

**CLOUD POINT EXTRACTION FOR THE DETERMINATION OF COPPER IN ENVIRONMENTAL SAMPLES BY FLAME ATOMIC ABSORPTION SPECTROMETRY****Ardeshir Shokrollahi, Mehrorang Ghaedi\* and Shiva Gharaghani**

Chemistry Department, University of Yasouj, Yasouj 75914-353, Iran

**Mohammad Reza Fathi**

Chemistry Department, University of Ahvaz, Ahvaz, Iran

**Mustafa Soylak**

Chemistry Department, University of Erciyes, 38039 Kayseri, Turkey

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A simple cloud point extraction procedure is presented for the pre-concentration of copper in various samples. After complexation by 4-hydroxy-2-mercapto-6-propylpyrimidine (PTU), copper ions are quantitatively extracted into the phase rich in Triton X-114 after centrifugation. Methanol acidified with 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> was added to the surfactant-rich phase prior to its analysis by flame atomic absorption spectrometry (FAAS). Analytical parameters including concentrations for PTU, Triton X-114 and HNO<sub>3</sub>, bath temperature, centrifugation rate and time were optimized. The influences of the matrix ions on the recoveries of copper ions were investigated. The detection limits (3SD<sub>b</sub>/m, n=4) of 1.6 ng mL<sup>-1</sup> along with enrichment factors of 30 for Cu were achieved. The proposed procedure was applied to the analysis of environmental samples.

Keywords: 4-hydroxy-2-mercapto-6-propylpyrimidine; cloud point extraction; copper ion.

**INTRODUCTION**

Copper has received considerable attention owing to its uses in metallurgy and chemical industries. Moreover, it is an essential constituent of about thirty enzymes and glycoproteins and is required for the synthesis of hemoglobin and for some biological processes. Also promotes iron absorption from the gastrointestinal system, is involved in the transport of iron from tissues into plasma, helps to maintain myelin in the nervous system, is important in the formation of bone and brain tissues and is necessary for other many important functions. When levels of Cu exceed certain values, however, defense mechanisms to protect against excess Cu are overcome and toxicity results. For this reason, several methods for the determination of copper ion are available for copper ion determination.<sup>1, 2</sup>

The determination of trace copper in biological samples is particularly difficult because of the complex matrix and the usually low concentration of copper, which requires sensitive instrumental techniques and frequently a pre-concentration step.<sup>3-6</sup> Micelles and other organized amphiphilic assemble 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.<sup>7-12</sup>

Separation procedures based on the peculiar properties of aqueous non-ionic and zwitterionic surfactant solution have also been proposed as an alternative to the use of traditional organic solvents. Aqueous solutions of almost all non-ionic surfactants become turbid when heated to a temperature known as the cloud point. Above this temperature, the isotropic micellar solution separates into two transparent liquid phases: a surfactant-rich phase of very small volume composed mostly of the surfactant plus a small amount of water, and an aqueous phase, in equilibrium with

the former, which contains a surfactant concentration close to its critical micellar concentration, is the base of cloud point extraction (CPE). The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient, and of lower toxicity to the environment than those extractions that use organic solvents. The CPE phenomenon has been used for the extraction and pre-concentration of metal cations<sup>13-19</sup> after the formation of sparingly water-soluble complexes. CPE has been shown to be an effective sample pre-concentration technique for improving sensitivity and selectivity prior to atomic spectrometry.

In the present work a simple, selective and sensitive CPE method for pre-concentration and determination of copper ion in various real samples using PTU as selective and sensitized complexing agent was established.

**EXPERIMENTAL****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. Deionised water was used for all dilutions. Copper standard solution was prepared by dissolving appropriate amount of nitrate salt of copper(II). 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-Hydroxy-2-mercapto-6-propylpyrimidine, acetonitril and methanol solvents were purchased from Merck Company.

**Instrumentation**

A Shimadzu UV-Vis 160 spectrophotometer was used to measure the absorbance of complex in Triton X-100 media. A 691

\*e-mail: m\_ghaedi@mail.yu.ac.ir

pH/Ion meter with a combined glass and calomel electrode has been used for measurement and adjustment of test solutions pH. The evaluation of ions content were carried out on a Shimadzu 680 A or a Perkin–Elmer 603 atomic absorption spectrometer with a hollow cathode lamp and a deuterium background corrector, at respective resonance line using an air–acetylene flame.

### Procedure

A typical cloud point experiment required the following steps: an aliquot of 15 mL of a solution containing  $\text{Cu}^{2+}$ , 0.15% Triton X-114 and 1.3 mM of PTU was adjusted to pH 6.0 with an acetate buffer. 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 4000 rpm, for 15 min. The whole system was cooled in an ice-bath so 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 0.5 M  $\text{HNO}_3$  in methanol and then the copper content was readily evaluated by FAAS.

### Pretreatment of samples

Analysis of water samples for determination of copper ions content was performed as following: 400 mL of sample was poured in a beaker and 8 mL concentrated  $\text{HNO}_3$  and 3 mL of 30% (v/v)  $\text{H}_2\text{O}_2$  for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one tenth volume. After adjustment of samples pH to desired value the CPE were performed according to general described procedure.<sup>3</sup>

Homogenized soil sample 20 g or blood sample 20 mL was weighed accurately and in a 200 mL beaker was digested in the presence of an oxidizing agent with addition of 10 mL concentrated  $\text{HNO}_3$  and 2 mL  $\text{HClO}_4$  70% 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 given at Section 2.3 was applied. Copper levels in the final solutions were determined by FAAS.

Spinach sample was purchased from Gachsaran Iran. Afterwards, it was taken in small mesh. For the digestion of the sample, the procedure given by Ghaedi<sup>7</sup> was applied. A 40 g of spinach 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, treated with 10.0 mL concentrated nitric acid and 3 mL 30%  $\text{H}_2\text{O}_2$  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 in water, filtered and by keeping the pH at 6.0 made up to 25 mL by addition of KOH and acetate buffer. The dissolved solution was suitably diluted and presented procedure was applied.

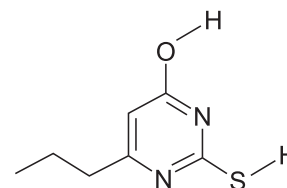
A 20 g of tablet chocolate sample was ashed in silica crucible for 4 h on a hot plate and the charred material was transferred to furnace for overnight heating at 450 °C. The residue was cooled and treated with 10.0 mL concentrated nitric acid and 3 mL 30%  $\text{H}_2\text{O}_2$  again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 0.5 mL concentrated hydrochloric acid and 1–2 mL 70% perchloric acid and evaporated to fumes, so that all the copper metal changes to copper ions. The solid residue was dissolved in water and filtered and by keeping the pH at 6.0 made up to 25 mL by

addition of KOH and acetate buffer. Then the procedure was applied. Copper levels in the final solutions were determined by FAAS.

A 50 g of liver were taken and dried for 48 h in an oven at 120 °C to remove the water content and to obtain a constant weight (about 68% water). Dried liver sample transferred into a glass flask. For the digestion of the sample, the procedure given by Ghaedi *et al.*<sup>4</sup> was applied. A concentrated acid mixture of 3 mL  $\text{H}_2\text{SO}_4$ , 15 mL  $\text{HClO}_4$ , and 15 mL  $\text{HNO}_3$  was added and left to stand over night. The solution was kept in an oil bath at 50 °C until the foaming stopped. Then the temperature was increased to 150 °C and heating was continued until the evolution of brown fumes of nitrogen oxides ceased. When a dark brown in mixture was appeared, the flask was cooled for about 2 min then a 5 mL of nitric acid had to be added. Heating was continued until nitrogen oxides fumes were longer given off. Appearance of white fume of perchloric acid in 1 mL solution is an indication of complete digestion. The solid residue was dissolved in water and filtered and by keeping the pH at 6.0 made up to 25 mL by addition of KOH and acetate buffer. Then the procedure was applied. Copper levels in the final solutions were determined by FAAS.

## RESULTS AND DISCUSSION

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

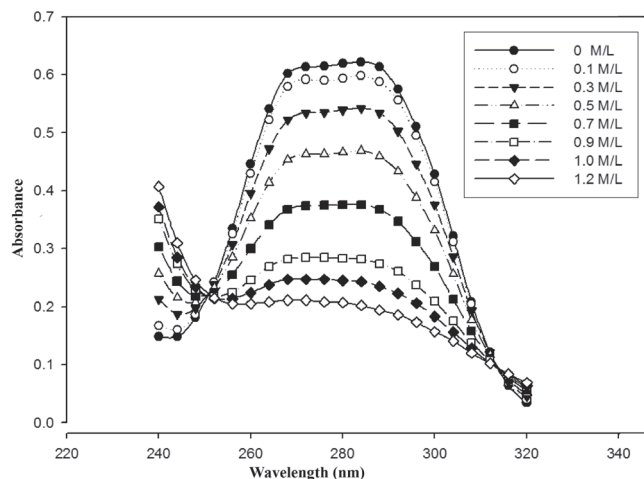


Scheme 1. 4-Hydroxy-2-mercapto-6-propylpyrimidine (PTU)

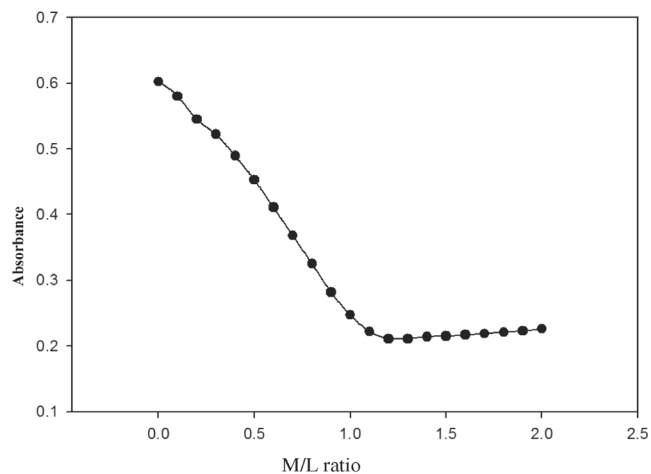
In preliminary experiments typical complexation between copper ion and PTU was examined using spectrophotometry, and the nature of respective complex was investigated using the mole ratio method under the established experimental conditions by Kinfite program.<sup>20</sup> In order to confirm this result and ascertain the nature and structure of the extracted species, to the fixed amount of PTU different mole ratio of copper ion was added and corresponding data are presented in Figures 1, 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 PTU molecules with the one molecule of copper ion. This reagent has sufficient hydrophobicity to be used as a complexing agent in cloud point extraction.

### Effect of pH

The cloud point extraction of copper ion was performed in solutions of pH ranging from 3 to 8. Extraction recovery depends on the pH at which complex formation occurs. The effects of pH on the extraction of copper complex are given in Figure 3. In the



**Figure 1.** Absorbance spectra of complex of PTU ( $1 \times 10^{-3}$  M) with copper ion ( $1 \times 10^{-3}$  M) in acetonitril in different mole ratio



**Figure 2.** Mole ratio plot of  $1 \times 10^{-3}$  M of PTU in acetonitril and various concentration of  $\text{Cu}^{2+}$   $1 \times 10^{-3}$  M, mole ratio plot

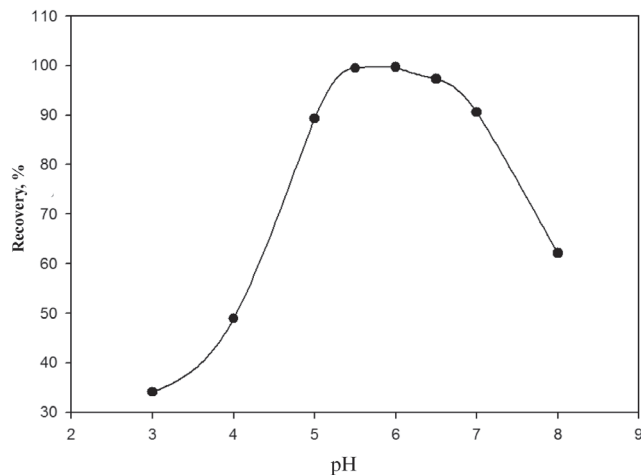
**Table 1.** Logarithm of stability constants assembling for the interaction of  $\text{Cu}^{2+}$  with PTU in acetonitril

Complex nature		
$\text{Cu}^{2+}$	PTU	Log Kf
1	1	$5.000 \pm 0.004$
1	2	$3.001 \pm 0.003$

pH range 5.5–6.0, extraction was quantitative. The decrease in recoveries at pH > 6.0 is probably due to the precipitation of copper ions in the form of hydroxide, and at pH < 5.5 may be due to competition from hydronium ion toward ions for complexation with PTU or decomposition of complex at pH values smaller than 5.5, which led to the decrease in recoveries. In subsequent experiments were performed at pH 6.0.

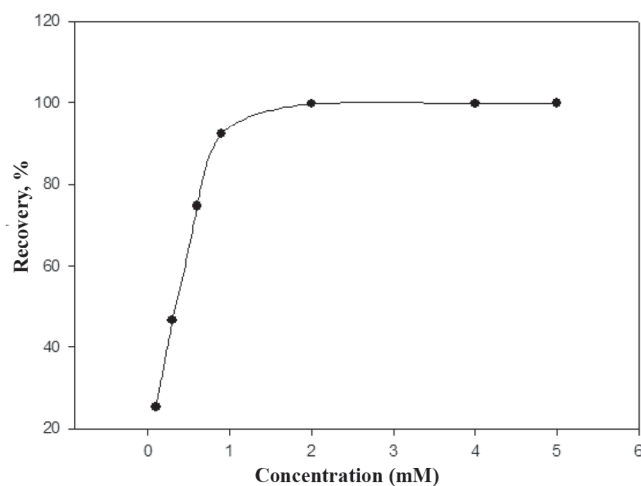
#### Effect of PTU concentration on copper CPE recovery

The concentration of PTU was evaluated over the range 0.1–5.0 mM. For this study, 15 mL of a solution containing  $0.2 \text{ ng mL}^{-1}$  copper ion in 0.15% (v/v) Triton X-114 with various amounts of PTU was subjected to the cloud point preconcentration process.



**Figure 3.** Effect of pH on Copper Ion Recovery, Condition: 15 mL  $0.2 \text{ } \mu\text{g mL}^{-1}$   $\text{Cu}^{2+}$  ion at various pH, 0.15% (v/v) Triton X-114, 0.2 mM PTU, 1.0% (w/v) NaCl, eluting solution 0.5 mL of 0.5 M  $\text{HNO}_3$  in methanol

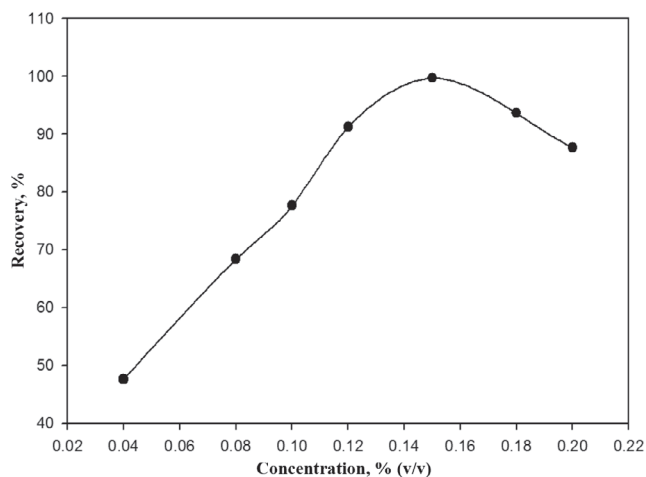
The extraction recovery as a function of the PTU concentration is shown in Figure 4. There was no significant difference in the results between 2.0–5.0 mM considering the average copper ion recovery. A concentration of 2.0 mM of PTU was chosen for subsequent experiments.



**Figure 4.** Effect of PTU concentration on Copper Ion Recovery, Condition: 15 mL  $0.2 \text{ } \mu\text{g mL}^{-1}$   $\text{Cu}^{2+}$  ion at pH 6.0, 0.15% (v/v) Triton X-114 different concentration of PTU, 1.0% (w/v) NaCl, eluting solution 0.5 mL of 0.5 M  $\text{HNO}_3$  in methanol

#### Effect of Triton X-114 concentration

The preconcentration efficiency was evaluated using Triton X-114 concentrations ranging from 0.04 to 0.2% (v/v). The results are demonstrated in Figure 5. The highest copper ion recovery was obtained with 0.15% (v/v) Triton X-114. By decreasing the surfactant concentration to 0.04% (v/v) the recovery was reduced. The copper ion recovery also decreased for a higher Triton X-114 concentration (0.2% v/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.<sup>21,22</sup> At lower Triton X-114 concentrations (below 0.04% v/v), the preconcentration efficiency of the complex was very low, probably



**Figure 5.** Effect of amount of Triton X-114 on the recoveries of copper. Condition: 15 mL 0.2  $\mu\text{g mL}^{-1}$   $\text{Cu}^{2+}$  ion at pH 6.0, 0.2 mM PTU, 1.0% (w/v) NaCl, eluting solution 0.5 mL of 0.5 M  $\text{HNO}_3$  in methanol

due to assemblies that were inadequate to quantitatively entrap the hydrophobic complex.<sup>23</sup> A surfactant concentration of 0.15% (v/v) for Triton X-114 was selected for all further works.

#### Effect of NaCl concentration

Studies on the effects of some additives, such as anionic and non-ionic surfactants and electrolytes, as NaCl,  $\text{KNO}_3$  and  $\text{MgCl}_2$ , on the cloud point behavior of non-ionic surfactants have been reported.<sup>24-26</sup> It was observed that the presence of electrolytes decreases the cloud point (salting-out effect), resulting in a more efficient extraction. The lower cloud point is attributed to electrolytes promoting dehydration of the poly(oxyethylene) chains.<sup>27</sup> According to Hiller *et al.*<sup>26</sup> the salting-out phenomenon is directly related to desorption of ions to the hydrophilic parts of the micelles, increasing inter-attraction between micelles and consequently leading to the precipitation of surfactant molecules. Based on this discussion, NaCl was investigated as electrolyte in the concentration range from 0.5 to 5% (w/v) and the highest copper ion recovery was obtained at 1% (w/v) NaCl concentration. The signal decreased considerably for increasing NaCl concentrations (2–5% w/v). 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, 1% (w/v) NaCl concentration was used in all further experiments.

#### Effect of methanol

Since the surfactant-rich phase obtained after the cloud point preconcentration contains a high concentration of Triton X-114 and, at the same time, the volume obtained is rather small (0.5 mL), methanol containing 0.5 mol  $\text{L}^{-1}$   $\text{HNO}_3$  was added to the surfactant-rich phase after phase separation. Moreover, it was necessary to decrease the viscosity of the rich phase without excessive dilution of the micelle to facilitate the introduction of the sample into the atomizer of the spectrometer. There is an optimum volume (0.5 mL) with respect to the copper ion recovery. Smaller volumes of methanol were not tested because in this case it was not possible to quantitatively transfer the rich phase from test tubes to the graduated

tubes and measuring the absorbance. Larger volumes of acidified methanol dilution are clearly predominated resulting in a gradual absorbance reduction. A 0.5 mL volume of methanol was therefore used throughout the remaining experiments.

#### Effect of temperature

The cloud point temperature of Triton X-100 is 67.3 °C, however, room temperature is the preferred cloud point temperature for analytical purposes. In order to decrease the cloud point temperature of micellar solution of Triton X-100, NaCl solution was used. The effect of additives organic or inorganic on cloud point temperature of micellar solution of surfactants is reported in the literature.<sup>9,22</sup> The incubation time and equilibration temperature above the cloud point were thoroughly optimized. It was desirable to employ the shortest incubation time and the lowest possible equilibration temperature, which compromise completion of the reaction and efficient separation of phases. It was observed temperatures in the range of 40–45 °C are adequate for Cu analysis. Higher temperatures lead to the decomposition of Cu-PTU complexes and the reduction of analytical signal. At lower temperatures the separation of the two phases is not complete. The incubation time is kept at 20 min which is sufficient for the completion of the physicochemical processes.

#### Effect of centrifuge time and rates

It is required to preconcentrate trace amount of copper ion with high efficiency in short time. Therefore, CPE on a set of experiments of 15 mL sample at pH 6.0, 2.0 mM PTU, 0.2  $\mu\text{g mL}^{-1}$  copper(II) and 1% NaCl by heating 45 °C and centrifuging in various rate and time further cooling in various time has been carried out. The results indicate the experiment in the optimized reagent concentration after heating for 15 min in 45 °C and centrifuging by 15 min in 4500 rpm and cooling in 15 min in ice-bath lead to high recovery of copper ion in short time.

#### Effect of foreign ions

The influences of some alkaline and alkaline-earth ions and transition metal ions on the copper ion recovery of the analyte ion were investigated by the presented CPE procedure. The results are given in Table 2. The tolerance limit is defined as the ion concentration causing a relative error smaller than  $\pm 5\%$  related to the preconcentration and determination of Cu(II). Copper ion was quantitatively recovered in the presence of large amounts of alkaline and alkaline earth ions and some transition metal ions. The matrix ion contents in the final solutions were found to be significantly lower and suitable for atomic absorption spectrometric determinations.

**Table 2.** Effects of the matrix ions on the recoveries of the examined metal ions (N=3)

Ion	Added As	Tolerance Limit Ion $\text{mg L}^{-1}$
$\text{Cl}^-$ , $\text{K}^+$ , $\text{Na}^+$	KCl, NaCl	1000
$\text{Mg}^{2+}$	$\text{MgCl}_2$	1000
$\text{HCO}_3^-$	$\text{NaHCO}_3$	1000
$\text{PO}_4^{3-}$	$\text{Na}_3\text{PO}_4$	1000
$\text{Zn}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Ca}^{2+}$ ,	Nitrate salt	750
$\text{Pb}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Co}^{2+}$ , $\text{Fe}^{3+}$ ,		
$\text{Fe}^{2+}$ , $\text{Ag}^+$ , $\text{Al}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Hg}^{2+}$		

## Characteristics of the method

Calibration graphs were obtained by preconcentrating 2.0 mL of standard solution in the presence of 0.15% (v/v) Triton X-114, pH 6.0, 2.0 mM PTU with 1% w/v NaCl, under the experimental conditions specified in the optimized procedure section. The solutions were introduced into the flame atomic absorption spectrometry by conventional aspiration. Table 3 gives the characteristic performance of the proposed method of standard solutions subjected to the entire procedure.

## Accuracy and applications

We have explored the feasibility of the methodology using preconcentration with PTU in surfactant media for the determination of copper in different matrices treated according to Experimental section. The procedure was applied to the determination of copper ion in different environmental samples, including waste water, river water, soil and blood sample, vegetable sample, liver sample and chocolate samples by standard addition method. Reliability was checked by spiking experiments and independent analysis. The results are presented in Table 4. The recovery of spiked samples is satisfactory reasonable and was confirmed using addition method,

**Table 3.** Optimum conditions for the presented CPE Method

Parameter	Optimum Value
pH	6.0
PTU concentration (mM)	2.0
Centrifuge condition	15 min at 4000 rpm
Eluting agent	0.5 mL of 0.5 mol L <sup>-1</sup> HNO <sub>3</sub> in methanol
Bath temperature	15 min on 45 °C
Cooling	15 min
Enrichment factor	30
RSD, %	< 1.4%
Limit of Detection (3SD <sub>b</sub> /m, n=4)	1.6 ng mL <sup>-1</sup>

**Table 4.** Recovery studies of copper in real samples

Sample	Added	Found	RSD %	Recovery %
Vegetable <sup>a</sup>	0	0.219	1.3	—
	0.4	0.634	0.9	103.8
Liver <sup>a</sup>	0	0.538	1.4	—
	0.3	0.853	0.8	105.0
River water <sup>b</sup>	0	79.3	1.1	—
	100	182.1	0.6	102.8
Soil <sup>a</sup>	0	0.213	1.4	—
	0.2	0.408	0.9	97.5
Blood <sup>b</sup>	0	79.8	1.3	—
	100	182.6	0.8	102.8
Chocolate <sup>b</sup>	0	0.145	1.4	—
	0.2	0.349	1.0	102.0
Tap water <sup>a</sup>	0	68.9	1.4	—
	100	171.3	0.9	102.4
Waste water <sup>a</sup>	0	88.9	1.3	—
	100	192.1	0.9	103.2

a) All values are mg g<sup>-1</sup> after suitable dilution; b) all values are µg L<sup>-1</sup>

which indicate the capability of the system in the determination of copper in environmental samples.

## CONCLUSION

A novel, sensitive and accurate cloud extraction procedure for copper by using PTU in various matrixes in low concentrations has been reported. The proposed method has the following advantages: simple, rapid and low analysis cost. The effect of matrix can be overcome by the method, and the results are satisfying. The method proposed here is rapid and has good reproducibility. The preconcentration factor and detection limits of the proposed method are comparable with various separation-preconcentration methods.<sup>13-15,28-34</sup> The low RSD of real sample analysis is an indication of methods versatility for real sample.

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