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Combination of cold-induced aggregation microextraction and central composite design for preconcentration and determination of copper in food and water samples

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ABSTRACT

An efficient, simple, and rapid cold-induced aggregation microextraction method was applied to preconcentrate copper (II) ions from water and food samples as a prior step to its determination by flame atomic absorption spectrometry. In this method, small amounts of 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF_6] and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [Hmim][Tf_2N] as hydrophobic ionic liquids (ILs) and extractant solvents were dissolved in the sample solution containing Triton X-114. After dissolving, the solution was cooled in an ice bath and a cloudy solution was formed of IL fine droplets due to the decrease of IL solubility. The effective parameters, such as pH, amount of chelating agent and IL, temperature, and concentration of salt were optimized by a fractional factorial design to identify the most important parameters and their interactions, and central composite methodology was used to achieve the optimum point of effective parameters to the response. Under the optimum conditions, the calibration graph was linear in the range of 2–100 $\mu g\,L^{-1}$ with a correlation coefficient of 0.996 and a limit of detection of 0.42 $\mu g\,L^{-1}$. The relative standard deviation was 2.61% ($n = 6$). The obtained enrichment factor was 75 for copper. The interference effect of anions and cations was also tested. The proposed method was compared with the other methods and applied to the analysis of several real and spiked samples and the satisfactory relative recoveries (96.5–101.3%) were obtained.

Keywords: Cold-induced aggregation microextraction; Flame atomic absorption spectrometry; Central composite design; Trace metal determination; Food samples

1. Introduction

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Today, with the rapidly increasing urban population and water resources becoming scarcer, there is a strong need to reconsider our consumption patterns and the way we use our water resources. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products [1]. The continued intake of copper by human beings leads to necrotic changes in the liver and kidney, mucosal irritation; widespread capillary damage, depression, weakness, lethargy, and anorexia, as well as damage to the

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gastrointestinal tract and lung cancer [2,3]. Corrosion in copper pipes also increases copper levels in drinking water. This calls for the urgent need to monitor and bring down copper ions to acceptable levels [4].

Despite developments in modern analytical instruments, direct determination of trace analytes at low concentrations in complex matrixes is often a problem for analytical chemists. Sample preparation is a bottleneck since the various steps often involve consuming large volumes of hazardous organic solvents, are time consuming and/or expensive. Hence, the development of isolation/pre-concentration procedures prior to trace element determination has been investigated in considerable detail in recent decades.

Many preconcentration techniques have been widely used for copper analysis in environmental samples, liquid–liquid extraction, coprecipitation, ion-pair extraction, and liquid membrane technology [5–8]. These classical methods of extraction are labor intensive and time - consuming. Furthermore, the majority of these techniques consume relatively large volumes of high - purity solvents with expensive disposal requirements, and the subsequent removal of solvents causes many environmental problems.

The search for the new solvent is the key to advancement in liquid phase microextraction. In this context, room temperature ILs, which are water and air-stable salts, composed of an organic cation and either and organic or an inorganic anion, have attracted much attention due to their special characterictics [9–11].

An efficient and simple method termed cold-induced aggregation microextraction (CIAME) was developed, which was based on the use of ILs in homogeneous liquid–liquid microextraction (HLLME) [12–14]. In this method, a very small amount of hydrophobic IL as an extractant solvent is dissolved in the sample solution containing Triton X-114. After dissolving, the solution is cooled in the ice bath and a cloudy solution is formed due to the solubility reduction of IL and fine droplets of it were formed. After centrifuging, the fine droplets of extractant phase settle to the bottom of the conical-bottom glass centrifuge tube.

This method is simple, rapid, and viscosity-independent for extraction and preconcentration of metal ions and organic compounds from water samples and is robust against high content of salt and water-miscible organic solvents. Additionally, in comparison with the organic solvent extraction, it is much safer since only small amounts of surfactant and IL are used which are being considered as “green solvent” for various separation processes and in comparison with IL-based DLLME, extraction recoveries of CIAME are relatively high.

Another important capability of this method is that it can be operated in continuous mode. If the solution is cooled during the centrifugation, fine droplets of extractant phase are continuously formed and analytes are extracted and transferred to the bottom of the centrifuge tube. In order to have a good recovery in case of microextraction in which the volume of the extractant solvent is very small, large distribution coefficient is necessary, unless the recovery is low and continuous microextraction is required.

Spectrophotometric methods and flame atomic absorption spectrometry (FAAS) are available techniques in many laboratories. So, they are frequently used for determination of heavy metals [15–18]. FAAS is usually less subjected to interferences than electrothermal atomic absorption or inductively coupled plasma mass spectrometry (ICP–MS) (difficulties in the determination are caused by matrix interferences, principally high salt content). Typically, 1–4 mL of a sample solution is used for FAAS determination of a single element. For a small sample volume, because of high dilution, the concentration of measured elements may be lower than the detection limit. Therefore, by means of minimizing sample consumption while retaining high sensitivity for the measurement is of considerable importance. This limitation can be compensated by using a microsample introduction system (so-called flame microsampling) [19].

Multivariate techniques have been widely applied in optimization of methods in analytical chemistry [20,21]. Recently, factorial design was used several times for optimization of preconcentration procedures for metal determination using FAAS [22–24].

In this work, CIAME was combined with FAAS by using microsample introduction system for determination of copper in foods and water samples using diethyldithiocarbamate (DDTC) as a complexing agent. The optimization step was performed by a central composite fractional factorial design.

2. Experimental

2.1. Instrumentation

A Varian SpectrAA-400 atomic absorption spectrometer equipped with a deuterium background correction and an air–acetylene burner was used for the analysis. A copper hollow-cathode lamp operated at 4 mA was used as the radiation source. Measurements were carried out in the peak height mode at 324.7 nm, Cu. The slit width was 0.5 nm. A Universal 320R refrigerated centrifuge equipped with an angle rotor (6-place, 9,000 rpm, Cat. No. 1620A) was from Hettich (Kirchlengern, Germany). A Metrohm digital pH-meter (model 692, Herisau, Switzerland) equipped with a glass combination electrode was used. A home-made microsample introduction system was used for aspiration of the extractant phase in FAAS [25].

2.2. Reagents and solutions

All reagents used were of analytical grade. Triple distilled water was used throughout the experiment. DDTC, acetone, ethanol, 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF_6] and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [Hmim][Tf_2N] and all salts used were obtained from Merck (Darmstadt, Germany). Triton X-114 was purchased from Fluka (Buchs, Switzerland).

A stock solution of copper (II) (1,000 mg L^{-1}) was prepared by dissolving an appropriate amount of Cu $(NO_3)\cdot 3H_2O$ and working standard solutions were obtained by appropriate stepwise dilution of the stock standard solutions. All stock and working standard solutions were stored in plastic (polypropylene) bottles, with leak-proof screw cap, which were cleaned before use by soaking them in 10% nitric acid solution for at least 24 h, and then rinsing them thoroughly with triple distilled water. A 10^{-2} mol L^{-1} DDTC solution was prepared by dissolving the appropriate amount in water. The viscosity of ILs is high and their handling is difficult, so working solutions ([Hmim][PF_6], 0.8 mg μL^{-1} and [Hmim] [Tf_2N], 0.5 mg μL^{-1}) were prepared in acetone.

2.3. CIAME procedure

The sample or standard solution containing Cu (II), DDTC)7×10^{-5} mol L^{-1}), ($C_8H_5KO_4$-HCl) buffer (pH = 4), sodium nitrate (0.21%, w/v), and Triton X-114 (0.05%, w/v) were poured into a 10 mL conical-bottom glass centrifuge tube. [Hmim][PF_6] (48 mg) and [Hmim] [Tf_2N] (5 mg) were added and the volume of the solution was adjusted to 10.0 mL by triple distilled water. After that, the tube was kept in a thermostated bath at 45°C for 5 min. After shaking, it was placed in an ice-water bath for 10 min and a cloudy solution was formed. Then, the mixture was centrifuged for 5 min at 5,000 rpm. As a result, fine droplets of IL settled at the bottom of the centrifuge tube. Bulk aqueous phase was removed simply by inverting the tubes. Afterwards, IL-phase was dissolved in 100 μL of pure ethanol and aspirated into the atomic absorption spectrometer.

2.4. Real samples preparation

The practical applicability of the recommended method was evaluated by extracting Cu from water and food samples. Potato, broccoli, and green tea were purchased from local supermarkets in Tehran. At first, these samples were cleaned with double-distilled water and then dried at 110°C. Five hundred milligrams of samples were placed in separate 50 mL beakers, 15 mL of concentrated nitric acid was added, and the beakers were covered with glass watch and heated on a hot plate (130°C for 3 h). The samples were then cooled, 5 mL of concentrated perchloric acid was added and the mixtures were heated again until the solutions became clear. The glass watches were removed and the samples were cooled and then transferred into 100 mL volumetric flasks by rinsing the interior of the beakers with water. The resulting solutions were diluted to the mark, and the recommended procedure was followed [26].

Water samples including water wall, tap water, sea water (Caspian Sea), and river water (Babolrood) were selected and the proposed CIAME method was applied to determine the copper content. After sampling, they were filtered through filter paper to remove suspended particulate matter. Finally, aliquots of 10 mL of each sample solution were used and the proposed method was applied to extraction of copper ions from the water samples under optimum conditions.

2.5. Optimization strategy

The optimization step was carried out by using a central composite fractional factorial design. Considering the proposed preconcentration procedure, variables chosen for optimization were pH, amount of chelating agent, salt concentration, amount of IL, and temperature. Maximum and minimum levels of each factor (Table 1) were established according to works described in literature and previous papers. To examine the combined effect of the five independent variables on the response, a central composite fractional factorial design with a total of 36 experiments were performed. All experiments were carried out in

Table 1
Factors and levels used in the central composite design

Variables		Coded factors level				
	Symbols	−2 (low)	−1	0	1	2 (high)
pH	A	1	2	3	4	5
amount of DDTC (μL)	B	10	30	50	70	90
Temperature (°C)	C	20	30	40	50	60
Amount of IL (μL)	D	30	40	50	60	70
Concentration of salt (% w/v)	E	0	0.2	0.4	0.6	0.8

random order and divided into two blocks, using a 10 mL sample solution containing a concentration of 50 μg L^{-1}.

3. Results and discussion

3.1. Selection of IL

For selection of a suitable IL some considerations were recommended. In this work, we focused on the ILs containing imidazolium cation. Imidazolium-ILs containing PF_6^- as anion are hydrophobic, relatively inexpensive, and liquid in the experimental conditions, so they are suitable for LLE. Among [Bmim][PF_6], [Hmim][PF_6], and [Omim][PF_6] according to physicochemical properties like density, viscosity, and water solubility, with regard to the fact that the sample volume was 10 mL, [Hmim][PF_6] was chosen as the extractant solvent.

3.2. Selection of anti-sticking agent

According to reported works in literature, after centrifugation, it was observed that some amount of the IL-phase sticks on the wall of the centrifuge tube. In order to overcome this problem, a non-ionic surfactant was added into the sample solution. In the presence of the non-ionic surfactant and during the phase separation, molecules of the surfactant surrounded the fine droplets of IL. Hence, interactions of IL with the wall of the centrifuge tube decreased and consequently, IL-phase did not stick on the wall of the centrifuge tube.

The effects of two non-ionic surfactants (Triton X-114 and Triton X-100) were investigated and compared. In the presence of Triton X-100, the absorbance decreased; while in the case of using Triton X-114, the absorbance increased. So, Triton X-114 was chosen as the anti-sticking agent at the optimum concentration of 0.05% (w/v).

3.3. Selection of diluting agent

For AAS, the solvent should have good nebulization and burning characteristics, having not too low-boiling point and compatibility with direct injection into FAAS. To select the best diluting agent, effect of ethanol and acetone was studied individually and IL-phase was diluted by 100 μL of the each solvent. Both acetone and ethanol could dissolve the settled IL-phase. However, ethanol was preferred to acetone due to major compatibility with FAAS. In addition, ethanol showed better repeatability in absorbance and sharper peaks than acetone. Therefore, 100 μL of ethanol was chosen to dilute the settled phase.

3.4. Optimization of the preconcentration procedure by using factorial design

For optimization of the preconcentration procedure, a fractional factorial design (2^{5-1}) was performed, involving the mentioned variables. The central composite design can be described with Eq. (1), resulting from adjustment of the quadratic model.

$$\begin{aligned} R &= 0.099 + 0.027A + 0.028B + 0.024C \\ &+ 0.097D - 0.024E - 0.004143AB - 0.022AC \\ &+ 0.023AD - 0.008626AE - 0.009757BC \\ &+ 0.044BD - 0.030BE \\ &+ 0.017CD - 0.001824CE - 0.045DE + 0.005088A^2 \\ &+ 0.004346B^2 + 0.014C^2 + 0.044D^2 - 0.0047E^2 \end{aligned}$$

Parameters of the equation were obtained by multiple regression analysis of the experimental data, where *R* is the predicted response in a real value. The mathematical model was evaluated by using the analysis of variance (ANOVA) and the analysis of the residues generated between predicted values and observed values (Table 2). Results demonstrated that the employed mathematical model suited well with the obtained values. The results were interpreted by using graphs obtained from the model. The three-dimensional (3D) central composite design plots of the response, using Eq. (1) when one of the variables is fixed at the central point and the other two are allowed to vary, are shown in Fig. 1. The plots depicted interaction between effective parameters.

Separation of metal ions by CIAME involves prior formation of a complex with sufficient hydrophobicity and subsequent extraction into a small volume of the sedimented phase. The pH value plays a unique role in the metal chelate formation and the subsequent extraction. The effect of pH in the range of 1.0–5.0 on the formation of Cu–DDTC complex and the extraction of copper ions in water samples was investigated. As can be seen, the signal intensity of Cu was improved with the increase of pH from 1 to 4. When pH was higher than 4, the signal of Cu started to decrease with the increasing pH. Because of the precipitation of this cation, thus, pH of 4 was selected for the following experiment (Fig. 1(a)).

The effect of DDTC concentration was examined, too. According to Fig. 1(b), the absorption increased by increasing the DDTC concentration, as it was expected. We investigated DDTC concentration in the range of 1.0×10^{-5}–9.0×10^{-5} mol L^{-1}. Maximum absorbance was obtained at a concentration of 7×10^{-5} mol L^{-1} of the ligand and after that, the absorbance stayed approximately constant.

In the presence of high content of salt, the solubility of [Hmim][PF_6] increases and phase separation does

Table 2
ANOVA for response surface reduced cubic model ANOVA table

Source	Sum of square	df[a]	Mean square	*F*-value	*P*-value Prob > *F*	
Block	7.442E−003	1	7.442E−003			
Model	0.46	20	0.023	10.15	<0.0001	Significant
A	0.016	1	0.016	7.27	0.0174	
B	0.017	1	0.017	7.62	0.0153	
C	0.013	1	0.013	5.95	0.0286	
D	0.22	1	0.22	97.16	<0.0001	
E	0.013	1	0.013	5.75	0.0309	
AB	2.303E−004	1	2.303E−004	0.10	0.7546	
AC	7.322E−003	1	7.322E−003	3.23	0.0938	
AD	7.884E−003	1	7.884E−003	3.48	0.0832	
AE	1.146E−003	1	1.146E−003	0.51	0.4885	
BC	1.277E−003	1	1.277E−003	0.56	0.4652	
BD	0.026	1	0.026	11.37	0.0046	
BE	0.012	1	0.012	5.31	0.0371	
CD	4.413E−003	1	4.413E−003	1.95	0.1845	
CE	5.122E−005	1	5.122E−005	0.023	0.8826	
DE	0.032	1	0.032	13.96	0.0022	
A2	8.266E−004	1	8.266E−004	0.36	0.5554	
B^2	5.906E−004	1	5.906E−004	0.26	0.6176	
C^2	6.450E−003	1	6.450E−003	2.85	0.1136	
D^2	0.063	1	0.063	27.82	0.0001	
E^2	7.053E−004	1	7.053E−004	0.31	0.5856	
Residual	0.032	14	2.265E−003			
Lack of Fit	0.014	6	2.405E−003	1.11	0.4313	Not significant
Pure Error	0.017	8	2.160E−003			
Core Total	0.50	35				

[a]Degree of freedom.

not occur, but according to common ion effect, solubility decreases in the presence of IL with common ion (such as [Hmim][Tf_2N]). This is one of the interesting properties of ILs. In the presence of [Hmim][Tf_2N], a lower amount of [Hmim][PF_6] was required for the phase separation. The effect of the amount of IL ([Hmim][PF_6]), in the range of 24–72 mg was investigated. Fig. 1(b) shows that the optimum amount of [Hmim][PF_6] for the complete extraction was 48 mg in the presence of [Hmim][Tf_2N].

$NaNO_3$ was chosen in order to study the salt effect in the range of 0–0.8% (w/v). Absorbance slightly increased as a result of the salting-out effect. A concentration of 0.21% (w/v) $NaNO_3$ was selected for subsequent experiments to increase the recovery (Fig. 1(c)).

According to (Fig. 1(c)), before shaking the solution containing IL, it was heated in the range of 20–70°C. In this range, the absorbance was approximately constant. Since ILs dissolved more easily at temperatures of above 30°C, the temperature of 45°C was chosen for the heating step.

3.5. Analytical features

Under optimum conditions, the calibration curves were observed as linear in the concentration range of 2–100 μL^{-1} Cu by using 10 mL of the solution. The correlation coefficient of the calibration curve equation was 0.996, which indicates that a good linear regression was established between the absorbances and the concentrations. The detection limit, calculated according to three times the standard deviation of the blank signals with the preconcentration step, was 0.42 $\mu g\,L^{-1}$ for Cu. The precision expressed as a relative standard deviation (RSD) for six replicate measurements of the concentration of 15 $\mu g\,L^{-1}$ was 2.61%.

The enrichment factor was calculated by the ratio of slope of preconcentrated samples to those obtained without preconcentration and it was 75.

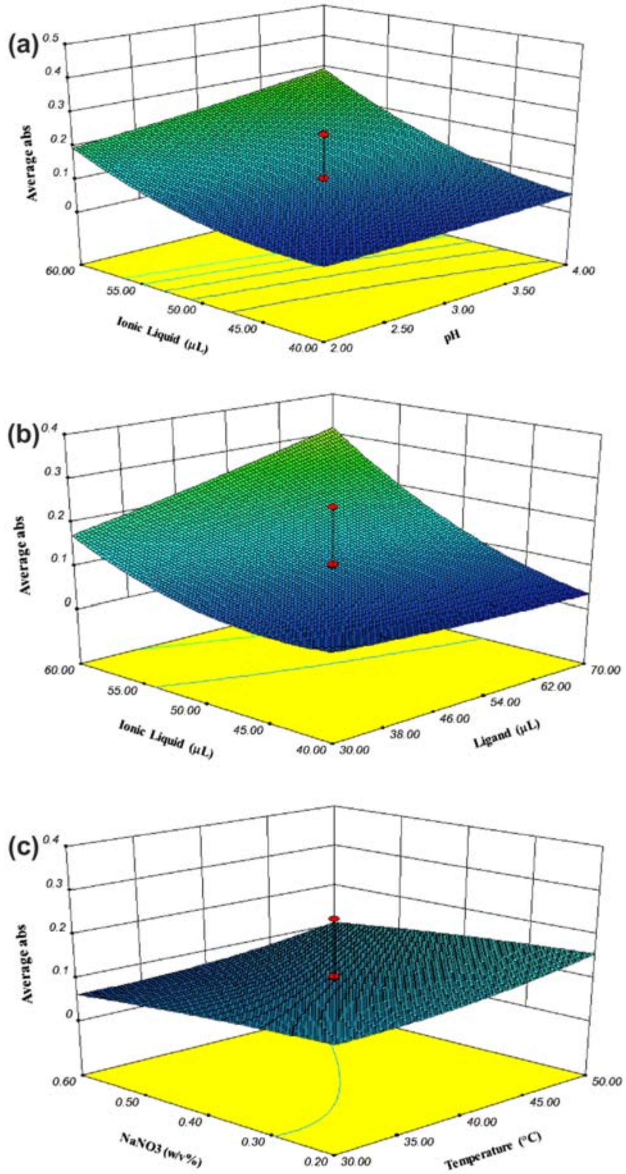

Fig. 1. The 3D central composite design plots for effects of variables on the response: (a) effect of the concentration of ligand and pH on the absorbance. Experimental conditions: Sample volume: 10 mL, [Hmim][PF_6]: 48 mg concentration of $NaNO_3$: 0.21% (w/v), temperature: 45˚C, concentration of analyte: 50 $\mu g\,L^{-1}$ (b) effect of the amount of IL and concentration of ligand on the absorbance. Experimental conditions: Sample volume: 10 mL, concentration of $NaNO_3$: 0.21% (w/v), pH: 4, temperature: 45˚C, concentration of analyte: 50 $\mu g\,L^{-1}$ and (c) effect of two variables (temperature and salt concentration) on the absorbance. Experimental conditions: Sample volume: 10 mL, [Hmim][PF_6]: 48 mg, DDTC concentration: 7×10^{-5} mol L^{-1}, pH: 4, concentration of analyte: 50 $\mu g\,L^{-1}$.

3.6. Effect of foreign ions

The interference in the present method was investigated. The interference was due to the competition of other metal ions for the chelating agent and their subsequent co-extraction with Cu. In these experiments, a solution containing 10 ng mL^{-1} of Cu and interfering ions were treated according to the recommended procedure. The tolerance limit was defined as the concentration of added ions that caused less than ±5%. The results showed that at least 5,000 $\mu g\,mL^{-1}$ of Na^+, K^+, SO_4^{2-}, NO_3^-, and Cl^-, 2,000 $\mu g\,mL^{1-}$ of Ca^{2+} and Mg^{2+} and 100 $\mu g\,mL^{-1}$ of Al^{3+}, SiO_4^{2-}, and PO_4^{3-} had no remarkable interferences with the determination of Cu. Co^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, and Pb^{2+} could be tolerated up to 5 $\mu g\,mL^{-1}$ and $Cr^{3+}$and Fe^{3+} could be tolerated up to 1 $\mu g\,mL^{-1}$.

3.7. Comparison with other methods

Table 3 compares the characteristic data of the proposed method with other preconcentration methods for Cu^{2+} reported in the literature. As it can be seen, the proposed method possesses a lower limit of detection and a higher enrichment factor than most reported methods with only 10 mL of the sample solution and it is suitable for determination of trace amounts of Cu^{2+} in water and food samples.

3.8. Analytical application

The proposed method was applied to determine Cu^{2+} ions in water and food samples. The accuracy of the method was investigated with known amounts of Cu^{2+} ions. Copper ions were also determined in all the samples by inductively coupled plasma optic emission spectrometry (ICP-OES), not presenting statistical difference between obtained results. All these results are presented in Table 4. The percentage recovery (R) was calculated by using the equation: $R = 100(C_s - C_0)/m$, where C_s is a value of metal in a spiked sample, C_0 is a value of the metal in the sample, and m is an amount of the spiked metal. These results demonstrated that the proposed procedure could be satisfactorily used for analysis of water and food samples.

4. Conclusions

In this study, an efficient and simple mode of HLLME based on IL named CIAME was developed for preconcentration of copper from water and food samples as a prior step to its determination by FAAS. Copper was employed as a test analyte and DDTC as the complexing agent to assess the extraction procedure. This method is simple, rapid, safe, and robust against high content of salt and water-miscible organic solvents. The variables influencing the proposed mic-

Table 3
Comparison of CIAME with other methods for determination of copper

Method	SV[a]	EF[b]/PF[c]	RSD[d]	LOD[e]	Ref.
SPE/ICP-OES[f]	25	54	3.76	0.26	[27]
HLLME[g]/FAAS	5	25	7.6	1.74	[28]
CPE[h]/UV–vis spectrometry	25	22	2.8	5	[29]
DLLME[i]/FAAS	12	42–48	5.1	3	[30]
D-CPE[j]/FAAS	10	22	2.7	0.5	[31]
CIAME/FAAS	10	75	2.61	0.42	This work

[a] Sample volume.
[b] Enrichment factor.
[c] Preconcentration factor.
[d] Relative standard deviation.
[e] Limit of detection.
[f] Solid phase extraction and inductively coupled plasma optical emission spectrometry.
[g] Homogeneous liquid–liquid extraction.
[h] Cloud point extraction.
[i] Dispersive liquid–liquid microextraction.
[j] Displacement cloud point extraction.

Table 4
Analytical results for Cu^{2+} determination in food and water samples by proposed and ICP–OES methods

Sample	Added	Found	Recovery (%)	ICP-OES
Potato ($\mu g\, g^{-1}$)	0	3.28 ± 0.09	–	3.5 ± 0.08
	10	13.15 ± 0.36	98.7	13.43 ± 0.34
Broccoli ($\mu g\, g^{-1}$)	0	4.30 ± 0.12	–	4.12 ± 0.10
	10	14.17 ± 0.41	98.3	14.10 ± 0.38
Green tea ($\mu g\, g^{-1}$)	0	6.42 ± 0.17	–	6.48 ± 0.19
	10	16.20 ± 0.43	98.6	16.29 ± 0.46
Tap water ($\mu g\, L^{-1}$)	0	7.10 ± 0.20	–	7.20 ± 0.17
	10	17.00 ± 0.48	99	17.15 ± 0.44
Wall water ($\mu g\, L^{-1}$)	0	3.50 ± 0.10	–	3.37 ± 0.12
	10	13.63 ± 0.38	101.3	13.47 ± 0.35
Sea water ($\mu g\, L^{-1}$)	0	2.47 ± 0.07	–	2.45 ± 0.08
	10	12.30 ± 0.33	98.3	12.36 ± 0.35
River water ($\mu g\, L^{-1}$)	0	2.30 ± 0.06	–	2.4 ± 0.05
	10	11.95 ± 0.32	96.5	12.25 ± 0.30

roextraction method have been studied. The dynamic range of the method was comprised between 2 and 100 $\mu g\, L^{-1}$, the detection limit and enrichment factor were 0.42 $\mu g\, L^{-1}$ and 75 for copper, respectively. The proposed method was compared with the other methods and applied to the analysis of various real samples and the satisfactory relative recoveries (96.5–101.3%) were obtained.

In comparison with cloud point extraction (CPE), the background is too low in the case of saline solutions, because of a very low solubility of water in ILs. Also, owing to a high viscosity of ILs, removal of bulk aqueous phase is easier. This method is more suitable for the extraction of heat-susceptible species in comparison with CPE. By flame microsampling technique, the consumption of the extractant phase was minimized and the enrichment factor of the microextraction technique was improved. Also an injection of a small volume (50 µL) of the extractant phase into the flame provides very smooth and spike-like signal profiles. A fractional factorial design enabled the optimization step to be faster. Therefore, the detailed effect of factors on each other and also on the efficiency could be seen. This helped us to choose, more precisely, the best experimental conditions for effective factors with minimal experimental trials.

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