APPLICATION OF TRITON X-100 COATED POLY VINYL CHLORIDE AS NEW SOLID PHASE FOR PRECONCENTRATION OF Fe^{3+}, Cu^{2+} AND Zn^{2+} IONS AND THEIR FLAME ATOMIC ABSORPTION SPECTROMETRIC DETERMINATIONS

Mehrorang Ghaedi[1*] and Ebrahim Niknam[1]

[1]Chemistry Department, Yasouj University, Yasouj 75914-353, Iran

ABSTRACT. A selective, sensitive and efficient method for preconcentration of trace amounts of Cu(II), Fe(II) and Zn(II) ions based on the uptake of their complexes with 3-((indolin-3-yl)(phenyl)methyl)indoline (IYPMI) loaded on Triton X-100 coated poly vinyl chloride has been reported. The influences of the analytical parameters including pH, ligand amount, surfactant type and concentration, eluting condition and sample volume on metal ions recovery were investigated. The method has been successfully applied for the extraction of these ions content in some real samples of soil and plants. The extraction efficiency was > 97% with low relative standard deviation (RSD < 2.4%) and the preconcentration factor of 90 (5 mL elution volume for a 450 mL of sample volume).

KEY WORDS: Surfactant coated PVC, Atomic absorption spectrometry, Solid phase extraction

INTRODUCTION

The surface water quality in a region is largely determined both by natural (weathering process soil corrosion) and anthropogenic processes; in particular, municipal and industrial wastewater discharge constitutes sources of toxic heavy metals. Heavy metals are present in natural water and industrial wastewater, soil sample and plants samples. The presence of heavy metals in surface water and ground water poses a major inorganic contamination problem [1-3]. Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions because of the relatively simple and inexpensive equipment. However, direct determination of metal ions at trace levels by FAAS is limited not only due to insufficient sensitivity, but also by matrix interference [4-7]. For this reason, preliminary separation and preconcentration of trace elements from the matrix is frequently necessary to improve the detection limit and the selectivity.

Solid-phase extraction (SPE) with respect to liquid-liquid extraction has unique advantages such as reducing analysis time, easy manipulation, lesser amount of solvent, no disposal of large quantities of organic solvents, higher concentration factor, no problem with the miscibility of solvent, easy adaptable for very selective extraction, easy automatisation without problems such as incomplete phase separations, not quantitative recoveries and emulsion formation. This technique has been widely used for separation and preconcentration of metal ions [7-11].

Generally, the design of a stable and selective solid phase sorbents for separation and preconcentration of a target metal ion depends on different factors related to the nature of solid support, its surface area and reactivity [12] as well as other important factors related to the organic complexing agent bound to the solid substrate. These factors include the structure of the immobilized organic compound as a whole, the nature of the incorporated donor atoms (O, N, P and S), the positioning of the functional groups along the surface of the solid support and the steric requirements of the complex formed after uptake of the desired metal ion [13]. For this purpose, various sorbents [14-22] have been used. Since, our survey through literature did not show any application of 3-((indolin-3-yl)(phenyl)methyl)indoline (IYPMI) on PVC as solid phase, therefore, this new sorbent was applied for preconcentration and determination of the trace amount of Fe^{3+}, Cu^{2+} and Zn^{2+} ions.

_____

*Corresponding author. E-mail: m_ghaedi@mail.yu.ac.ir

EXPERIMENTAL

Instruments

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

Reagent and solutions

Acids and bases, nitrate of metal ions including lead, cadmium, mercury, cobalt, nickel, copper, zinc, magnesium, calcium, strontium, barium, silver, sodium and potassium and surfactants including sodium dodecyl sulfate (SDS), Triton X-100, cetyltrimethylammonium bromide (CTAB) and n-dodecytrimethylammonium bromide (DTAB) with the purity of analytical grade was purchased from E. Merck, Darmstadt, Germany and were used as received. Doubly distilled deionized water was used throughout. The pH adjustment was carried out by addition of dilute nitric acid or potassium hydroxide. Poly vinyl chloride high molecular weight was purchased from Fluka (Switzerland). The ligand was synthesized according to literature (Scheme 1) [23].
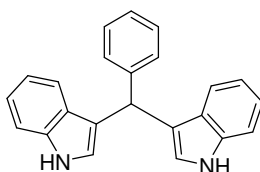
Scheme 1. The structure of ligand.

Preparation of IYPMI coated PVC

60 mg of Triton X-100 and 40 mg of IYPMI was added to 40 mL of water solution containing 1.25 g PVC particles and its pH was adjusted to 10 by addition of dilute KOH. While shaking the suspension with a stirrer the pH was adjusted to 2 with 2 M hydrochloric acid. Acidification leads to decrease in ligand and surfactant solubility and simultaneously the surfactant will be coated on surface of PVC via adsorption or micelle formation and ligand will be trapped in the interior core of respective aggregate of surfactant. After mixing for 15 min, the supernatant solution was discarded and the remaining was used as solid phase. When kept in a refrigerator the sorbent is stable at least for 1 week.

Measurement of amount of IYPMI loaded on the T-X100 coated PVC

A 10 mL of 0.005 M NaOH solution containing 40 mg of IYPMI was added to 1.25 g of PVC and 60 mg of Triton X-100 in a 25 mL vial and while shaking the pH was adjusted to 2.0. After shaking for 1 h, a portion of the supernatant liquid was diluted to the appropriate volume and the absorbance of the solution was measured at maximum wavelength of the ligand. Comparisons of the absorbance of supernatant solution with absorbance of IYPMI solution at similar conditions indicate the amount of IYPMI adsorbed on T-X100 coated PVC. The change in color of PVC is an indication of ligand immobilization on PVC.

Test works

The pH of 200 mL of sample solutions containing analyte ions was adjusted to 7 by addition of HCl or KOH solution and the solutions were contacted for 60 min with solid phase at 300 rpm in a beaker and stirred by a magnetic stirrer. After preconcentration, the retained ions were then eluted with 5 mL of 4 M nitric acid and analytes content in the eluent were determined by flame atomic absorption spectrometer at conditions mentioned by manufacture.

Pretreatment of real samples

All the real samples were prepared according to our previous publications [24-27]. The certified liver sample was also digested in the manner described below. Triplicate samples (weight of 10 mg) were weighed in glass flasks and 5-10 mL of concentrated HNO_3 was added. The flasks were capped and then digested at 60-70 °C for 1-2 h until semi-dryness. The digests were treated with 5 mL nitric acid and a few drops of H_2O_2, heated on a hot plate at approx. 80 °C until the color of the digestion solution became bright yellow. Then the sample was cooled, and diluted to a volume of 25 mL in volumetric flasks with the distilled water. Then the procedure described above was applied.

For digestion of orange juice samples, 5.0 g of the orange juice samples were accurately weighed and added with 5 mL of concentrated HNO_3 in the digestion vessel and a heating program was executed. After then, 1 mL of H_2O_2 (30% w/v) was added and heated for 2 h in 650 °C. The residue was cooled and filtered and then the procedure described above was applied.

5 g of homogenized soil sample was weighed accurately and in a 200 mL beaker. The digestion procedure was carried out by heating the sample for 1 h after addition of 10 mL concentrated HNO_3 and 2 mL $HClO_4$ 70% (w/v) was added and heated for 1 h. 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 described above was performed.

Lotus trees sample (from Gachsaran, Iran) were taken in small mesh. A 40 g sample 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 and treated with 10.0 mL concentrated nitric acid and 3 mL 30% (w/v) H_2O_2 again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. 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 and filtered and the pH was adjusted at 10.0 by addition of KOH and diluted to 25 mL. Then, the procedure described above was performed.

RESULTS AND DISCUSSION

Based on the well known hard-soft acid-base theory, the existence of a donating nitrogen atom in the flexible structure of ligand was expected to increase the stability constant of complexes of the ligand (IYPMI) with Fe^{3+}, Cu^{2+} and Zn^{2+} ions over other metal ions including alkali, alkaline earth and many transition and heavy metal ions.

Therefore, it has been used as efficient sorbent for solid phase extraction of these mentioned ions. In this regard the influence of effective variables including pH, amount of sorbent and eluting solution condition was optimized.

Effect of different surfactant and amount of Triton X-100

In order to conduct an efficient and repeatable solid phase extraction the composition of solid phase must be optimized. In this regard solid phase composed of 60 mg of various surfactant including SDS, Triton X-100, CTAB and DTAB at fixed value of ligand (40 mg) and PVC (1.25 g) was prepared then procedure described in previous section was carried out at pH 7 and respective results are presented in Table 1. Quantitative results were obtained with Triton X-100. This result is probability due to the fact that expected neutral complex could be efficiently trapped in to the interior core of micelles or ad-micelled coated on the surface of PVC as support. In all the optimization study the volume of sample solution was 200 mL.

Table 1. Effect of surfactant type on ions recovery.

Surfactant	Zn	Cu	Fe
SDS	98	74	65
Brij 58	38	35	34
CTAB	45	43	40
Triton-X100	99	98	97

While cross-linked PVC retained only a little amount of these metal ions (less than 10%), Triton X-100-coated PVC (less than 40%) for these ions, ligand loaded on Triton X-100-coated PVC is capable for quantitative extracting of these ions from the sample solutions. Therefore, addition of ligand and Triton X-100 is necessary and their amounts must be optimized. The influence of amount of Triton X-100 on the recovery of ions enriched on solid phase via complexation was investigated by contacting 200 mL of a solution containing 40 μg of each ion with solid phase containing different amount of Triton X-100 and 1.25 g of PVC and 40 mg IYPMI at pH 7.0. The results are depicted in Figure 1. As can be seen, by using 60 mg of Triton X-100, complete and reversible uptake-elution of metal ions could be achieved. The retention of metal ions on hemi-micelles, which have a hydrophobic surface, was clearly dependent on analyte complex polarity. The formation of minute amounts of ad-micelles was essential to achieve complete ad-solubilization of these ions as respective complex (which probably are neutral). Probably due to insufficiency of eluting solution for reversible elution of the retained metal ions, at surfactant concentrations higher than 60 mg a decrease in the percentage of ions recovery was observed.
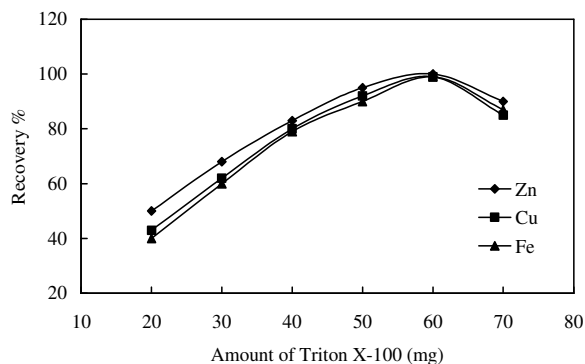

Figure 1. Effect of Triton X-100 concentration on ions recovery.

Influences of pH

One of the most important factors in a solid phase extraction procedure is the pH of the aqueous phase for the quantitative recoveries. This could be attributed to the fact that these metal ions

were presented in free cation form in an acidic medium, i.e. pH ≤ 7.0, and then the charge intensity of the functional groups of solid materials played a crucial role in the metal sorption. The effect of solution pH on the ions uptake was investigated within the range of 3.0-10.0.

It can be seen in Figure 2, the metal ions recoveries were increased from pH 2.0 to 7.0 and a decline in the efficiency appeared with further increasing the pH value. This could be attributed to the fact that these metal ions were presented in free cation form in an acidic medium, i.e. pH ≤ 7.0 and then the charge intensity of the functional groups of solid materials played a crucial role in the metal sorption. As a function of pH value, the dissociations of the acidic functional groups on the ligand, which providing binding sites for the metal ions, were governed by the acidity of the solution. At a low pH value, e.g. 3.0, the dissociations were suppressed greatly due to the excess H^+ in the sample solution and therefore nearly no sorption took place. The increase of pH value facilitated the dissociation of functional groups and thus more binding sites were released for the sorption of metals. As a result, increased retention efficiency was achieved. However, an even higher pH value, 7.0, tended to cause the precipitation of $M(OH)_n$, which resulted in the heterogeneity of the sample flow and the contamination of sorbent surface and hence a slight decline of the retention efficiency. Consequently a sample pH value of 6.0 was employed for the ensuing investigations. Therefore, the pH 7.0 was chosen throughout the subsequent experiments.
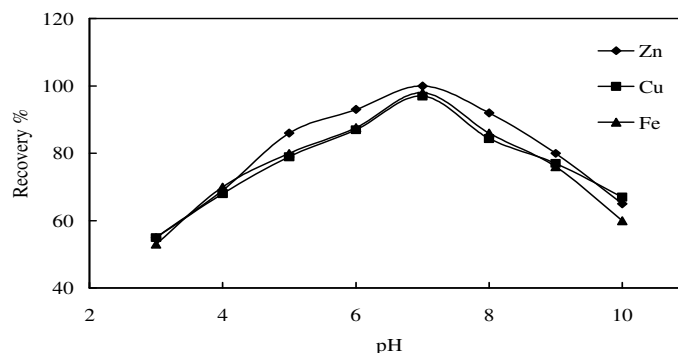

Figure 2. Effect of pH on analytes ion recovery (n = 3).

Effects of amounts of IYPMI

The ligand concentration plays an important role in the retention of analytes because in its absence the solid phase does not retain the metal ions completely. The amount of solid phase filled to the column is a main parameter for the quantitative recoveries of analyte ions.

To investigate the influence of amount of IYPMI on the recovery of these ions, a set of similar experiments at fixed value of PVC (1.25 g) and Triton X-100 (60 mg) containing various amount of ligands by addition of 2.0-7.5 mL of 1.0% (w/v) solution (20-75 mg of ligand) were conducted according to procedure described in the experimental section and respective results are presented in Figure 3. As it can be seen, with increasing the IYPMI amount up to 40 mg an increase in recoveries can be achieved and further increase lead to decrease in efficiency of ions extraction. Quantitative recoveries for the analytes were obtained using 40 mg of IYPMI. The composition of the complex produced is critical in attaining highest extraction percentages. At higher amount of ligand probably due to formation of charged complex, the extraction efficiency of these ions was decreased.
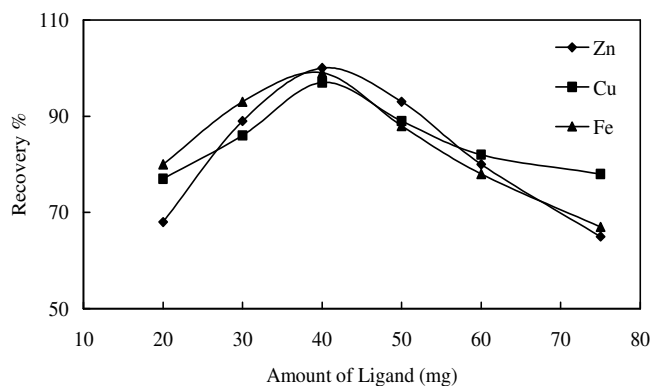
Figure 3. Effect of amount of IYPMI on analytes ions recovery (n = 3).

Choice of eluent

The choice of a suitable eluent is another important factor for obtaining efficient and selective recovery of analytes. As could be seen from Figure 2, the uptake of these metal ions was negligible at pH < 3, therefore, the acidic eluents is the best solution for obtaining efficient extraction. Due to this point, various eluent solutions given in Table 2 were used for elution of ions which retained on Triton X-100 coated PVC due to chelation with IYPMI. Quantitative recoveries for copper, zinc and iron ions were obtained only with 4 M HNO_3. Recoveries were not quantitative using other examined eluents. The effect of eluent volume and concentration on the recoveries of the analytes was also studied by using various volume of 4 M HNO_3 and 5 mL of different concentration of HNO_3. It was found that quantitative recoveries could be obtained with 5.0-10.0 mL of 4 M HNO_3. Therefore, the volume of 5.0 mL of 4 M HNO_3 was used in the subsequent experiments.

Table 2. Effect of type and concentration of eluting agent on recovery of analytes.

Eluent	Recovery %		
	Zn	Cu	Fe
H_3PO_4 (4 M)	30	25	22
HCl (4 M)	87	58	61
H_2SO_4 (4 M)	14	13	37
CH_3COOH (4 M)	39	21	14
HNO_3 (1 M)	50	35	40
HNO_3 (2 M)	73	62	57
HNO_3 (3 M)	85	80	79
HNO_3 (4 M)	97	98	97
HNO_3 (5 M)	89	92	91

Influence of shaking time and rate

It is required to preconcentrate trace amount of metal ions with high efficiency in short time. To determine the rate of loading of metal ions on the modified Triton X-100 loaded PVC, batch experiments were carried out at regular time intervals (5-120 min) and stirring rate between 100-400 rpm. At the beginning of uptake process, very high uptake rates were observed and then plateau values (i.e. adsorption equilibrium) were completely reached in about 20-30 min for copper and zinc at stirring rate of 300 rpm and about 60 min for Fe^{3+} ions. The batch system

studies showed that equilibrium time was significantly short. By taking into account these results, modified Triton X-100 coated PVC could be used as useful and efficient adsorbent for ions preconcentration after 60 min contacting at attiring rate of 300 rpm.

Effects of amounts of PVC

The influence of the amounts of PVC as support on trace metal ions enrichment as solid phase was also investigated. The results show that up to 1.25 g of PVC, efficiency of extractions increase and further addition has not significantly enhanced the recoveries of analytes. The recoveries of analytes above 1.25 g of solid phase were below 95% with 5 mL of the eluent. In the proposed procedure, 1.25 g of PVC is recommended (Figure 4) as support for an efficient and reversible extraction of metal ions.
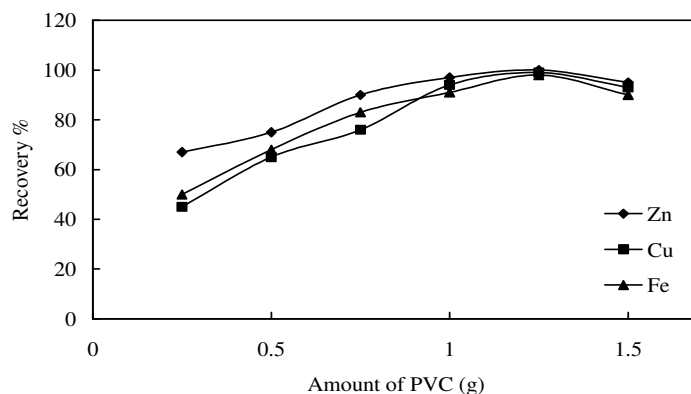

Figure 4. Effect of PVC amount on analytes ions recovery (n = 3).

Interference

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interference may be attributed to the preconcentration step, in which the cations may react with ligand and anions which may form stable complex with metal ions (both lead to decrease in extraction efficiency). The possible interference of other metal ions and of a few anions on the recovery of copper, zinc and iron was investigated. A relative error of less than 5% was considered to be within the range of experimental error. At the given level no significant interference was observed in the determination of these ions. Thus, the interference-free determination level of present system indicates that high concentration of matrix salts, have minimal effect on ions species relative to matrix ions (Table 3).

Table 3. Effects of the interfering ions on the recoveries of the examined metal ions.

Ion[*]	Interfering ion/analyte amount	Recovery %		
		Fe	Cu	Zn
$Ba^{2+}, Mg^{2+}, Ca^{2+}, Ti^{3+}, Na^+, K^+, Li^+, Al^{3+}$		97	98	97
	1000	96	97	96
		97	98	98
$Pb^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+}, Ni^{2+}$	250	95	96	96
CH_3COO^-	900	95	95	98
Ag^+	150	97	94	95
Mn^{2+}, SO_4^{2-}	600	95	96	97
Cl^-	400	97	98	97

[*]The relative standard deviations were between 1-2.5%.

Reusability of the solid phase

The reusability of the solid phase was tested by loading metal ions several times on a solid phase from a solution having a concentration of 2-50 µg L^{-1} for stirring in 60 min at 300 rpm and then adsorbed ions were eluted by the general procedure. It was found that the uptake capacity after 5 times of uptake and elution does not vary more than 5%. Therefore, these SPE are suitable for repeated use without considerable loss of uptake capacity.

Analytical features

By employing the optimum experimental conditions, the calibration graphs obtained for copper, zinc and iron, respectively, were given as, A = 4.128 [Cu mg L^{-1}] + 0.263 (R^2 = 0.997, n = 4), A = 0.86 [Fe mg L^{-1}] - 0.005 (R^2 = 0.9994, n = 4), A = 6.184 [Zn mg L^{-1}] + 0.013 (R^2 = 0.998, n = 4) in the interval of 10 up to 400 µg L^{-1} for copper(II) and zink(II) ion and from 20 up to 400 µg L^{-1} for iron(III) ions. The experimental preconcentration factors [28, 29] calculated as the ratio of the slope of the calibration graph with and without preconcentration were 45 for zinc, 43 for copper and 39 for iron, while the preconcentration factor as the volume of initial solution (450 mL) to the volume of eluting solution (5 mL) for all ions is 90.

The limit of detection (LOD) of a method is the lowest analyte concentration that produces a response detectable above the noise level of the system, typically, three times the standard deviation (s) of the blank (n = 10), were found to be 1.0 µg L^{-1} for Zn(II), 1.25 µg L^{-1} for Cu(II) and 2.9 µg L^{-1} for Fe(III). The empirical limit of quantification (LOQ) is the lowest level of analyte that can be accurately and precisely measured, were found to be 10 µg L^{-1} for Zn(II) and Cu(II) and 20.0 µg L^{-1} for Fe(III) ions.

Table 4. Recovery of analytes from spiked samples by using proposed method (n = 3).

Ion	Added, µg mL^{-1}	Found, µg mL^{-1}	RSD %	Recovery %
CRM 185 liver[a]				
Fe	0	-----	---	---
Cu	0	2.06	0.9	102.0
Zn	0	1.97	1.0	101.5
Orange juice[b]				
Cu	0	0.166	1.1	----
	0.2	0.371	0.8	102.5
Zn	0	0.297	1.0	-----
	0.2	0.505	0.8	104.0
Fe	0.0	0.683	0.8	----
	0.2	0.890	0.6	103.5
Soil sample[c]				
Fe	0.0	0.170	1.3	---
	0.2	0.376	1.0	103.0
Cu	0.0	0.214	1.2	----
	0.2	0.422	0.9	104.0
Zn	0.0	0.149	1.2	-----
	0.2	0.356	1.0	103.5
Lotus (tree) sample[c]				
Fe	0.0	0.250	1.2	---
	0.2	0.458	0.8	104.0
Cu	0.0	0.260	1.3	----
	0.2	0.471	1.1	105.5
Zn	0.0	0.144	1.3	-----
	0.2	0.352	0.9	104.0

[a] 0.5 g of certified sample in 100 mL sample solutionm, [b] 20 mL oranje juice in 100 mL sample, [c] 10 g sample in 100 mL sample solution; in all case final volume is 5 mL.

Accuracy of the method

In order to evaluate the accuracy of the proposed procedure the certified reference liver samples were analyzed. The reliability of the presented method was also checked by spiking experiments and independent analysis. The results for real samples analysis of certified reference liver, soil, lotus tree and orange juice are presented in Table 4. The recovery of metal spikes added to the samples was investigated and it was found to be satisfactorily reasonable, since a good agreement was obtained between the added and measured analyte amounts. The recovery values obtained for the added standards were higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects. In all the real sample analysis 25 mL of stock solution of real sample was diluted in 50 mL volumetric flask and procedure described in experimental section was carried out.

A comparison of the proposed system with other preconcentration procedures using several sorbents is given in Table 5. The proposed preconcentration system shows good enrichment factors with reasonable preconcentration time over other preconcentration methods. Consumptive index (CI) is another efficient way to evaluate the performance of preconcentration system [40]. CI is expressed by volume of analyte solution (V, mL) and the experimental preconcentration factor (EPF) ratio (CI = V/EPF), thus indicate the necessary volume to obtain one unit of enrichment factor. As seen from the Table 5, the detection limit for proposed method is comparable to those given by many methods. In addition, enrichment factor can be improved by using larger sample volumes. It is important to emphasize that CI values obtained in the present study are lower than that of the most procedure.

Table 5. Comparison of proposed paper with previously reported preconcentration system of some metal ions using chemically modified sorbents and detection by FAAS.

Metal	Sorbent	Sample volume (mL)	Enrichment factor	LOD ($\mu g\ L^{-1}$)	P.T. (min)	CI (mL)	Ref.
Cu, Ni, Pb, Co	DHMP loaded-activated carbon	1300	260	2.9/3.5/8.4/3.4	-	5.0	30
Pb, Cu, Ni, Co, Cd	Functionalized-silica gel	25-100	-	22.5/1.0/2.9/0.95/1.1	6.25-25	-	31
Cu, Cd, Co, Pb, Zn, Mn	Quinalizarin functionalized-XAD-2	1000	1000/50/40/50/100/65	2.0/1.3/5.0/15.0/1.0/1.6	8.5/5.3/10.2/15/7.4/14.1	10/20/25/20/10/15.4	32
Cu, Fe, Zn	Bacillus thuringiensis israelensis	250	37	1.14, 2.01 and 0.14	50	0.18/0.57	33

CONCLUSIONS

The proposed solid phase extraction method is simple, accurate, economical and can be applied for the determination of copper, zinc and iron in environmental samples. The system showed reproducibility and reliability in analytical data, with an RSD value of lower than 5% on triplicate experiment. Solid phase composed of 60 mg of Triton X-100, 1.25 g PVC and 40 mg of ligand can be used for as least 5 experiments without any loss in its sorption behavior. The system was successful in preconcentration of analytes from large sample volume (450 mL). The proposed preconcentration/separation method could be applied to the highly saline samples and the samples contain some transition metals at mg L^{-1} levels. 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 for preconcentration of analyte ions in various environmental samples including soil, lotus tree and orange juice and certified liver samples.

REFERENCES

1. Kazi, T.G.; Arain, M.B.; Jamali, M.K.; Afridi, H.I.; Jalbani, N.; Baig, A. *Ecotox. Environ. Safety* **2009**, 72, 301.
2. Soylak, M.; Elci, L.; Dogan, M. *Talanta* **1995**, 42, 1513.
3. Ghaedi, M.; Shokrollahi, A. *Fresenius Environ. Bull.* **2006**, 15, 1373.
4. Shamsipur, M.; Ghiasvand, A.R.; Sharghi, H.; Naemi, H. *Anal. Chim. Acta* **2000**, 408, 271.
5. Soylak, M.; Elci, L.; Dogan, M. *Anal. Lett.* **2000**, 33, 513.
6. Soylak, M.; Elci, L.; Dogan, M. *Fresenius Environ. Bull.* **1996**, 5, 148.
7. Yamini, Y.; Tamaddon, A. *Talanta* **1999**, 49, 119.
8. Soylak, M.; Elci, L.; Dogan, M. *Anal. Lett*. **1997**, 30, 623.
9. Mahmoud, M.E.; Gohar, G.A. *Talanta* **2000**, 51, 77.
10. Koejan, R.; Prjeszlakowski, S. *Talanta* **1992**, 39, 63.
11. Ghaedi, M.; Shokrollahi, A.; Kianfar, A.H.; Mirsadeghi, A.S.; Pourfarokhi, A.; Soylak, M. *J. Haz. Mat*. **2008**, 154, 128.
12. Soylak, M.; Saracoglu, S.; Elci, L.; Dogan, M. *Int. J. Environ. Anal. Chem.* **2002**, 82, 225.
13. Budhiraja, R.P. *Separation Chemistry*, New Age International Publishers: New Delhi; **2004**.
14. Ferreira, S.L.C.; Andrade, H.M.C.; dos Santos, H.C. *J. Coll. Interf. Sci.* **2004**B, 270, 276.
15. Ghaedi, M.; Ahmadi, F.; Soylak, M. *Ann. Chim.* **2007**, 97, 277..
16. Akl, M.A.A.; Kenawy, I.M.M.; Lasheen, R.R. *Microchem. J.* **2004**, 78, 143.
17. Fan, Z.; Hu, B.; Jiang, Z. *Spectrochim. Acta B* **2005**, 60, 65.
18. Dubey, R.K.; Bhalotra, A.; Gupta, M.K.; Puri, B.K. *Microchem. J.* **1998**, 58, 117.
19. Otero-Romani, J.; Moreda-Pineiro, A. *Anal. Chim. Acta* **2005**, 536, 213.
20. Feri, T.; Pangiorgio, S. *Anal. Chim. Acta* **1996**, 321, 185.
21. Anthemidis, A.N.; Zachariadis, G.A.; Stratis, J.A. *Talanta* **2002**, 58, 831.
22. Thurman, E.M.; Mills, M.S. *Solid-Phase Extraction: Principles and Practices*, John Wiley and Sons: New York; **1998**.
23. Niknam, K.; Zolfigol, M.A.; Sadabadi, T.; Nejati, A. *J. Iran. Chem. Soc*. **2006**, 3, 318.
24. (a) Ghaedi, M.; Ahmadi, F.; Soylak, M. *J. Haz. Mat.* **2007**, 147, 226; (b) Ghaedi, M.; Niknam, K.; Shokrollahi, A.; Niknam, E. *J. Chinese Chem. Soc.* **2009**, 56, 150.
25. Ali, S.S.; Kazi, T.G.; Kazi, G.H. *Hamdard Medicus* **1999**, 4, 61.
26. (a) Ghaedi, M.; Shokrollahi, A.; Fathi, M.R.; Gharaghani, S.; Soylak, M. *Quim. Nova* 2008, 31, 70; (b) Ghaedi, M.; Shokrollahi, A.; Kianfar, A.H.; Pourfarokhi, A.; Khanjari, N.; Mirsadeghi, A.S.; Soylak, M. *J. Hazard. Mater.* **2009**, 162, 1408.
27. Fili, S.P.; Oliveira, E.; Oliveira, P.V. *J. Braz. Chem. Soc.* **2003**, 14, 435.
28. Fang, Z. *Flow Injection Separation and Preconcentration*, Wiley: New York; **1993**.
29. Enríquez-Domínguez, M.F. *Analyst* **1998**, 123, 105.
30. Ghaedi, M.; Ahmadi, F.; Shokrollahi, A. *J. Haz. Mat.* **2007**, 142, 272.
31. Ngeontae, W.; Aeungmaitrepirom, W.; Tuntulani, T. *Talanta* **2007**, 71, 1075.
32. Kumar, M.; Rathore, D.P.S.; Singh, A.K. *Fresenius J. Anal. Chem.* **2001**, 370, 198.
33. Lemos, V.A.; Baliza, P.X. *Talanta* **2005**, 67, 564.