Cloud-Point Extraction for On-Line Trace Determination of Copper(II) by Flame Atomic Absorption Spectrometry

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A cloud point extraction-flow injection procedure is proposed for on-line determination of trace amounts of copper(II) by flame atomic absorption spectrometry. Copper(II) was extracted using the non-ionic surfactant, Triton X-114 after complex formation with N-phenyl benzohydroxamic acid at pH 5 in the presence of sodium sulfate as a salting-out agent at 25 °C. After the cloud point having been obtained in the reaction coil at room temperature, the surfactant-rich phase containing the complex was collected in a mini-column packed with cotton. Then, the complex was eluted into the nebulizer of flame atomic absorption spectrometer by passing ethanol containing 1% (v/v) nitric acid. The chemical and flow variables including pH, reagent and surfactant concentrations, sample and eluent flow rates affecting the extraction and determination were optimized and the enhancement factor was estimated to be 45. The sample throughput (15 h^{-1}) was greater than batch technique. The calibration graph was linear in the range of 5-220 μg l^{-1}. A good precision for 50 μg l^{-1} copper(II) (1.9% RSD, n = 8) and detection limit ($3S_b$ m^{-1}) 1.00 μg l^{-1} were obtained. The accuracy was assessed by the analysis of a standard reference material (NBS-364) and the obtained results were in good agreement with certified amounts of copper. The proposed method was applied to the determination of copper(II) in water and hair samples.

Keywords: Salt induced cloud point extraction, Flow injection, Copper(II), FAAS

INTRODUCTION

Although trace amount of copper is vital for many biological systems, its higher concentration is considered as a widespread anthropogenic pollutant [1,2]. Thus, its determination at trace level is important due to the increasing concern for environmental pollution.

Analytical techniques such as electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma mass spectrometry (ICP-MS) are the techniques available for direct determination of trace metals with sufficient sensitivity. Flame atomic absorption spectrometry (FAAS) is a more readily accessible technique and has wide applications for determination of metal ions in solutions, because of its speed and availability in most routine laboratories [3]. The technique is less subject to interferences than are ETAAS and ICP-MS. However, it has the major drawback of low sensitivity for direct determination of metals in many matrices. Therefore, for ultra trace determination of metals, a preconcentration and matrix elimination steps are required.

Liquid-liquid extraction (LLE) [4] and solid phase extraction (SPE) using different modified sorbents [5-8] are widely used for this purpose. Cloud point extraction (CPE) is a green method because, unlike organic solvents used in LLE, surfactants are non-toxic, non-volatile and nonflammable. Another advantage of CPE is the high preconcentration factor that can be obtained starting from the small initial volumes of

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the sample and by collecting the metal in a small volume (≈0.5 ml) of the surfactant phase [9-12]. A considerable interest in the micellar extractions of trace metal ions is expressed in the literature [13-17]. However, the laborious sample preparation and calibration procedures for manual batch operations are not attractive.

Flow-injection analysis (FIA) is a powerful tool for automatic rapid sample pretreatment and non-chromatographic separation before analyte is determined by a variety of methods [18]. Moreover, in on-line FI-CPE, the centrifugation procedure is avoided, making the extraction simpler and the analysis time shorter [19,26]. According to most on-line CPE reports in the literature, spectrophotometric and chemiluminescence detection techniques have been used for this purpose [19-21]. Flow injection atomic absorption spectrometric (FIAAS) systems offer an improvement in nebulization efficiency and the ability to easily adjust the signal magnitude [22]. The most common sample pretreatment method used in FIAAS systems is on-line solid phase extraction [23-25], where the analysis is relatively fast, but the sorbent modification and conditioning are time consuming. Recently, we reported the use of dithizone as a complexing agent for CPE-FIAAS of silver ions, where the cloud point and phase separation were obtained at 40 °C [26].

In order to achieve a considerable distribution ratio of the metal ion and consequently an efficient extraction, a lipophilic regent is required. Hydroxamic acids are important group of reagents in analytical chemistry, which form lipophilic complexes with metal ions and have been used in separation and determination of several metal ions [27,28]. No attempt has been made for the use of hydroxamic acids, especially N-phenylbenzohydroxamic acid (PBHA) as complexing agent in CPE-FIAAS of metal ions. The present work aimed at investigating the ability of PBHA as a chelating agent for on-line CPE-FIAAS extractive determination of copper as well as the effect of the salting-out agent on the extraction efficiency at room temperature rather than elevated temperature. The time of analysis and sample throughput for FI-CPE were compared with that of conventional manual CPE.

EXPERIMENTAL

Apparatus

A Varian Model SpectrAA220 (Mulgrave, Vic., Australia)

flame atomic absorption spectrometer equipped with a deuterium lamp background corrector was used for the analysis of copper(II). A copper hollow cathode lamp operating at 324.7 nm was used as the radiation source. The operating conditions were those recommended by the manufacturer, unless specified otherwise.

A peristaltic pump (Alitea C-6 XV, Sweden) furnished with silicon tubes were used to propel the solutions. The reaction coil was of PTFE tubing (i.d. 0.5 mm). A mini-column (collection column, CC), consisting of a cylindrical glass tube (3 cm × 4 mm) packed with cotton, was used as FIA sample loop. A six-channel rotary valve was used for loading/ injection steps. A Julabo MP5 thermostatic bath was operated to reach the cloud point temperature when the room temperature was below 25 °C. The pH measurements were accomplished with a Metrohm model 692 pH/ion meter furnished with a combined glass electrode.

Reagents

All chemicals and reagents were of analytical reagent (AR) grade, and all aqueous solutions were prepared in doubly distilled de-ionized water. Triton X-114 was obtained from Fluka and used as received. The stock standard solution of copper(II) (1000 mg l^{-1}) and the salts Na_2SO_4, NaCl and $NaNO_3$ were obtained from Merck (Darmstadt, Germany). The solutions of other metal ions were prepared from their respective salts. Working standard solutions were prepared by appropriate dilution of the stock standard solutions. PBHA was synthesized by the reaction of N-phenyl hydroxylamine and benzoyl chloride [29], and its solution (1×10^{-2} M) was prepared by dissolving 0.106 g of the reagent in 15 ml absolute ethanol diluted to 50 ml with distilled water. Acetate buffer solution (pH 5) was prepared by mixing appropriate volumes of sodium acetate (0.1 M) and hydrochloric acid (0.1 M) solutions. A low-alloy steel sample *i.e.* NBS-364 was obtained from National Bureau of Standards, USA.

Procedure

The FIA system was operated in the time-based mode as follows: In the extraction stage (Fig. 1a), the sample or standard solution containing the analyte (5-220 μg l^{-1}), 0.06% (v/v) Triton X-114 and PBHA (1×10^{-4} M), whose pH was adjusted to 5 by using acetate buffer, was loaded into FI manifold for 2.0 min at the rate of 5 ml min^{-1}. The sample
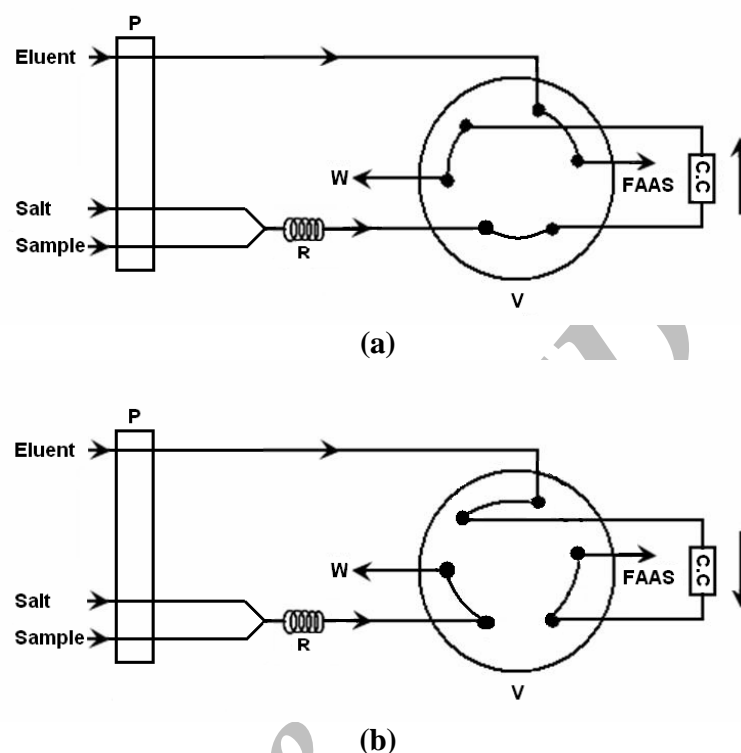
Fig. 1. Schematic diagram of the CPE- FIAAS manifold for the preconcentration and determination of copper(II). P: peristaltic pump; R: reactor; V: valve; FAAS: flame atomic absorption spectrometer; CC: collection column; W: waste. Valve in the (a) loading position and (b) elution position.

solution was merged with the sodium sulfate solution (5 ml min^{-1}) to decrease the cloud point temperature of Triton X-114 below the room temperature, and to facilitate phase separation inside the reaction coil (R) at 25 °C (optimum temperature to obtain the cloud point). The mixture then passed through the CC, where the surfactant-rich phase containing the complex was collected, while the aqueous phase was discharged (W). After completion of sample loading, the valve was switched on to the injection position (Fig. 1b) for 5 s, and the complex in the CC was eluted with ethanol containing 1% (v/v) nitric acid (5 ml min^{-1}) in the reverse direction (to minimize the dispersion), and carried into the nebulizer of FAAS. The absorption signals were processed at the peak height mode by using the instrument software. The average values of peak height were obtained for three replicate measurements.

Sample Preparation

Water samples (tap, river, spring and sea waters) were filtered through a 0.45 μm pore size nylon filter to remove any suspended particulate matter. 10 ml of each sample was analyzed by the proposed method.

Dark hair sample was collected from the vertex of the scalp of a 30-year-old man. The sample was washed according to the procedure proposed by the International Atomic Energy Agency (IAEA) [30]. 1.0 g of dried sample was digested as reported elsewhere [14]. 10 ml aliquots of the final clear solution obtained were analyzed by the prescribed procedure.

Standard alloy sample (0.05 g) was dissolved in 10 ml nitric acid (65%) and 10 ml concentrated perchloric acid in a Pyrex beaker on a hot plate (220 °C). The solution was heated to near dryness and, after cooling to room temperature, the contents were transferred into a 250 ml calibrated flask using small portions of 0.1% HNO_3. The volume was made up to the mark with 0.1% HNO_3 in the presence of 0.2% sodium fluoride to mask iron.

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RESULTS AND DISCUSSION

Optimization of Chemical Variables

PBHA is an acidic reagent (pK_a, 8.15) and its dissociation equilibrium depends on the pK value as well as pH of the solution. Hence, its complex formation and extraction behavior is also pH dependent. The effect of pH of the sample solution on the peak absorption was studied in the pH range of 1 to11 by using HCl (0.1 M) and NaOH (0.1 M). As can be seen from Fig. 2, pH 3-7 is the optimum range for copper(II) extraction. At pH values lower than 3 the ligand is protonated, hence the extraction yield and consequently the absorbance decrease, while at pH values higher than 8 the decrease in absorbance can be attributed to both dissociation of PBHA and hydrolysis of copper ion. However, pH 5 was chosen to enhance the selective extraction of copper(II) from its co-existing metal ions such as Fe(III), Zn(II), Co(II), Ni(II) and Pb(II).

The amount of chelating reagent is one of the factors affecting the kinetics of chelate formation and extraction efficiency of metal ion, hence the influence of PBHA concentration on the extraction efficiency of copper(II) was investigated in the range of 2×10^{-5}-5×10^{-4} M. It was observed that the extraction yield and absorbance signal of copper increased with increasing the concentration of the reagent. At concentrations higher than 0.6×10^{-4} M the absorbance signal showed insignificant changes, hence 1×10^{-4} M was used in subsequent experiments to assure efficient extractions.

The effect of surfactant concentration was investigated on both FI-CPE and manual CPE. In the former case, it was found that the maximum absorbance was obtained for 0.06% (v/v) Triton X-114 and larger concentrations led to the decrease in absorbance signals. Larger concentrations increased the volume of surfactant-rich phase within the mini-column, resulting in dilution of the extracted sample; therefore, 0.06% (v/v) Triton X-114 was chosen. In the latter case using 15 ml sample solution with the same pH and PBHA concentration as that in FI-CPE, the highest absorbance signal was obtained with 0.2% (v/v) Triton X-114 after 5 min equilibration at 40 °C. Since the volume of surfactant-rich phase is proportional to the surfactant concentration in the original solution, higher preconcentration factor is expected from FI-CPE [19]. The cloud point temperature (CPT) of
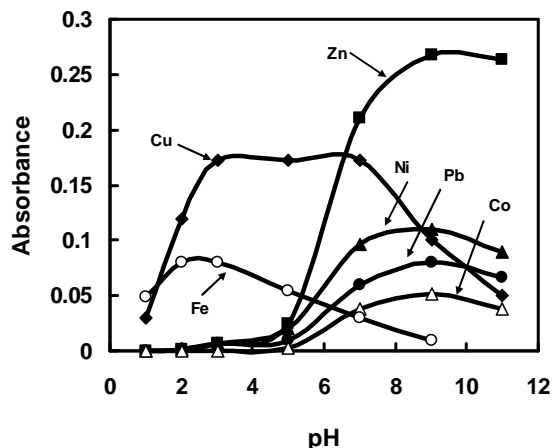

Fig. 2. Effect of pH on the extraction/preconcentration of copper(II), Ni(II), Pb(II), Co(II), Fe(III) (80 μg l^{-1} each) and Zn(II) (40 μg l^{-1}). Conditions: PBHA (1×10^{-4} M); Triton X-114 (0.07 %v/v); the flow parameters are same as Figs. 3 and 4.

Triton X-114 is 23-25 °C.

It is also known that the presence of organic polar solvents such as ethanol or acetone increase the CPT, though it can be expected to be compensated for by this organic solvent effect in the presence of an electrolyte. Therefore, the salting-out effect [31] was studied in both the absence and presence of different concentrations of $NaNO_3$, Na_2SO_4 and NaCl (0.05-1 M each) at 25 °C. It was found that Na_2SO_4 resulted in the highest absorption signal, and the signals increased with increasing the salt concentration. This effect must be due to the enhanced hydrophobic interactions among the surfactant aggregates and the analyte as well as the decrease in the cloud point temperature of Triton X-114 in the presence of Na_2SO_4. At higher concentrations than 0.4 M, the signals decreased considerably, hence 0.3 M was chosen as the optimum concentration. On the other hand, the absence of salt decreased the signal by 65%. It is interesting to note that high concentration of salt can increase the density of water drops accompanied by the surfactant rich phase, and hence disturb the phase separation. Reduction of signals in the absence of salt is due to an increase in cloud point temperature leading to incomplete phase separation at 25 °C.

Optimization of FI Variables

In our previous investigation into different filtering

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materials, it was found that cotton resulted in the best reproducibility [26]. Aliquots of standard solutions containing 80 μg l^{-1} of copper(II), 1×10^{-4} M PBHA, Triton X-114 (0.06% v/v) and Na_2SO_4 (0.3 M), buffered at pH 5 were passed through the column packed with cotton at the flow rate of 4 ml min^{-1} for 120 s. The retained complex was then eluted with ethanol containing 1% (v/v) nitric acid at the flow rate of 4 ml min^{-1} for 5 s.

The copper elution from the CC was studied using different solvents such as pure ethanol, methanol and their nitric acid solutions (0.1% to 3% v/v), at the rate of 4 ml min^{-1}. The complete elution and highest absorption signal were obtained with ethanol containing nitric acid. Since the concentration variation of nitric acid from 1% to 3% did not cause any significant change in the absorption signal, ethanol containing 1% (v/v) nitric acid was chosen for subsequent experiments (Fig. 3).

In FI-CPE, the extraction efficiency depends on the column length and the amount of cotton packed in the column. On the basis of our previously reported findings [26], a 3.0 cm column length was used in this work. The amount of cotton in the mini-column is important in collecting the surfactant-rich phase; hence, it was optimized for the selected column length by testing different amounts of dry cotton (50-100 mg). The best results were obtained when *ca.* 80 mg cotton leading to a column density of $\approx$0.21 mg mm^{-3}, was used. The larger amounts of cotton led to reduction of the signal due to the blockage of tubes and insufficient elution of the retained complex, while smaller amounts resulted in low absorbance due to inefficient collection.

The sample flow rate was studied in the range of 1 to 8 ml min^{-1}. It was observed that the analytical signals were constant up to the rate of 5 ml min^{-1} and decreased slightly by increasing the sample flow rate to above 6 ml min^{-1}, which must be due to the incomplete reaction in the coil as well as insufficient detainment of the micellar phase on the mini-column. So, the sample flow rate of 5 ml min^{-1} was selected for further studies to compromise for higher enrichment and shorter analytical time.

The performance of the flow system was investigated by varying the sample loading time from 30 to 240 s. The analytical signals increased with an increase in loading time up to 120 s, above which there was no significant change in
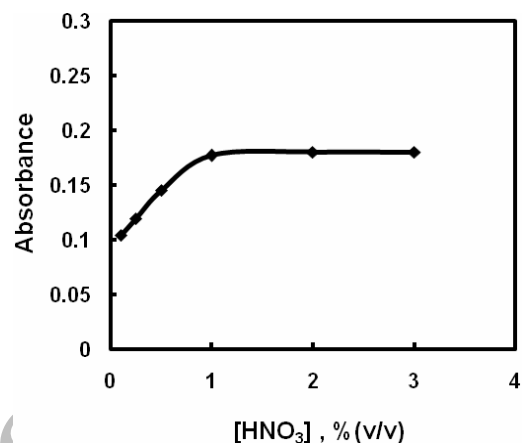

Fig. 3. Effect of HNO_3 concentration on the elution of copper. Conditions: initial concentration of copper(II), 80 μg l^{-1}; pH, 5; column, 3 cm $\times$ 4 mm packed with 75 mg cotton; sample flow rate, 4 ml min^{-1}; sample loading time, 120 s; eluent flow rate, 4 ml min^{-1}.

the signals (Fig. 4), which can be attributed to the adsorption saturation of the column. Hence, the loading time of 120 s was chosen.

The influence of elution rate was also investigated in the range of 2-8 ml min^{-1}. Figure 5 shows that the absorption peak increased with an increase in the flow rate and reached a maximum at flow rates in the range of 5-8 ml min^{-1}. At flow rates below 5 ml min^{-1}, the signal decreased considerably resulting in broader peaks. This must be due to the incompatibility between elution and nebulization flow rates, which can cause a significant dispersion when the eluent flow rate is smaller than the nebulizer flow rate. One may declare that the signals as well as the theoretical preconcentration factor ($V_{original}/V_{preconcentrated}$), could be enhanced at lower flow rates by using 10 cm straight tubing for connecting the valve to the nebulizer [22]. However, the lower elution flow rates increased the total analysis time. Hence, a flow rate of 5 ml min^{-1} was selected for elution.

Analytical Characteristics of the Method

The calibration graph was linear over the range of 0.005-0.220 μg ml^{-1} for 2 min of preconcentration time. The calibration graph equation obtained under the optimal
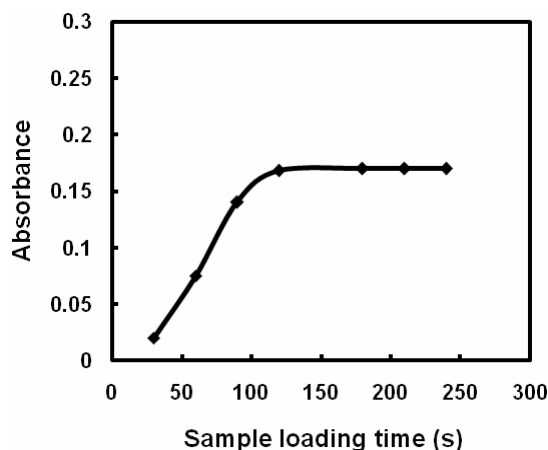
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Fig. 4. Effect of sample loading time on the absorbance of copper. Conditions: initial concentration of copper(II), 80 μg l^{-1}; pH, 5; column, 3 cm × 4 mm packed with 75 mg cotton; sample flow rate, 4 ml min^{-1}; eluent, 1% (v/v) HNO$_3$ in ethanol (4 ml min^{-1}).

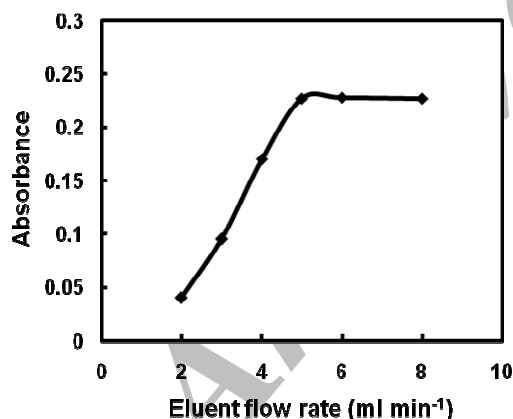**Fig. 5.** Effect of eluent flow rate on the absorbance of copper Conditions: initial concentration of copper(II), 80 μg l^{-1}; pH, 5; column, 3 cm × 4 mm packed with 80 mg cotton; sample flow rate, 5 ml min^{-1}; sample loading time, 120 s; eluent, 1% (v/v) HNO$_3$ in ethanol.

chemical and flow conditions was: A = 2.7905 ± 9.0 × 10^{-3}C + 0.0038 ± 1.0 × 10^{-3}, where C is the concentration of copper(II) in μg ml^{-1}, (R^2 = 0.9996). The precision for 8 replicate

measurements at 0.05 μg ml^{-1} was 1.9% relative standard deviation. The limit of detection (LOD), defined as C$_{LOD}$= 3S$_b$ m^{-1}, (where S$_b$ is the standard deviation of the blank (n = 8), and m is the slope of the calibration curve), was found to be 1.00 μg l^{-1}. The calibration graph was also obtained with standard solutions of copper(II) (in the concentration range of 0.3-10.0 μg ml^{-1}) without preconcentration, as A = 0.0607 ± 1.0 × 10^{-3} C + 0.0053 ± 4.2 × 10^{-3}, (R^2 = 0.9993). The RSD% and LOD were 1.0% (n = 6 at 5 μg ml^{-1} copper) and 230 μg l^{-1} (n = 6), respectively. The enhancement factor calculated as the ratio of the slopes of calibration curves obtained with and without preconcentration, and preconcentration factor were found to be 45 and 24, respectively for 10 ml sample solution. The sample throughput was 15 h^{-1}, (mean time of analysis 4 min).

Selectivity of the Method for Copper

In view of the high selectivity provided by FAAS, the interferences studied were those related to the extraction step, *i.e.* the co-existing metal ions and the cations that may react with PBHA, as well as the anions that may react with copper(II) and reduce the extraction efficiency. Accordingly, the method was applied to 10 ml of sample solutions containing 80 μg l^{-1} copper(II), 1 × 10^{-4} M PBHA and interferent ions in different interferent-to-analyte ratios in the presence of 0.06% (v/v) Triton X-114 at pH 5. Table 1, depicts the tolerance limits of the diverse ions, *i.e.* interferent-to-analyte ratios in which relative error was less than ±5%. As can be seen, Fe^{3+} interferes at low ratios. This interference can be eliminated in the presence of sodium fluoride as masking agent.

Determination of Copper in Real Samples and the Method Validation

In order to assess the applicability of the proposed method, it was applied to the samples of river water, sea water, spring water, tap water and human hair. The results are shown in Table 2. The validation of the method was performed by the recovery experiments for spiked samples (Table 2) as well as by the analysis of a standard reference material, NBS-364 with a copper content of 2.4 mg g^{-1}. The content of copper found by the present method was 2.30 ± 0.12 mg g^{-1} (t-test at P = 0.05, n = 3). The results obtained were in good agreement with the added and certified amounts of copper, which indicates the

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Table 1. Tolerance Limits of Diverse Ions in Determination of 80 μg l^{-1} of Copper

Tested ions	Mole ratio, Interferent/analyte[a]
Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, SCN$^-$	1000
CH$_3$COO$^-$, Cl$^-$, PO$_4^{3-}$	
Pb^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}	400
Ce(IV), Cd^{2+}, V(V)	60
U(VI), Mo(VI)	20
Fe^{3+}	3

[a]Highest ratio which gives an error less than 5%.

Table 2. Determination and Recovery of Copper(II) in Real Samples

Sample	Copper(II), (μg l^{-1})		Recovery (%)
	Added	Found	
Tap water[a]	-	30.5 ($\pm$0.7)[b]	-
	5	35.9 ($\pm$0.7)	101.1
	10	39.8 ($\pm$0.6)	98.3
River water[a]	-	6.5 ($\pm$0.9)	-
	5	11.2 ($\pm$0.7)	97.4
	10	16.7 ($\pm$0.6)	101.2
Spring water[c]	-	n.d[d]	-
	5	5.3 ($\pm$0.6)	106.0
	10	10.3 ($\pm$0.7)	103.0
Sea water[e]	-	n.d	-
	5	4.9 ($\pm$0.6)	98.0
	10	10.2 ($\pm$0.7)	102.0
	Copper(II), (μg g-1)		
Human hair[f]	-	9.0 ($\pm$ 0.9)	
	4.0	13.1 ($\pm$ 0.8)	100.7

[a]Samples from Zanjan city and province. [b]Values in the parentheses are standard deviations for triplicate analysis. [c]Sample collected from Cheshme gholamali, Ghazvin province. [d]Not detected. [e]Caspian sea water sample. [f]30-year-old man hair.

reliability and capability of the method for the determination of copper in real samples.

CONCLUSIONS

The lipophilicity of PBHA and its tolerance for the interferences caused by the co-existing metal ions make it feasible for CPE and selective towards copper(II). With the aid of salting-out effect, heating of the system was avoided and the cloud point was obtained at room temperature which consequently made the procedure more convenient as compared to our earlier reports [26,32]. The developed FIAAS

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Table 3. Comparison of the Present Method with Previously Reported Ones

Method	System	LR (µg l^{-1})	PF/EF	LOD (µg l^{-1})	S.V (ml)	RSD (%)	Ref.
On-line SPE/FAAS	C18/NN	-	19	2.00	3.25	1.7	[25]
SPE/Spect.	Neocuproine	3-100	-	1.13	500	-	[5]
CPE/FAAS	DDTP	5-200	-	0.94	10	3<	[14]
CPE/FAAS	MPKO	10-250	30	1.60	15	1.2	[15]
CPE/FIAAS	PBHA	5-220	45	1.00	10	1.9	This method

L.R: linear range; PF/EF: preconcentration/enhancement factor; S.V: sample volume; NN: 1-nitrozo-2-naphthol; Spect: spectrophotometry; MPKO: methyl-2-pyridylketone oxime; DDTP: O, *O*-diethyldithiophosphate.

system yielded good results in terms of selectivity, accuracy and precision for the rapid determination of copper(II) in real samples, which were compared with the previously reported methods. The results are presented in Table 3 [5,14,15,25]. As can be seen, our results are comparable with, and in some cases better than, the reported ones. The FI system in this work afforded a mean time of analysis of 4 min and a sample throughput of 15 h^{-1}, which is much better than the manual CPE performed here (mean time of analysis, 30 min; sample throughput, 2 h^{-1}). The limit of detection of the method can be lowered by using ETAAS or ICP-MS techniques.

ACKNOWLEDGEMENTS

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