetic amino acids onto hydrous γ-Al_2O_3, J. Colloid Interface Sci. 105 (1985) 197–215.

[35] A.R. Bowers, C.P. Huang, Adsorption characteristics of metal-EDTA complexes onto hydrous oxides, J. Colloid Interface Sci. 110 (1986) 575–590.

[36] Y. Mao, B.M. Fung, A study of the adsorption of acrylic acid and maleic acid from aqueous solutions onto alumina, J. Colloid Interface Sci. 191 (1997) 216–221.

[37] M. Hiraide, M.H. Sorouraddin, H. Kawaguchi, Immobilization of dithizone on surfactant-coated alumina for preconcentration of metal lons, Anal. Sci. 10 (1994) 125–128.

[38] G. Absalan, M.A. Mehrdjardi, Separation and preconcentration of silver ion using 2-mercaptobenzothiazole immobilized on surfactant-coated alumina, Sep. Purif. Technol. 33 (2003) 95–101.

[39] M. Hiraide, J. Hori, Enrichment of metal-APDC complexes on admicelle-coated alumina for water analysis, Anal. Sci. 15 (1999) 1055–1058.

[40] S. Dadfarnia, A.M.H. Shabani, M. Gohari, Trace enrichment and determination of silver by immobilized DDTC microcolumn and flow injection atomic absorption spectrometry, Talanta 64 (2004) 682–687.

[41] T. Saitoh, S. Matsushima, M. Hiraide, Concentration of polyaromatic hydrocarbons in water to sodium dodecyl sulfate-γ-alumina admicelle, J. Chromatogr. A 1069 (2005) 271–274.

[42] X. He, S. Hu, K. Liu, Y. Guo, J. Xu, S. Shao, Oxidized Bis(indolyl)methane: A Simple and Efficient Chromomeric-Sensing Molecule Based on the Proton Transfer Signaling Mode, Org. Lett. 8 (2006) 333–336.

[43] M. Hiraide, M.H. Sorouradin, H. Kawaguchi, Immobilization of dithizone on surfactant-coated alumina for preconcentration of metal lons, Anal. Sci. 10 (1994) 125–128.

[44] 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, Fresenius Environ. Bull. 14 (2005) 1158–1163.

[45] H. Karimi, M. Ghaedi, A. Shokrollahi, H.R. Rajabi, M. Soylak, Development of a selective and sensitive flotation method for determination of trace amounts of cobalt, nickel, copper and iron in environmental samples, J. Hazard. Mater. 151 (2008) 26–32.

[46] J.L. Manzoori, M.H. Sorouraddiin, A.M. Haji Shabani, Determination of mercury by cold vapor atomic absorption spectrometry after preconcentration with dithizone immobilized on surfactant-coated alumina, J. Anal. At. Spectrom. 13 (1998) 305–308.

[47] 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.

[48] S. Dadfarnia, A.M. Salmanzadeh, A.M. Haji Shabani, Immobilized 1,5-diphenylcarbazone as a complexing agent for on-line trace enrichment and determination of copper by flow injection–atomic absorption spectroscopy, J. Anal. At. Spectrom. 17 (2002) 1434–1438.

[49] J.P. Xiao, Q.X. Zhou, H.H. Bai, Preconcentration of copper with multi-walled carbon nanotubes pretreated by potassium permanganate cartridge for solid phase extraction prior to flame atomic absorption spectrometry, Chin. Chem. Lett. 18 (2007) 714–717.

[50] R.J. Gohari, K.A. Gorouh, Modified bentonite as sorbent for removal of Tl+ and Bi 3+ from water samples, Asian J. Chem. 19 (2007) 4837–4840.

[51] S.J. Shahtaheri, M. Khadem, F. Golbabaei, A. Rahimi-Froushan, M.R. Ganjali, P. Norouzi, Solid phase extraction for evaluation of occupational exposure to Pb (II) using XAD-4 sorbent prior to atomic absorption spectroscopy, Int. J. Occup. Saf. Ergon. 13 (2007) 137–145.

[52] K. Kiran, K. Janardhanam, Determination of trace metals in water samples by flame atomic absorption spectrometry using column solid-phase extraction, Asian J. Chem. 19 (2007) 3468–3474.

[53] M. Soleimani, A. Morsali, A. Khani, New reagent for solid phase extraction and atomic absorption determination of trace amount of Fe(III) in water samples, Asian J. Chem. 19 (2007) 3554–3560.

[54] H. Bag, A. Elci, L. Elci, Determination of lead, iron, manganese and zinc in sea water samples by atomic absorption spectrometry after preconcentration with chromosorb 105, Eurasian J. Anal. Chem. 1 (2006) 42–54.

[55] 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.