



Cloud point extraction and flame atomic absorption spectrometry combination for copper(II) ion in environmental and biological samples

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ABSTRACT

A cloud point extraction procedure was presented for the preconcentration of copper(II) ion in various samples. After complexation by 4-(phenyl diazenyl) benzene-1,3-diamine (PDBDM) (chrysoidine), copper(II) ions were quantitatively recovered in Triton X-114 after centrifugation. 0.5 ml of methanol acidified with 1.0 mol L⁻¹ HNO₃ was added to the surfactant-rich phase prior to its analysis by flame atomic absorption spectrometry (FAAS). The influence of analytical parameters including ligand, Triton X-114 and HNO₃ concentrations, bath temperature, heating time, centrifuge rate and time were optimized. The effect of the matrix ions on the recovery of copper(II) ions was investigated. The detection limit (3S.D._b/m, n = 10) of 0.6 ng mL⁻¹ along with preconcentration factor of 30 and enrichment factor of 41.1 with R.S.D. of 1.0% for Cu was achieved. The proposed procedure was applied to the analysis of various environmental and biological samples.

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1. Introduction

Copper is an essential element for enzymes, but above a healthy limit it accumulates in the liver, causing diarrhea, vomiting, transpiration and, depending on its concentration, death from bleeding [1]. When levels of Cu exceed certain values, however, defense mechanisms to protect against excess Cu are overcome and toxicity results [2,3]. Frequently, a preconcentration step is required for the determination of ultra-trace amounts of copper by FAAS not only because the amount of the metal present in water samples may be close to or even below the detection limit but also because the matrix of saline water samples may cause serious interference [4–8].

Micelles and other organized amphiphilic assemblies are increasingly utilized in analytical chemistry especially in separation and preconcentration procedures. Their unique micro-heterogeneous structures capable of selective interaction with different solute molecules can strongly modify solubility, chemical equilibrium, kinetics and the spectroscopic properties of analytes and reagents [8–12]. Compared with other extraction methods such

as liquid–liquid extraction, cloud point extraction (CPE) exhibits much more environmentally friendly properties, and it is safer because small volumes of noxious surfactants are used instead of toxic organic solvents. The surfactant is easily introduced into FAAS by manual injection after diluting it with methanolic solution containing nitric acid. CPE is an attractive technique that reduces the consumption and exposures to a solvent and it also reduces disposal costs and extraction time that has been used for preconcentration of metal ions after the formation of sparingly water-soluble complexes [13–18]. Triton X-114 was chosen as the non-ionic surfactant because of its low cloud point temperature and high density of the surfactant-rich phase as well as its low cost commercially and lower toxicity. The efficiency of the cloud point extraction depends on the hydrophobicity of the ligand and of the complex formed, on the apparent equilibrium constants in the micellar medium and on the formation kinetics of the complex and on the transference between the phases [19,20].

Chrysoidine is used as a dye for silk and cotton; in oils, fats and waxes for polishes, paper, leather, inks, wood and biological stains [21]. It is also used to dye maggots used as fishing bait. Up to a threefold excess risk for using bronze maggots for more than 5 years was reported in one case–control study [22].

Therefore, in the present work using PDBDM, a simple, selective and sensitive CPE method for preconcentration and determination of copper(II) ions in various real samples has been established.

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2. Experimental

2.1. Reagents and materials

All chemicals used in this work were of analytical reagent grade and purchased from Merck (Darmstadt, Germany). They were used without further purification. Deionized water was used for all dilutions. Copper(II) ion standard solution was prepared by dissolving appropriate amount of nitrate salt of copper(II) ion. A 1.0% (v/v) Triton X-114 from E. Merck, Darmstadt, Germany was prepared by dissolving 1.0 mL of Triton X-114 in distilled water in 100 mL volumetric flask with stirring. 4-(Phenyl diazenyl) benzene-1,3-diamine (PDBDM) (chrysoidine) (molecular weight 262.74, dye content 97.5%, supplied by Loba Chemie) is used in this study. Methanol solvents were purchased from Merck Company. Cloud points of Triton X-114 in aqueous solution are 24 °C [23]. For all the experiments, surfactants and dye are used without further purification.

2.2. Instrumentation

A Shimadzu AA-680 atomic absorption spectrometer equipped with deuterium background correction and copper hollow-cathode lamp was used for absorbance measurements at wavelength of 324.8 nm according to instrument instruction. The instrumental parameters were adjusted according to the manufacturer's recommendations. A 30 E 148 Scheme fan or Hettich centrifuge was used to accelerate the phase separation process. A Metrohm 692 pH meter furnished with a combined glass-saturated calomel electrode was used for pH measurements.

2.3. Spectrophotometric titrations

Standard stock solutions of ligand ($1.0 \times 10^{-2} \text{ mol L}^{-1}$) and the Cu^{2+} ions ($1.0 \times 10^{-2} \text{ mol L}^{-1}$) were prepared by dissolving appropriate and exactly weighed (with an accuracy of $\pm 0.0001 \text{ g}$) amount of pure solid compounds in pre-calibrated 25.0 mL volumetric flasks and diluted to the mark with deionized water. Working solutions were prepared by appropriate dilution of the stock solutions. According to the spectra reported (Fig. 1), titration of the ligand solution ($8.0 \times 10^{-5} \text{ mol L}^{-1}$, 2.75 mL) was carried out by the addition of micro-liter amounts of a concentrated standard solution of the metal ion ($8.0 \times 10^{-4} \text{ mol L}^{-1}$) using a pre-calibrated micro-syringe, followed by absorbance intensity reading at $25.0 \pm 0.1 \text{ }^\circ\text{C}$ at the related λ_{max} 's (302 nm) (Fig. 1).

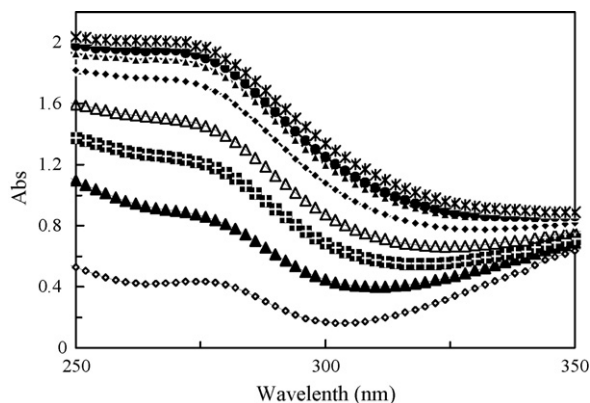
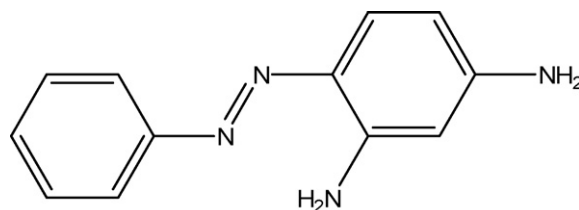


Fig. 1. Absorbance spectra of complex of PDBDM ($8.0 \times 10^{-5} \text{ mol L}^{-1}$) with copper(II) ion ($8.0 \times 10^{-5} \text{ mol L}^{-1}$) in pH 10.0 in different mole ratio.



Scheme 1. Structure of chrysoidine (PDBDM).

2.4. Procedure

A typical cloud point experiment required the following steps: an aliquot of 15 mL of a solution containing $0.13 \mu\text{g mL}^{-1}$ of copper(II) ion, 0.05% Triton X-114 and 0.15 mmol L^{-1} of PDBDM was adjusted to pH 10.0 with the addition of KOH. The mixture was shaken for 1 min and left to stand in a thermo-stated bath at 45 °C for 15 min. Separation of the phases was achieved by centrifugation at 3500 rpm for 15 min. The whole system was cooled in an ice-bath for 15 min that the surfactant-rich phase would regain its viscosity. In this way, the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved in 0.5 mL of 1.0 mol L^{-1} HNO_3 in methanol and then the copper content was readily evaluated by FAAS.

2.5. Application of real samples

The real samples including water, soil, blood, liver, meat and spinach samples were treated according to previous publication [23–27]. Then the procedure given in Section 2.4 was performed.

3. Results and discussion

Nowadays, spectrophotometric investigation of complexation using the kinfitt program [28] has been used to evaluate the stability constant of respective complexes of ligand with metal ions.

As shown in Scheme 1, due to the existence of donating nitrogen atom as well as $-\text{NH}$ group in PDBDM was expected to increase both the stability and selectivity of its copper(II) ion complex over other metal ions, especially alkali and alkaline earth cations. It occurred to us that the presence of some constituents with non-cyclic sulfur-containing ligand and hydroxyl group in addition to the Π electrons results in selective interaction with Cu^{2+} while oxygen atoms of the ligands mostly interact with this ion through ion–dipole interactions, while all resulting in fast complexation and higher sensitivity.

In preliminary experiments typical complexation between copper(II) ion and PDBDM was examined using spectrophotometry, and the nature of respective complex was investigated using the mole ratio method under the established experimental conditions by Kinfitt program. In order to confirm this result and ascertain the nature and structure of the extracted species, to the fixed amount of PDBDM different mole ratio of copper(II) ion was added and corresponding data is presented in Figs. 1 and 2 and relative formation constant are presented in Table 1. As it can be seen, a mole ratio of 2 can be achieved, indicating the association of two PDBDM molecules with one molecule of copper(II) ion. This reagent has sufficient hydrophobicity to be used as a complexing agent in cloud point extraction.

Table 1

Logarithm of overall stability constants for the interaction of copper(II) ion with PDBDM in aqueous solution at pH 10.0

Complex nature Cu^{2+}	PDBDM	$\log \beta$
1	1	5.117 ± 0.013
1	2	9.121 ± 0.004

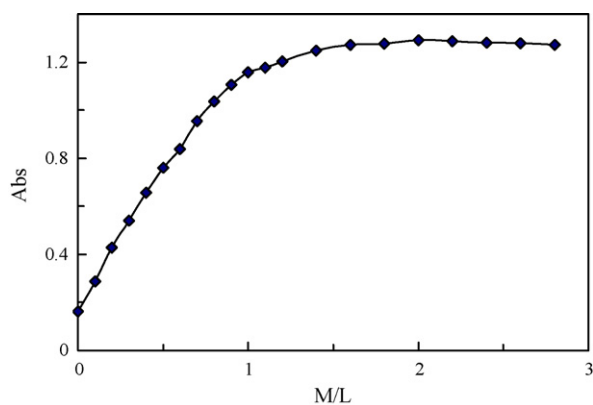


Fig. 2. Mole ratio plot of $8.0 \times 10^{-5} \text{ mol L}^{-1}$ of PDBDM in pH 10.0 and various concentrations of Cu^{2+} $8.0 \times 10^{-4} \text{ M}$, mole ratio plot at wavelength of 302 nm.

In this regard, using chrysoidine a simple, efficient and selective CPE of copper(II) ion has been carried out. In order to obtain sensitivity of method and efficiency for copper(II) ions extraction including pH, ligand and surfactant quantities, incubation time, temperature, viscosity, sample volume, and interfering ions must be investigated.

3.1. Effect of pH

The formation of metal–chelate and its chemical stability are the two important influence factors for CPE. The pH plays a unique role on metal–chelate formation and subsequent extraction, and is proved to be a main parameter for CPE. Extraction yield depends on the pH at which complex formation is carried out. In this view, a set of similar experiments in the pH range of 4.0–11.0 was conducted according to described procedure in Section 2 and respective results illustrated in Fig. 3. The results show pH value of 10.0 seems to be optimum for the complete removal of the Cu(II) ion concentration by CPE. These results can be explained considering pK value of the PDBDM dye which is found to be around 6.0. At lower pH (less than pK value), the dye is protonated, and its ionic characteristics increase leading to less solubilization of the dye in the hydrophobic micelles. At higher pH (above pK value), the dye is de-protonated and it behaves like a hydrophilic molecule and easily gets solubilized in the micelles. The dye solubility and extraction to surfactant rich phase is higher in basic pH, therefore, synergically improved the copper(II) ion extraction to surfactant rich phase. On the other hand, at $\text{pH} > 10.0$ the signal decreases yielding lower recovery and absorbance due to precipitation of Cu(II) ions in the form of hydroxides. Owing to this behavior, pH 10.0 was selected for the subsequent studies.

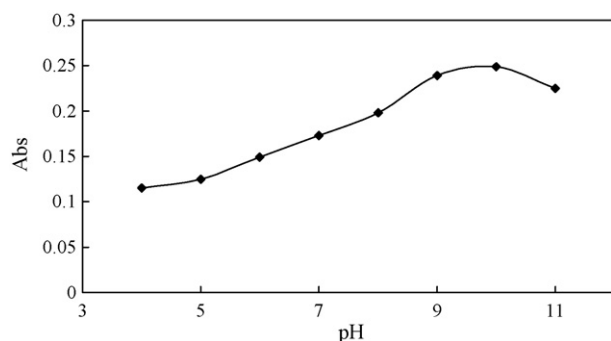


Fig. 3. Effect of pH on copper(II) ion recovery, condition: 15 mL $0.1 \mu\text{g mL}^{-1}$ Cu^{2+} ion at various pH, 0.05 (w/v) Triton X-114, 0.15 mmol L^{-1} PDBDM, 0.1 mol L^{-1} NaCl, eluting solution 0.5 mL of 0.5 mol L^{-1} HNO_3 in methanol.

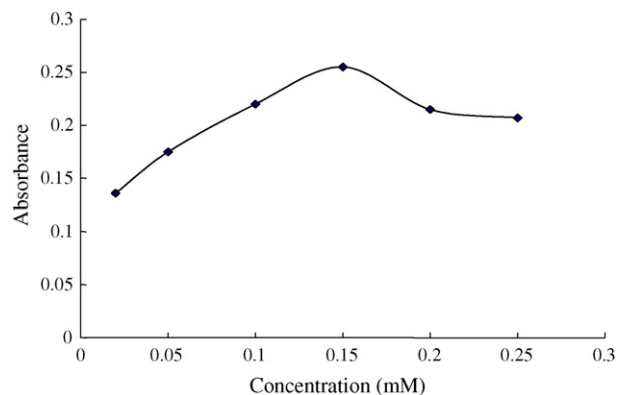


Fig. 4. Effect of PDBDM concentration on copper(II) ion recovery, condition: 15 mL $0.13 \mu\text{g mL}^{-1}$ Cu^{2+} ion at pH 10.0, 0.05 (w/v) Triton X-114, different concentrations of PDBDM, 0.1 mol L^{-1} NaCl, eluting solution 0.5 mL of 0.5 mol L^{-1} HNO_3 in methanol.

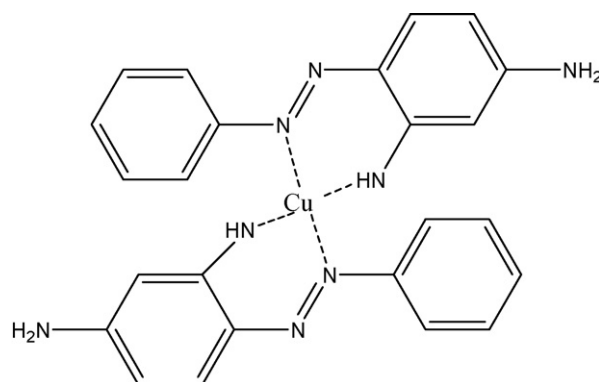
3.2. Effect of PDBDM concentration

The effect of concentration of the chelating agent on the analytical responses was subsequently studied. Therefore, a set of similar experiments at $0.13 \mu\text{g mL}^{-1}$ Cu^{2+} , 0.05% (w/v) Triton X-114 and pH 10.0 various amount of PDBDM was conducted and respective results were presented in Fig. 4. As it can be seen the method sensitivity will be improved up to 0.15 mmol L^{-1} of PDBDM. The extraction yield as a function of the concentration of the complexing agent is shown in Fig. 4. The sensitivity increases up to 0.15 mmol L^{-1} PDBDM concentration.

A concentration of 0.15 mmol L^{-1} for PDBDM was chosen to account for other extractable species that might potentially interfere with the assaying of copper(II) ion. The composition of the complex produced is critical in attaining highest extraction percentages. At higher ligand consideration due to possible charged species formation and inability to extract in surfactant rich phase sensitivity and extraction efficiency will be reduced [29,30]. The schematic diagram for complexation are presented in Scheme 2.

3.3. Effects of equilibration temperature and time

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of extraction and efficient separation of phases. The dependence of extraction efficiency upon equilibration temperature and time above the cloud point in the range of 30–55 °C and 5–30 were thoroughly optimized, respectively. The results showed that an equilibration temperature of 45 °C and an equilibration time of 15 min were adequate to achieve quantitative



Scheme 2. Schematic diagram of copper complexation with PDBDM.

extraction. It was found that 45 °C is adequate for these analyses. An equilibration time of 15 min was chosen as the optimal to achieve maximum sensitivity. Unreasonably high temperatures are not suitable in the proposed analytical method since they could create stability problems for chelates and chelating agents, while at higher temperature, CMC of non-ionic surfactants decreases [31]. Moreover, non-ionic surfactants appear relatively more hydrophobic at higher temperatures, due to an equilibrium shift that favors dehydration of the ether oxygens [32]. This leads to an increase in the number concentration of micelles. As reported previously [32], the solubilization capability of the micellar solution increases with temperature leading to an increase in the dye extraction.

3.4. Effect of dilution condition

Accordingly, after phase separation it is necessary to decrease the viscosity of the surfactant-rich phase to facilitate handling and introduction into the atomizer. The addition of a diluting solution in the surfactant-rich phase is always indispensable in order to obtain a clear and homogenous solution of low viscosity compatible with the requirements of flame and plasma nebulizer. Most commonly, a methanolic solution of 1.0 mol L⁻¹ HNO₃, as diluting agent, is included in analytical schemes to accommodate this need. There is an optimum volume for added methanol with respect to the analytical signals. This should be a compromise between the capability of methanolic solution to lower the viscosity, thus improving the homogeneity of the solution, and the amount of organic solvent that can be tolerated without problems by some detectors (for example, flame and plasma in atomic detectors).

3.5. Effect of Triton X-114 concentration

The preconcentration efficiency was evaluated using Triton X-114 concentrations ranging from 0.015% to 0.09% (w/v). The results are demonstrated in Fig. 5. The highest copper(II) ion recovery was obtained with 0.05% (w/v) Triton X-114. By decreasing the surfactant concentration to 0.015% (w/v) the recovery was reduced. The copper(II) ion recovery also decreased for a higher Triton X-114 concentration (0.05%, w/v). This result might be related to the presence of the high amount of surfactant, resulting in an increase in the volume of the surfactant-rich phase. In addition, the viscosity of the surfactant-rich phase increases, leading to poor sensitivity [33,34]. At lower Triton X-114 concentrations (below 0.015%, w/v), the preconcentration efficiency of the complex was very low, probably due to assemblies that were inadequate to quantitatively entrap the hydrophobic complex [35]. A surfactant concentration of 0.05% (w/v) for Triton X-114 was selected for all further works.

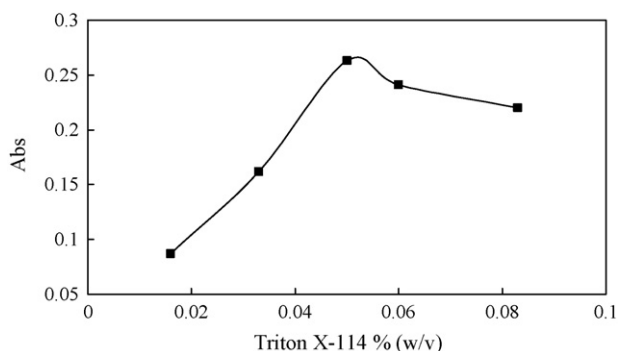


Fig. 5. Effect of amount of Triton X-114 on the recoveries of copper(II) ion, condition: 15 mL 0.13 μg mL⁻¹ Cu²⁺ ion at pH 10.0, 0.15 mmol L⁻¹ PDBDM, 0.1 mol L⁻¹ NaCl.

Table 2

Effects of the matrix ions on the recovery of the copper (II) ions

Ion	Added as	Tolerance limit ion (the fold)
PO ₄ ³⁻ , Mg ²⁺ Cl ⁻ , K ⁺ , Na ⁺ , Ba ²⁺ , Ca ²⁺ , HCO ₃ ⁻	Na ₃ PO ₄ , MgCl ₂ , KCl, NaCl, Ba(NO ₃) ₂ , Ca(NO ₃) ₂ , NaHCO ₃	1000
Zn ²⁺ , Cd ²⁺ , Pb ²⁺ , Ni ²⁺ , Co ²⁺ , Fe ³⁺ , Ag ⁺ , Al ³⁺ , Cr ³⁺ , Hg ²⁺	Nitrate salt	800

Table 3

Characteristics performance of the presented CPE method

Parameter	Optimum value
Detection limit	n = 10
Preconcentration factor	30
Enrichment factor	41.1
Linear range (μg mL ⁻¹)	0.01–0.26
R.S.D. (%)	1.0
Limit of detection (ng mL ⁻¹) (3S.D. _b /m, n = 4)	0.6

3.6. Effect of NaCl concentration

NaCl was investigated as electrolyte in the concentration range from 0.01 to 0.5 mol L⁻¹ and the highest sensitivity and copper(II) ion recovery was obtained at 0.1 mol L⁻¹ NaCl concentration. The signal decreased considerably for increasing NaCl concentrations (0.01–0.5 mol L⁻¹). This effect might be explained by the additional surface charge when the NaCl concentration is very high, thus changing the molecular architecture of the surfactant and consequently the micelle formation process. It is necessary to emphasize that different blank solutions were also evaluated and no significant signal was obtained. In this way, 0.1 mol L⁻¹ NaCl concentrations were used in all further experiments.

3.7. Effect of centrifuge time and rates

It is required to preconcentrate trace amount of copper(II) ion with high efficiency in short time. Therefore, CPE on a set of experiments of 15 mL sample at pH 10.0, 0.15 mmol L⁻¹ PDBDM, 0.13 μg mL⁻¹ copper(II) ion, 0.05% (w/v) for Triton X-114 and 0.1 mol L⁻¹ NaCl by heating at 45 °C and further centrifuging in various rates and times has been carried out. The results indicate the experiment in the optimized reagent concentration after heating for 15 min at 45 °C and centrifuging by 15 min in 3500 rpm and cooling in 15 min in ice-bath lead to high recovery of copper(II) ion in short time.

Table 4

Recovery studies of copper in real samples (amounts for solid samples: 4.0 g, final volume: 5 mL)

Sample	Added (μg L ⁻¹)	Found (μg L ⁻¹)	R.S.D. (%)	Recovery (%)
Vegetable	0	28.9	1.4	–
	100	131.2	1.1	102.3
Liver	0	29.1	1.3	–
	100	131.2	1.0	102.1
Meat	0	30.6	1.3	–
	100	132.3	0.9	101.7
Lotus (tree)	0	17.7	1.3	–
	100	119.2	1.0	101.5
Soil	0	18.0	1.4	–
	100	121.0	1.0	103.0
Blood	0	112.1	1.3	–
	100	215.4	0.9	103.0
Tap water	0	6.2	1.4	–
	100	108.2	1.1	102.0

Table 5
Comparative data from some recent studies on preconcentration–separation of copper

Technique	System	PF	Detection limit ($\mu\text{g/L}$)	Reference
CPE	1-(2-Thenoyl)-3,3,3-trifluoracetone/Triton X-114	96	$0.4 \mu\text{g L}^{-1}$	[36]
CPE	2-(2'-Benzothiazolylazo)-5-(N,N-diethyl)aminophenol/Triton X-114	29	$0.1 \mu\text{g g}^{-1}$	[37]
Precipitation	2-[2'-(6-methyl-benzothiazolylazo)]-4-aminophenol	40	$0.5 \mu\text{g L}^{-1}$	[38]
Slotted tube atom trap	–	–	$30 \mu\text{g L}^{-1}$	[39]
SPE	Amberlite XAD-4 functionalized with 3,4-dihydroxybenzoic acid	91	$0.1 \mu\text{g L}^{-1}$	[40]
SPE	Silica-coated magnetic nanoparticles (SCMNPs) modified with γ -mercaptopropyltrimethoxysilane	476	0.092 ng L^{-1}	[41]
CPE	4-(Phenyl diazenyl) benzene-1,3-diamine/Triton X-114	30	$0.6 \mu\text{g L}^{-1}$	This work

CPE: cloud point extraction, SPE: solid phase extraction, PF: preconcentration factor.

3.8. Interferences

The effects of representative potential interfering species were tested. The tolerance limits of the coexisting ions, defined as the largest amount making change the recovery of copper(II) ion less than 5%, are given in Table 2. They show that the recovery is quantitative and satisfactory in the presence of most foreign cations and the major cations in the water and real samples have no obvious influence on CPE of copper(II) ion under the selected conditions.

3.9. Calibration, precision and detection limits

Calibration curves were obtained by the preconcentration of 15 mL of a standard sample solution in the presence of 0.05% Triton X-114 in medium at pH 10.0. The samples were introduced into the flame by conventional aspiration following the addition in 0.5 mL of 1.0 mol L^{-1} HNO_3 , methanol solution in. In this case, linear relationships between the absorbance measured and the concentration of metal placed in solution were obtained. Table 3 gives the parameters of the calibration curve; the relative standard deviation obtained for 10 replicates subjected to the complete procedure and the detection limits. Preconcentration of 15 mL of sample in the presence of 0.05% Triton X-114 permitted the detection of 0.6 ng mL^{-1} for copper(II) ion.

The preconcentration factors as the ratio of initial volume to final volume and enrichment factor as the ratio of the concentration of the analyte after preconcentration to that before preconcentration which give the same absorbance were 30 and 41.1 for copper(II) ion, respectively. However, the higher preconcentration factors could be obtained by using larger sample volumes. Furthermore, the need-to-handle volume of the final methanolic solution was estimated to be sufficient for the analyte of copper(II) ion and therefore it had to be increased to allow multiple runs for the same samples.

3.10. Applications of the presented procedure

The reliability of the presented method was checked by spiking experiments and independent analysis. The results for this study are presented in Table 4. 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. Conclusion

In this work, the use of micellar systems as a separation and preconcentration for copper(II) ion offers several advantages including low cost, safety, preconcentrated copper(II) ion with high recovery and very good extraction efficiency. We have proposed the use of cloud point extraction as an alternative method for the preconcentration of copper(II) ion as a prior step for their determination by flame atomic absorption spectrometry. The proposed method can be applied to the determination of trace of copper(II) ion in various real samples. The separation occurred efficiently, resulting in good enrichment factor and low LOD. In contrast to some other preconcentration techniques, no organic solvent is employed; therefore, the environmental pollution is limited to a small amount of surfactant. The methodology offers a simple, rapid, inexpensive and nonpolluting alternative to other preconcentration techniques. The method is relatively rapid as compared with previously reported procedures for the enrichment of analyte ions (Table 5). The presented method can be successfully applied to the preconcentration and determination of analyte ions in different real samples. The detection limits of analytes are superior to those of preconcentration techniques [36–43].

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