

## Research Article

# Preconcentration of Copper Using 1,5-Diphenyl Carbazide as the Complexing Agent via Dispersive Liquid-Liquid Microextraction and Determination by Flame Atomic Absorption Spectrometry

Reyhaneh Rahnama, Elaheh Shafiei, and Mohammad Reza Jamali

Department of Chemistry, Payame Noor University, P.O. Box 19395-3697, Tehran, Iran

Correspondence should be addressed to Reyhaneh Rahnama; r\_rahnama@ymail.com

Received 4 March 2012; Revised 21 September 2012; Accepted 2 October 2012

Academic Editor: Aniello Anastasio

Copyright © 2013 Reyhaneh Rahnama et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We report a simple and sensitive microextraction system for the preconcentration and determination of Cu (II) by flame atomic absorption spectrometry (FAAS). Dispersive liquid-liquid microextraction is a modified solvent extraction method and its acceptor-to-donor phase ratio is greatly reduced compared with other methods. In the proposed approach, 1,5-diphenyl carbazide (DPC) was used as a copper ion selective complexing agent. Several variables such as the extraction and dispersive solvent type and volume, pH of sample solution, DPC concentration, extraction time, and ionic strength were studied and optimized for a quantitative preconcentration and determination of copper (II) and at the optimized conditions: 60  $\mu\text{L}$ , 0.5 mL, and 5 mL of extraction solvent (chloroform), disperser solvent (ethanol), and sample volume, respectively, a linear calibration graph was obtained over the concentration range of 10–200  $\mu\text{g L}^{-1}$  for Cu (II) with  $R^2 = 0.9966$ . The limit of detection ( $3S_b/m$ ), and preconcentration factor are 2  $\mu\text{g L}^{-1}$  and 25, respectively. The relative standard deviation ( $n = 10$ ) at 100  $\mu\text{g L}^{-1}$  of Cu (II) is 2.5%. The applicability of the developed technique was evaluated by application to spiked environmental water samples.

## 1. Introduction

Sample preparation is an important analytical step especially for the determination of trace analytes in complex sample matrices commonly encountered in environmental and biological analysis [1]. Solvent extraction has been one of the most extensively studied and widely applied methods in preconcentration and separation procedures for the determination of trace elements due to its simplicity, convenience, wide scope, and so forth. Separation and preconcentration procedures using solvent extraction, generally, result in a high-enrichment factor, owing to the difference between the volumes of the aqueous and organic phases. Although this procedure is operated in batch mode, it is time consuming and produces large amounts of potentially toxic organic solvents as waste.

Modern trends in analytical chemistry are directed towards the simplification and miniaturization of sample preparation, as they lead inherently to a minimum solvent and reagent consumption and drastic reduction of laboratory wastes [2, 3]. Considering this aspect, for reducing the analysis step, increasing the sample throughput, and improving the quality and the sensitivity of the analytical methods, several microextraction techniques such as cloud point extraction (CPE) [4, 5], homogeneous liquid-liquid extraction (HLLE) [6, 7], liquid-phase microextraction (LPME) [8, 9], and solid-phase microextraction (SPME) [10] are being developed.

A novel microextraction technique as a high performance and powerful preconcentration method termed dispersive liquid-liquid microextraction (DLLME) was demonstrated by Assadi and colleagues previously [18]. This method is a simple and fast microextraction technique based on the use

TABLE 1: Comparison of DLLME with other extraction methods for determination of copper in water samples.

Method	LOD <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	R.S.D. <sup>b</sup> (%)	PF <sup>c</sup>	Sample volume (mL)	Reference
Online SPE-FAAS	3	3.3	16	13.6	[11]
SPE-FAAS	5.2	2.6	2	10	[12]
Online SPE-FAAS	10	3.4	16	4	[13]
CPE-spectrophotometry	5	2.8	22 <sup>d</sup>	25	[14]
SPE-FAAS	3	<5	20	250	[15]
SPE-FAAS	3.9	4.3	10	100	[16]
SPE-FAAS	2.5	3.3	25	50	[17]
DLLME-FAAS	2	2.5	25	5	Present work

SPE: solid phase extraction, FAAS: flame atomic absorption spectrometry, CPE: cloud point extraction, <sup>a</sup>Limit of detection, <sup>b</sup>Relative standard deviation, <sup>c</sup>Preconcentration factor, <sup>d</sup>Enhancement factor.

of an appropriate extractant, that is, a few microliters of an organic solvent and a disperser solvent with high miscibility in both extractant and aqueous phases. When the mixture of extractant phase and disperser is rapidly injected into the sample, a high turbulence is produced. This turbulent regimen gives rise to the formation of small droplets, which are dispersed throughout the aqueous sample. After the formation of a cloudy solution, the surface area between the extracting solvent and the aqueous sample becomes very large; therefore, the equilibrium state is achieved quickly and, as such the extraction time is very short. In fact, this is the principal advantage of DLLME. After centrifugation of the cloudy solution, a sedimented phase is settled in the bottom of a conical tube and used with the most appropriate analytical technique. For the determination of metal trace elements, a complexing reagent should be dissolved in the mixture [19]. Simplicity of operation, rapidity, low cost, high recovery, high enrichment factor, and environmental benignity are the advantages of DLLME [18]. This technique has been applied to the determination of trace organic pollutants and metal ions in environmental samples [20, 21].

Copper is an essential trace element and adverse health effects can potentially be associated with both very low and very high intakes [22]. Human long-term exposure to copper can cause acute gastrointestinal effects. These include stomachaches, dizziness, vomiting, and diarrhea [23]. High uptakes of copper may cause liver and kidney damage and even death. Whether copper is carcinogenic has not been determined yet. Accurate estimates of inhalation and ingestion (food and drinking water) exposures are therefore needed in order to realistically assess any effects of the distribution of copper intakes. In this manner, the determination of trace amounts of copper in several matrices is fundamental to identify the metal contamination in environment, water, or human body. Several instrumental methods, including inductively coupled plasma mass spectrometry (ICP-MS) [24], inductively coupled plasma atomic emission spectrometry (ICP-AES) [25], flame [26, 27] and graphite [28] atomic absorption spectrometry (AAS), adsorptive stripping voltammetry [29], and so forth, have been applied for the quantitative analysis of copper in various media. The common availability of the instrumentation, the simplicity of procedures, speed, precision, and accuracy of the technique are key factors in the selection of the determination method.

Aforementioned methods, except FAAS, involve greater cost and increased instrumentation complexity that limit their widespread application to routine analytical works. FAAS is still being used because of its low cost, friendly operation, high sample throughput, and good selectivity. FAAS technique suffers from poor sensitivity in the determination of heavy elements in environmental samples like natural water and other real samples [30, 31]. This drawback can be overcome by the combination of a suitable preconcentration technique with subsequent AAS determination.

In the presented work, a dispersive liquid-liquid microextraction procedure has been proposed for the preconcentration of copper prior to flame atomic absorption spectrometric determination. 1,5-diphenyl carbazide (DPC) was selected as a chelating agent. In this work we use microsample introduction system for the analysis of solutions by FAAS [32]. DLLME-FAAS by microsample introduction is a sensitive, fast, and reproducible technique for the preconcentration and determination of metal ions in water samples. After the optimization of experimental variables and determination of analytical features, the applicability of the developed technique was evaluated by application to spiked environmental water samples.

## 2. Experimental

**2.1. Instrumentation.** A SensAA (GBC, Australia) atomic absorption spectrometer equipped with deuterium background correction and copper hollow cathode lamp was used for the determination of copper at a wavelength of 324.8 nm. The instrumental parameters were adjusted according to the manufacturer's recommendations. A home-made microsample introduction system was constructed from a polyethylene valve and was coupled to the nebulizer needle by a small length of the PTFE capillary tube. A Hettich centrifuge (Model EBA 20, Germany) was used for centrifuging. The pH values were measured with a Metrohm pH-meter (model: 827) supplied with a glass-combined electrode.

**2.2. Reagents and Solutions.** All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany). Stock standard solution ( $1000 \text{ mg L}^{-1}$  in  $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ ) of Cu (II) was prepared using  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The

TABLE 2: Determination of copper in water samples.

Sample	Cu (II) amount ( $\mu\text{g L}^{-1}$ )		Recovery (%)
	Added	Found	
Tap water (drinking water system of Behshahr, Iran)	0.0	n.d. <sup>a</sup>	—
	50.0	49.0 (2.6) <sup>b</sup>	98.0
	100.0	99.0 (2.5)	99.0
Mineral water (Damavand mineral water, Iran)	0.0	n.d.	—
	50.0	49.0 (2.5)	98.0
	100.0	96.0 (2.6)	96.0
River water (Tajan river, Sari, Iran)	0.0	n.d.	—
	50.0	47.5 (2.7)	95.0
	100.0	97.0 (2.5)	97.0
Sea water (Caspian sea water, Sari, Iran)	0.0	n.d.	—
	50.0	51.5 (2.8)	103.0
	100.0	102.0 (2.8)	102.0

<sup>a</sup> Not detected.

<sup>b</sup> RSD of three replicate experiments.

working standard solutions were prepared by appropriate stepwise dilution of the stock standard solution with doubly distilled water.

Other reagents used were chelating agent 1,5-diphenyl carbazide (DPC), hydrochloric acid, nitric acid, sodium hydroxide, ethanol, methanol, acetone, acetonitrile, chloroform, dichloromethane, carbon tetrachloride, and sodium nitrate was obtained from Merck (Darmstadt, Germany). Chlorobenzene was obtained from Fluka (Switzerland).

A solution of  $0.1 \text{ mol L}^{-1}$  DPC was prepared by dissolving appropriate amount of DPC in methanol.

All glassware was rinsed with ultrapure water, decontaminated for at least 24 h in 10% (v/v) nitric acid solution and rinsed again five times with ultra-pure water.

**2.3. Extraction Procedure.** A 5 mL water sample containing the target ion was placed in a 10 mL test tube with conical bottom. Then 0.1 mL of  $0.1 \text{ mol L}^{-1}$  sodium acetate/acetic acid buffer (pH = 6) and 0.1 mL of  $0.1 \text{ mol L}^{-1}$  DPC solution were added. A mixture consisting of 0.5 mL ethanol (dispersive solvent) and 60  $\mu\text{L}$  chloroform (extraction solvent) was injected rapidly into the sample using a 1 mL syringe (gastight, Hamilton, Nevada, USA). A cloudy solution (resulting from the dispersion of the fine droplets of chloroform in the aqueous sample) was formed in the test tube. In this step, the copper ions reacted with DPC and extracted into the fine droplets of chloroform. The mixture was then centrifuged at 5000 rpm for 5 min. After this process, the dispersed fine droplets of chloroform were sedimented at the bottom of the conical test tube. The sedimented chloroform was removed using a 100  $\mu\text{L}$  microsyringe and was made up to 200  $\mu\text{L}$  by adding a mixture of  $0.1 \text{ mol L}^{-1}$   $\text{HNO}_3$  in methanol. The final solution was injected manually into FAAS equipped with microsample introduction system.

### 3. Results and Discussion

Before the analysis of the real samples by this method, to ensure the attainment of maximum extraction recovery, the parameters affecting DLLME efficiency including pH, the chelating agent concentration, the type and the volume of the extraction solvent, the type and the volume of the dispersive solvent, the extraction time and the ionic strength were optimized. One-variable-at-a-time optimization was used to obtain optimum conditions. The procedural parameters included in the optimization are given in the following section in order to gauge the importance of each. Triplicate extractions were performed for all experiments, and the average of these results was reported in figures or tables. Finally, these optimal conditions were applied to extract and detect copper in the real water samples.

**3.1. Effect of pH.** The separation of metal ions by DLLME involves a prior formation of a complex with sufficient hydrophobicity and a subsequent extraction into the small volume of the sedimented phase. The pH value plays a unique role on both the metal-chelate formation and the extraction. The effect of pH, in the range of 1–11, adjusted with hydrochloric acid and sodium hydroxide, on the Cu-DPC complex formation and the extraction of copper in water samples was investigated. The results illustrated in Figure 1 showed that the extraction recovery rose from pH 1 to 5, held at pH 5–8, and then declined with pH higher than 8. The Competition between protons and copper ions could explain the weak recovery in acid medium. On further increase of pH, recovery decreased probably due to the formation of hydroxide of copper. Therefore, further works for microextraction were performed at pH 6.0 by adding the sodium acetate/acetic acid buffer solution.

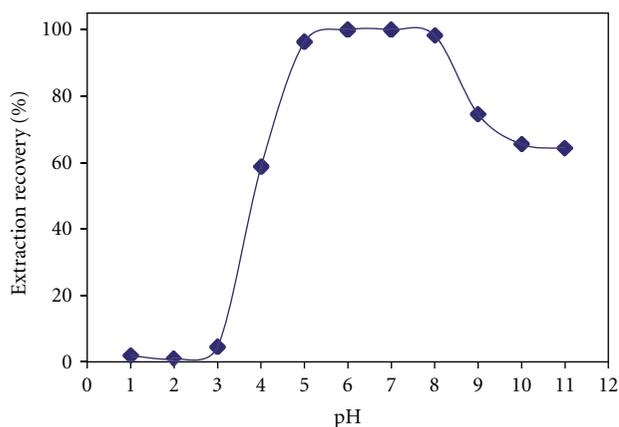


FIGURE 1: Effect of pH on the extraction recovery of copper. Extraction conditions: water sample volume, 5.0 mL; DPC,  $2 \times 10^{-3} \text{ mol L}^{-1}$ ; extraction solvent (chloroform) volume,  $60 \mu\text{L}$ ; dispersive solvent (ethanol) volume, 0.5 mL; concentration of copper,  $100 \mu\text{g L}^{-1}$ .

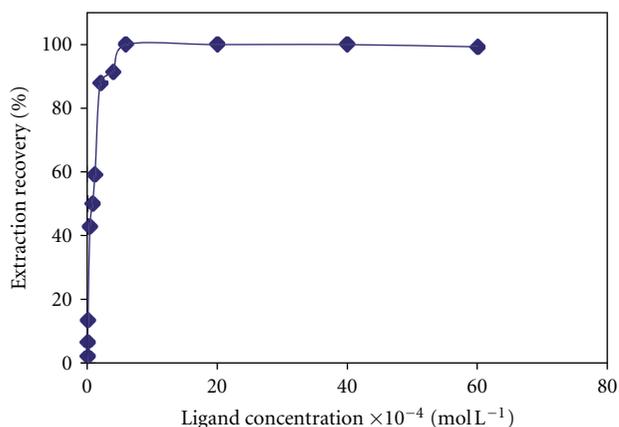


FIGURE 2: Effect of DPC concentration on the extraction recovery of copper. Extraction conditions: water sample volume, 5.0 mL; pH = 6; extraction solvent (chloroform) volume,  $60 \mu\text{L}$ ; dispersive solvent (ethanol) volume, 0.5 mL; concentration of copper,  $100 \mu\text{g L}^{-1}$ .

**3.2. Effect of DPC Concentration.** The influence of the amount of DPC was also evaluated in the range from  $4.0 \times 10^{-6}$ – $6.0 \times 10^{-3} \text{ mol L}^{-1}$ . The results are shown in Figure 2. It was observed that copper extraction improved, by increasing the DPC concentration, up to  $6.0 \times 10^{-4} \text{ mol L}^{-1}$  and remained constant. Lower extraction recovery at a concentration below  $6.0 \times 10^{-4} \text{ mol L}^{-1}$  is due to insufficient DPC concentration and incomplete formation of the complex. No significant changes were observed when higher concentrations of DPC were employed. Thus,  $2.0 \times 10^{-3} \text{ mol L}^{-1}$  DPC was chosen as the optimum to account for other extractable species.

**3.3. Selection of Extraction Solvent.** The type of extraction solvent used in DLLME is of essential consideration for efficient extraction. It should have low volatility, low toxicity,

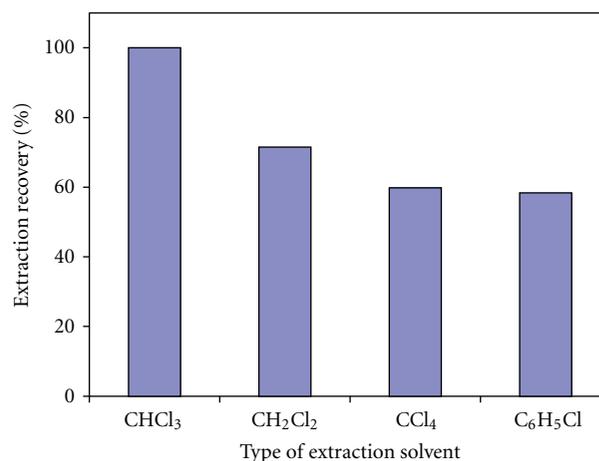


FIGURE 3: Effect of type of the extraction solvent on the extraction recovery of copper. Extraction conditions: water sample volume, 5.0 mL; pH = 6; DPC concentration,  $2 \times 10^{-3} \text{ mol L}^{-1}$ ; dispersive solvent (ethanol) volume, 0.5 mL; extraction solvent volume,  $60 \mu\text{L}$ ; concentration of copper,  $100 \mu\text{g L}^{-1}$ .

low water solubility and must not interfere with the analytical techniques used for the determination of analytes [18]. In the proposed method, the selected solvent also should have a density higher than water in order to sediment after centrifugation. Chlorobenzene (density,  $1.11 \text{ g mL}^{-1}$ ), carbon tetrachloride (density,  $1.59 \text{ g mL}^{-1}$ ), dichloromethane (density,  $1.32 \text{ g mL}^{-1}$ ), and chloroform (density,  $1.48 \text{ g mL}^{-1}$ ) were studied as extraction solvents using a mixture of 0.5 mL ethanol and  $60 \mu\text{L}$  of each extraction solvent. After DLLME, sedimented phase was made up to  $200 \mu\text{L}$  by adding acidic methanol and the solution was analyzed by FAAS. Figure 3 shows the effect of the type of extraction solvent on the extraction recovery of copper. As can be seen, recovery with chloroform is quantitative. Therefore, chloroform was selected as the extraction solvent for further experiments.

**3.4. Effect of the Volume of Extraction Solvent.** In order to examine the effect of the extraction solvent volume, solutions containing different volumes of chloroform (ranging from 40 to  $200 \mu\text{L}$ ) were subjected to the same DLLME procedure. The results are shown in Figure 4. According to results, by increasing the volume of chloroform from 40 to  $60 \mu\text{L}$ , the extraction recovery increased and then remained constant. It is clear that in solutions with low volumes of chloroform (lower than  $60 \mu\text{L}$ ) the amount of chloroform is not enough for the complete extraction of copper, hence, extraction recovery is low. Thereby,  $60 \mu\text{L}$  chloroform was used as extraction solvent in the subsequent experiments.

**3.5. Selection of Dispersive Solvent.** In DLLME, selecting an appropriate dispersive solvent is important, since dispersive solvent should be miscible with both extraction solvent and aqueous sample. For the sake of acquiring the most suitable dispersive solvent, four kinds of dispersive solvents, namely, acetonitrile, acetone, ethanol, and methanol were studied. Figure 5 shows the effect of the kind of dispersive solvent

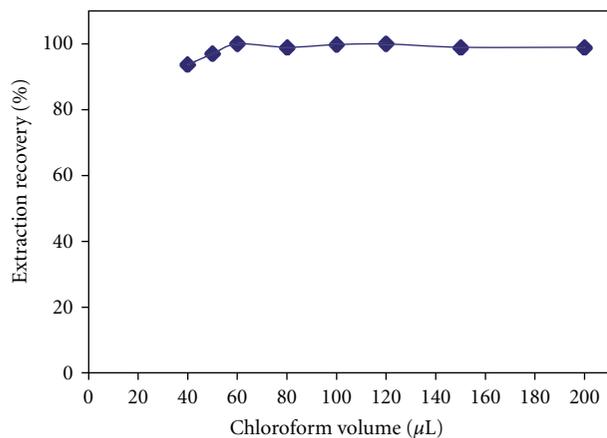


FIGURE 4: Effect of the volume of extraction solvent on the extraction recovery of copper. Extraction conditions: water sample volume, 5.0 mL; pH = 6; DPC concentration,  $2 \times 10^{-3} \text{ mol L}^{-1}$ ; extraction solvent, chloroform; dispersive solvent (ethanol) volume, 0.5 mL; concentration of copper,  $100 \mu\text{g L}^{-1}$ .

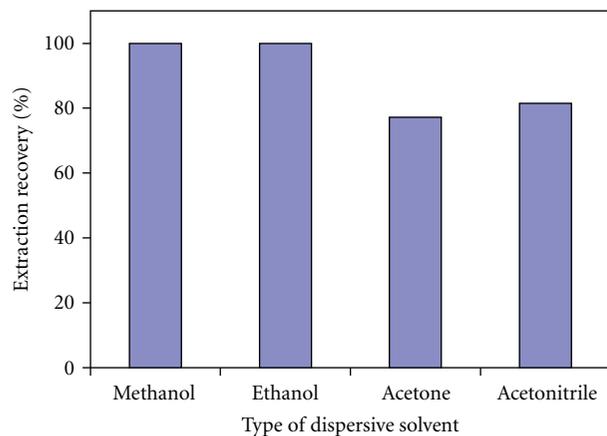


FIGURE 5: Effect of type of the dispersive solvent on the extraction recovery of copper. Extraction conditions: water sample volume, 5.0 mL; pH = 6; DPC concentration,  $2 \times 10^{-3} \text{ mol L}^{-1}$ ; extraction solvent (chloroform) volume,  $60 \mu\text{L}$ ; dispersive solvent volume, 0.5 mL; concentration of copper,  $100 \mu\text{g L}^{-1}$ .

on the extraction recovery of copper. It could be seen that ethanol and methanol could give the highest extraction recovery of the target analyte. Therefore, ethanol was selected as the dispersive solvent because of lower toxicity.

**3.6. Effect of the Volume of Dispersive Solvent.** The volume of dispersive solvent directly affects extraction solvent solubility in aqueous phase, thus, influencing the efficiency of the microextraction technique. Thus, ethanol volumes ranging within 0.25–1.5 mL were assayed. As can be seen from Figure 6, the extraction recovery reached its maximum value at 0.5 mL of the ethanol and then decreased by further increase in its volume. At low volume, ethanol could not disperse chloroform properly and the cloudy solution was not formed completely; at high volume, the solubility of the complex in

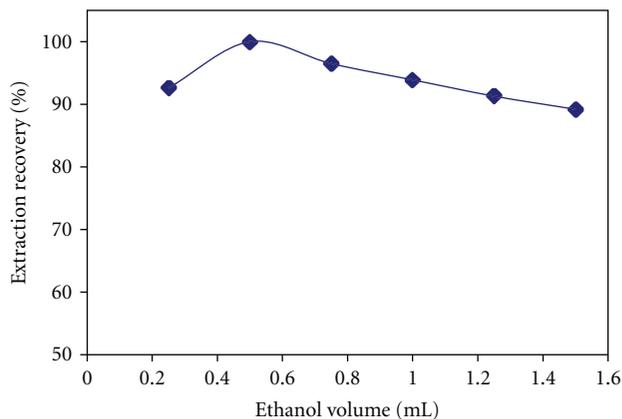


FIGURE 6: Effect of the volume of dispersive solvent on the extraction recovery of copper. Extraction conditions: water sample volume, 5.0 mL; pH = 6; DPC concentration,  $2 \times 10^{-3} \text{ mol L}^{-1}$ ; extraction solvent (chloroform) volume,  $60 \mu\text{L}$ ; dispersive solvent, ethanol; concentration of copper,  $100 \mu\text{g L}^{-1}$ .

water increased by the increase in the volume of ethanol. Therefore, 0.5 mL of ethanol was selected as the optimum volume of dispersive solvent.

**3.7. Effect of Extraction Time.** Extraction time is an important factor influencing the extraction recovery. In DLLME, extraction time is defined as the time between the injection of the mixture of dispersive and extraction solvent, and starting to centrifuge [18]. The effect of the extraction time on the extraction recovery of copper was investigated with the time varying from 0 to 30 min and the results displayed that the extraction time has no significant influence on the recovery of the analyte. This means that after the formation of the cloudy solution, the complex of metal ions and chelating reagent was formed instantly and, then, diffused into organic solvent quickly. Therefore, DLLME is a kind of fast equilibrium extraction technique.

**3.8. Effect of Centrifuging Rate and Time.** To achieve a good separation result, the effect of centrifugation rate and time on the extraction recovery was studied. The effect of centrifugation rate was investigated within the range of 1000–6000 rpm. It was found that over 4000 rpm, the organic phase completely settled; therefore, the rate of 5000 rpm was selected as the optimum point.

At the optimum rate, recovery was examined as a function of centrifugation time. Over 4 min, recovery was constant, indicating a complete transfer of the organic phase to the bottom of the centrifuge tube. So, the optimum centrifugation time was chosen as 5 min.

**3.9. Influence of Ionic Strength.** In order to investigate the influence of the ionic strength on the DLLME performance, several experiments were performed with different  $\text{KNO}_3$  concentrations (0.0–0.8  $\text{mol L}^{-1}$ ) while keeping other experimental parameters constant. According to the obtained experimental results, salt addition has no significant effect on

extraction recovery. Therefore, all the extraction experiments were carried out without adding salt.

**3.10. Interference Effects.** The effect of concomitant ions regularly found in natural water samples was evaluated by analyzing 5 mL of  $100 \mu\text{g L}^{-1}$  copper solution containing concomitant ions at different concentrations, and following the recommended extraction procedure. A variation on the recovery higher than  $\pm 5\%$  was considered as interference. The results have showed that a 1000-fold excess of alkali and alkaline earth cations (Na(I), K(I), Li(I), Ca(II)) and common anions (nitrate, iodide, bromide and phosphate); a 100-fold excess of cations Mn (II), Cd (II), Cr (VI), Ba (II), Co (II), Fe (III), Fe (II), Ag(I); a 80-fold excess of cation Mg (II); and a 50-fold excess of cations Pb (II), Cr (III), Al (III), Zn (II), Ni (II) did not affect the copper recovery. The above results indicate that none of the ions examined interfere in the extraction and determination of copper; thus, the developed method is applicable to the analysis of copper in various water samples.

**3.11. Analytical Performance and Comparison with Other Methods.** For the purpose of quantitative analysis, a calibration curve for copper was obtained by spiking the standards directly into distilled water and was extracted under optimal conditions. Linearity was observed over the range of  $10\text{--}200 \mu\text{g L}^{-1}$  with a correlative coefficient ( $R^2$ ) of 0.9964. The limit of detection (LOD), based on a signal-to-noise ratio (S/N) of 3, was  $2 \mu\text{g L}^{-1}$ . The precision of this method was determined by analyzing standard solution at  $100 \mu\text{g L}^{-1}$  of copper for ten times continuously, and the relative standard deviation (RSD) was 2.5%. The preconcentration factor was 25 for 5.0 mL sample solution.

As shown in Table 1, in comparison with other reported methods, the proposed method has low LOD and a good preconcentration factor. The method developed in this work is proposed as a suitable alternative to more expensive instruments for copper determination at trace levels. This methodology is a reproducible, simple, and low cost technique and does not require further instrumentation. These characteristics are of great interest for the routine laboratories in the trace analysis of metal ions.

**3.12. Analysis of Real Samples.** The proposed procedure has been applied to the determination of copper content in different water samples (tap, mineral, river, and sea water samples). The results are given in Table 2. According to the results, the concentration of copper in the analyzed water samples was below the LOD of the method.

The suitability of the proposed method for the analysis of natural water samples was checked by spiking samples with 50 and  $100 \mu\text{g L}^{-1}$  of copper. The results were tabulated in Table 2. According this table, the added copper ion can be quantitatively recovered from the water samples by the proposed procedure. These results demonstrate the applicability of the procedure for copper evaluation in water samples. The

recovery of copper added to the samples demonstrates the efficiency of the proposed method.

## 4. Conclusions

This work has been demonstrated as a new method of dispersive liquid phase microextraction combined with FAAS for the determination of copper in various water samples. This method is simple, rapid, and inexpensive and has a lower limit of detection and higher enrichment factor over other reported methods in the references. Especially, sample preparation time and consumption of toxic organic solvents are minimized in this method without affecting the sensitivity of the method. This is a novel method and is suitable for the simple and accurate evaluation of this element in a variety of water samples with satisfactory results.

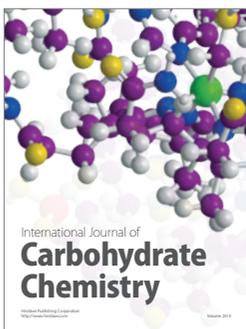
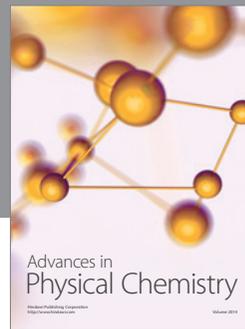
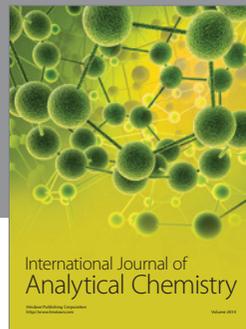
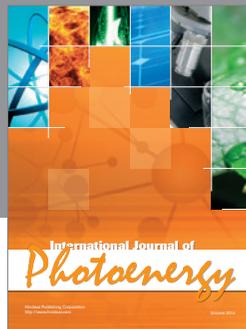
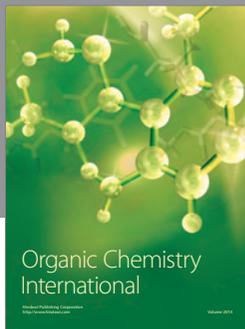
## Acknowledgment

The author thanks the research council at the Payame Noor University for financial support.

## References

- [1] Y. Saito, I. Ueta, M. Ogawa, M. Hayashida, and K. Jinno, "Miniaturized sample preparation needle: a versatile design for the rapid analysis of smoking-related compounds in hair and air samples," *Journal of Pharmaceutical and Biomedical Analysis*, vol. 44, no. 1, pp. 1–7, 2007.
- [2] M. Miro, J. M. Estela, and V. Cerda, "Recent advances in on-line solvent extraction exploiting flow injection/sequential injection analysis," *Current Analytical Chemistry*, vol. 1, no. 3, pp. 329–343, 2005.
- [3] A. N. Anthemidis and I. S. I. Adam, "Development of on-line single-drop micro-extraction sequential injection system for electrothermal atomic absorption spectrometric determination of trace metals," *Analytica Chimica Acta*, vol. 632, no. 2, pp. 216–220, 2009.
- [4] M. O. Luconi, M. Fernanda Silva, R. A. Olsina, and L. P. Fernández, "Cloud point extraction of lead in saliva via use of nonionic PONPE 7.5 without added chelating agents," *Talanta*, vol. 51, no. 1, pp. 123–129, 2000.
- [5] J. Chen and K. C. Teo, "Determination of cadmium, copper, lead and zinc in water samples by flame atomic absorption spectrometry after cloud point extraction," *Analytica Chimica Acta*, vol. 450, no. 1–2, pp. 215–222, 2001.
- [6] A. R. Ghiasvand, S. Shadabi, E. Mohagheghzadeh, and P. Hashemi, "Homogeneous liquid-liquid extraction method for the selective separation and preconcentration of ultra trace molybdenum," *Talanta*, vol. 66, no. 4, pp. 912–916, 2005.
- [7] H. Ebrahimzadeh, Y. Yamini, F. Kamare, and S. Shariati, "Homogeneous liquid-liquid extraction of trace amounts of mononitrotoluenes from waste water samples," *Analytica Chimica Acta*, vol. 549, no. 1, pp. 93–100, 2007.
- [8] F. Ahmadi, Y. Assadi, M. R. Milani, and M. Rezaee, "Determination of organophosphorus pesticides in water samples by single drop microextraction and gas chromatography-flame photometric detector," *Journal of Chromatography A*, vol. 1101, no. 1–2, pp. 307–312, 2006.

- [9] M. R. Khalili, Y. Yamini, S. Shariati, and J. A. Jonsson, "A new liquid-phase microextraction method based on solidification of floating organic drop," *Analytica Chimica Acta*, vol. 585, no. 2, pp. 286–293, 2007.
- [10] D. Djozan, Y. Assadi, and S. Hosseinzadeh, "Anodized aluminum wire as a solid-phase microextraction fiber," *Analytical Chemistry*, vol. 73, no. 16, pp. 4054–4058, 2001.
- [11] A. P. S. Gonz ales, M. A. Firmino, C. S. Nomura, F. R. P. Rocha, P. V. Oliveira, and I. Gaubeur, "Peat as a natural solid-phase for copper preconcentration and determination in a multicommutated flow system coupled to flame atomic absorption spectrometry," *Analytica Chimica Acta*, vol. 636, no. 2, pp. 198–204, 2009.
- [12] F. Sabermahani and M. A. Taher, "Application of a new water-soluble polyethylenimine polymer sorbent for simultaneous separation and preconcentration of trace amounts of copper and manganese and their determination by atomic absorption spectrophotometry," *Analytica Chimica Acta*, vol. 565, no. 2, pp. 152–156, 2006.
- [13] S. Walas, A. Tobiasz, M. Gawin, B. Trzewik, M. Strojny, and H. Mrowiec, "Application of a metal ion-imprinted polymer based on salen-Cu complex to flow injection preconcentration and FAAS determination of copper," *Talanta*, vol. 76, no. 1, pp. 96–101, 2008.
- [14] P. Liang and J. Yang, "Cloud point extraction preconcentration and spectrophotometric determination of copper in food and water samples using amino acid as the complexing agent," *Journal of Food Composition and Analysis*, vol. 23, no. 1, pp. 95–99, 2010.
- [15] N. Aydemir, N. Tokman, A. T. Akarsubasi, A. Baysal, and S. Akman, "Determination of some trace elements by flame atomic absorption spectrometry after preconcentration and separation by *Escherichia coli* immobilized on multiwalled carbon nanotubes," *Microchimica Acta*, vol. 175, no. 1-2, pp. 185–191, 2011.
- [16] E. Moniri, H. A. Panahi, M. Karimi, N. A. Rajabi, M. Faridi, and M. Manoochehri, "Modification and characterization of amberlite XAD-2 with calcein blue for preconcentration and determination of copper(II) from environmental samples by atomic absorption spectroscopy," *Korean Journal of Chemical Engineering*, vol. 28, no. 7, pp. 1523–1531, 2011.
- [17] J. L. Manzoori, M. Amjadi, and M. Darvishnejad, "Separation and preconcentration of trace quantities of copper ion using modified alumina nanoparticles, and its determination by flame atomic absorption spectrometry," *Microchimica Acta*, vol. 176, p. 437, 2011.
- [18] M. Rezaee, Y. Assadi, M. R. Milani Hosseini, E. Aghaee, F. Ahmadi, and S. Berijani, "Determination of organic compounds in water using dispersive liquid-liquid microextraction," *Journal of Chromatography A*, vol. 1116, no. 1-2, pp. 1–9, 2006.
- [19] F. Pena-Pereira, I. Lavilla, and C. Bendicho, "Miniaturized preconcentration methods based on liquid-liquid extraction and their application in inorganic ultratrace analysis and speciation: a review," *Spectrochimica Acta B*, vol. 64, no. 1, pp. 1–15, 2009.
- [20] E. Zeini Jahromi, A. Bidari, Y. Assadi, M. R. Milani Hosseini, and M. R. Jamali, "Dispersive liquid-liquid microextraction combined with graphite furnace atomic absorption spectrometry. Ultra trace determination of cadmium in water samples," *Analytica Chimica Acta*, vol. 585, no. 2, pp. 305–311, 2007.
- [21] R. R. Kozani, Y. Assadi, F. Shemirani, M. R. Milani Hosseini, and M. R. Jamali, "Determination of trihalomethanes in drinking water by dispersive liquid-liquid microextraction then gas chromatography with electron-capture detection," *Chromatographia*, vol. 66, no. 1-2, pp. 81–86, 2007.
- [22] C. Baird, *Environmental Chemistry*, Freeman and Longman, Essex, UK, 2nd edition, 1999.
- [23] H. A. McKenzie and L. E. Smythe, *Quantitative Trace Analysis of Biological Materials*, Elsevier, Amsterdam, The Netherlands, 1988.
- [24] J. Szpunar, J. Bettmer, M. Robert et al., "Validation of the determination of copper and zinc in blood plasma and urine by ICP MS with cross-flow and direct injection nebulization," *Talanta*, vol. 44, no. 8, pp. 1389–1396, 1997.
- [25] K. Sreenivasa Rao, T. Balaji, T. Prasada Rao, Y. Babu, and G. R. K. Naidu, "Determination of iron, cobalt, nickel, manganese, zinc, copper, cadmium and lead in human hair by inductively coupled plasma-atomic emission spectrometry," *Spectrochimica Acta B*, vol. 57, no. 8, pp. 1333–1338, 2002.
- [26] R. J. Cassella, O. I. B. Magalh es, M. T. Couto, E. L. S. Lima, M. A. F. S. Neves, and F. M. B. Coutinho, "Synthesis and application of a functionalized resin for flow injection/F AAS copper determination in waters," *Talanta*, vol. 67, no. 1, pp. 121–128, 2005.
- [27] C. A. Sahin, I. Tokgoz, and S. Bektas, "Preconcentration and determination of iron and copper in spice samples by cloud point extraction and flow injection flame atomic absorption spectrometry," *Journal of Hazardous Materials*, vol. 181, no. 1–3, pp. 359–365, 2010.
- [28] R. Manjusha, K. Dash, and D. Karunasagar, "UV-photolysis assisted digestion of food samples for the determination of selenium by electrothermal atomic absorption spectrometry (ETAAS)," *Food Chemistry*, vol. 105, no. 1, pp. 260–265, 2007.
- [29] S. Abbasi, H. Khani, and R. Tabaraki, "Determination of ultra trace levels of copper in food samples by a highly sensitive adsorptive stripping voltammetric method," *Food Chemistry*, vol. 123, no. 2, pp. 507–512, 2010.
- [30] M. Ghaedi, M. R. Fathi, F. Marahel, and F. Ahmadi, "Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry," *Fresenius Environmental Bulletin*, vol. 14, no. 12, pp. 1158–1163, 2005.
- [31] Y. Efendioglu, M. Yagan, and B. Batı, "Bi(III)4-methylpiperidinedithiocarbamate coprecipitation procedure for separation-pre-concentration of trace metal ions in water samples by flame atomic absorption spectrometric determination," *Journal of Hazardous Materials*, vol. 149, no. 1, pp. 160–165, 2007.
- [32] M. T. Naseri, P. Hemmatkhan, M. R. M. Hosseini, and Y. Assadi, "Combination of dispersive liquid-liquid microextraction with flame atomic absorption spectrometry using microsample introduction for determination of lead in water samples," *Analytica Chimica Acta*, vol. 610, no. 1, pp. 135–141, 2008.



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

