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In situ metathesis ionic liquid formation dispersive liquid–liquid microextraction for copper determination in water samples by electrothermal atomic absorption spectrometry

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ABSTRACT

In situ synthesis of ionic liquid extractant for dispersive liquid–liquid microextraction (*in situ* IL DLLME) combined with electrothermal atomic absorption spectrometry (ET AAS) for determination of copper in water samples was developed. Analytical signals were obtained without the back-extraction of copper from the IL phase prior to its determination by AAS. Some essential parameters of the microextraction and detection techniques such as the pH of sample solution, volume of components for *in situ* synthesis, matrix interferences and main parameters of graphite furnace atomizer have been studied. Under optimal conditions, high extraction efficiency for copper was achieved for the extraction of 0.7 μg L^{-1} in 10.0 mL of sample solution employing 8 μL of 1-hexyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl]imide ($HmimNTf_2$) as the extraction solvent. The detection limit was found as 0.004 μg L^{-1} with an enrichment factor of 200. The relative standard deviation (RSD) for seven replicate measurements of 0.7 μg L^{-1} in sample solution was 4%. The accuracy of the proposed method was evaluated by analysis of the Certified Reference Materials: NIST SRM 2709 (San Joaquin Soil), NBS SRM 2704 (Buffalo River Sediment), NRCC DOLT-2 (Dogfish Liver) and NIST SRM 1643e (Trace Element in Water). The measured copper contents in the reference materials were in satisfactory agreement with the certified values. The method was successfully applied to analysis of the tap, lake and mineral water samples.

1. Introduction

Copper is an essential element involved as a co-factor in a number of enzymatic reactions. However, its high concentrations in food and water are toxic. Long term exposure to copper can cause damage of infant liver at concentration 3 mg L^{-1} and single intake of water containing 30 mg L^{-1} copper results in vomiting, diarrhea and stomach cramps [1]. Many studies revealed its negative influence on different organisms. Copper is toxic to organisms including fish [2], amphipods [2,3] and algae [4]. Toxic properties of copper were noted at low μg per liter level to several dozens of μg per liter level. Influence of water pH and temperature on its toxicity was also confirmed [3,4].

Widespread copper utilization and its toxicity led to formation of regulations concerning its concentrations in both drinking and environmental water. US Environmental Protection Agency issued regulations limiting copper concentration in drinking water to 1.3 mg L^{-1} [5] and European proposals limit its content in fresh water to 1 μg L^{-1} and in sea water to 2.64 μg L^{-1} [6]. The necessity of copper control at low levels forces the usage of preconcentration procedures before its determination.

In the recent years a lot of new sample preparation techniques based on the copper extraction and microextraction have been proposed including solid-phase extraction [7–9] and dispersive liquid–liquid microextraction (DLLME) [10–15]. The DLLME technique streamlines the sample preparation step and can be used for isolation of both metal and organic analytes [16]. Most DLLME procedures require use of dispersion solvents to enable dissipation of extraction solvents in water samples and formation of a cloudy solution. At the same time the dispersion solvents increase solubility of analytes in the water matrix and generate additional wastes. Different procedures were developed to overcome these problems. Some researchers proposed usage of ultrasounds for dispersing the extraction solvent [17–19].

In another approach to DLLME the heating of the extraction solvent was used until its complete solubilization in the water matrix [20–22]. Mass transfer was improved but the procedure required much time for heating and cooling of the sample solution. The newest version of DLLME is an interesting alternative to the former techniques. The extraction solvent is formed *in situ* in relatively fast chemical reaction in a sample solution and no dispersion solvent is used. Only a few examples of that procedure

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can be found in the literature. Number of proposed *in situ* reactions is even more limited, as the researchers tend to use one type of reaction for a few studies [23–25].

This paper presents the development of *in situ* metathesis ionic liquid formation for DLLME isolation of copper from the water matrix. To our knowledge, the preconcentration of copper with *in situ* DLLME and its subsequent determination by electrothermal atomic absorption spectrometry (ET AAS) in organic phase without back-extraction has not been reported yet. A new procedure is proposed for *in situ* synthesis of ionic liquid.

2. Materials and methods

2.1. Instrumentation

All measurements were performed with an AAS 5EA spectrometer (Analytik Jena GmbH, Jena, Germany) equipped with deuterium source background correction, a transversely heated graphite atomizer and an MPE5 autosampler. Pyrolytically coated graphite tubes were employed exclusively. Copper hollow cathode lamp (Photron, Australia) was used as the radiation source. The operating conditions of the hollow cathode lamp were those recommended by the manufacturer. Compressed argon of UHP 5.5 purity obtained from Air Products (Warsaw, Poland) was employed as a protective and purge gas.

A centrifuge (Hettich EBA 20, Tuttlingen, Germany), generating a speed in the range from 500 to 6000 rpm, was employed for phase separation after extraction procedure.

The pH values were measured with a pH-meter (pH 211 Microprocessor, Hanna Instruments, Kehl, Germany) supplied with a glass-combined electrode.

A UniClever focused microwave sample preparation system (Plazmatronika, Wrocław, Poland) operating at 2450 MHz and 300 W maximum output was used to samples digestion. The computer-controlled system with continuous temperature, pressure and microwave power monitoring was equipped with high-pressure TFM-PTFE vessel and water cooling system. The vessel capacity was 110 mL and the maximum pressure and maximum temperature were 100 atm and 300 °C, respectively.

2.2. Reagents and solutions

Lithium bis[(trifluoromethyl)sulfonyl]imide ($LiNTf_2$), 1-hexyl-3-methylimidazolium chloride (HmimCl) and sodium diethyldithiocarbamate (DDTC) were from Sigma-Aldrich (St. Louis, MO, USA). Ethanol (absolute, *ca.* 99.5%) from J.T.Baker (Deventer, The Netherlands) was used as solvent for ionic liquid phase containing copper before ET AAS procedure. Working standard solutions were obtained by appropriate dilution of the stock standard solution ($1000\ mg\ L^{-1}$ solution of copper in 2% nitric acid, J.T.Baker). Solutions of $LiNTf_2$, HmimCl and DDTC were prepared in water at concentrations $0.2\ g\ mL^{-1}$, $0.45\ g\ mL^{-1}$ and $0.11\ g\ mL^{-1}$, respectively. All working standard solutions were prepared daily, the appropriate stock solution was diluted with high-purity water.

The pH of the sample solutions was adjusted with 65% HNO_3 and 30% NaOH (Suprapur, Merck, Darmstadt, Germany). Hydrogen peroxide 30% and 40% HF of the highest quality (Suprapur, Merck) were used for microwave-assisted digestion of SRMs.

High-purity water: deionized and doubly distilled water (quartz apparatus, Bi18, Heraeus, Hanau, Germany) was also used throughout the experiments. The interference study was performed with AAS standard solutions of the appropriate metals ($1000\ mg\ L^{-1}$, Certipur, Merck) and humic acid from Sigma-Aldrich.

2.3. Certified reference materials and real samples

Accuracy of the analytical procedure was verified using standard reference materials: DOLT-2 (Dogfish Liver) from the National Research Council of Canada (NRCC); SRM 1643e (Trace elements in water) and SRM 2709 San Joaquin Soil (Baseline Trace Element Concentrations) from the National Institute of Standards and Technology (NIST); SRM 2704 (Buffalo River Sediment) from the National Bureau of Standards (NBS).

During sample collection procedure all glass bottles were washed before using with 5% HNO_3 solution and then with high-purity water. Real water samples were collected from the several taps and lakes in Poznań city and from the points located around the city. Tap water was collected after 30 s running from the tap. Mineral water was purchased from a local store. All solid samples were analyzed after microwave-assisted digestion, water samples were analyzed directly without additional preparation.

2.4. Analytical procedures

2.4.1. Microwave-assisted digestion of SRMs

Approximately 250 mg of powdered standard reference material was placed in the TFM-PTFE vessel of the microwave digestion system and moistened by 1 mL of 30% H_2O_2. Then, 4 mL of 65% HNO_3 and 1 or 2 mL of 40% HF (for sediment or soil respectively) were added. The sample was heated for 20 min at 300 W. After digestion, the clear digested solution was transferred into 20 mL calibrated flask and diluted to volume with high-purity water. Before further analysis this solution was appropriately diluted depending on the concentration level of the element. In all cases, a corresponding blank was also prepared according to the above microwave-assisted digestion procedure.

2.4.2. Extraction and AAS determination procedures

Ten milliliters of a sample solution was poured into a centrifuge tube. The pH of the sample was adjusted to neutral if necessary. Then, 100 μL of DDTC solution was added. After 1 min 45 μL of HmimCl solution was pipetted. Next 100 μL of $LiNTf_2$ solution was added to start metathesis reaction. As a result 1-hexyl-3-methylimidazolium bis [(trifluoromethyl)sulfonyl]imide ($HmimNTf_2$) was formed. Five minutes later the mixture was centrifuged for 5 min at 5000 rpm and $HmimNTf_2$ containing copper-DDTC complex settled on the bottom of the tube. The bulk water phase was removed and the ionic liquid phase (about 8 μL) was dissolved in 40 μL of ethanol. In order to determine the analyte in the dissolved ionic liquid phase, 10 μL of the solution was injected into the graphite tube for ET AAS determination under the optimized conditions. Calibration was performed by the standard calibration technique using ethanol standards with addition of ionic liquid. The detailed graphite furnace temperature program used for the copper determination in analytical samples is shown in Table 1.

3. Results and discussion

The chemical and physical variables of *in situ* IL DLLME ET AAS method were optimized to achieve the best analytical performance by investigating each variable in turn with all other variables kept constant. This procedure allowed studying the individual effect of each variable on the analytical signals and extraction efficiency for copper. In order to investigate the microextraction of copper, parameters included the sample pH value, amount of components for *in situ* synthesis, DDTC concentration, complexation time as well as main parameters of graphite furnace atomizer have been studied. All experiments were performed with

Table 1
Operating conditions of the ET AA spectrometer used for copper determination after dispersive liquid–liquid microextraction with *in situ* metathesis ionic liquid formation.

AAS parameters	Values
Wavelength (nm)	324.8
Spectral band width (nm)	0.8
Lamp current (mA)	3.0
Furnace program steps	
Drying	90 °C, ramp 10 °C s^{-1}, hold 5 s
Drying	120 °C, ramp 10 °C s^{-1}, hold 10 s
Drying	400 °C, ramp 50 °C s^{-1}, hold 20 s
Pyrolysis	1100 °C, ramp 500 °C s^{-1}, hold 10 s
Atomization	2100 °C, ramp 1900 °C s^{-1}, hold 3 s
Cleanout	2450 °C, ramp 1000 °C s^{-1}, hold 4 s
Sample volume (μL)	10
Measurement mode	Peak height

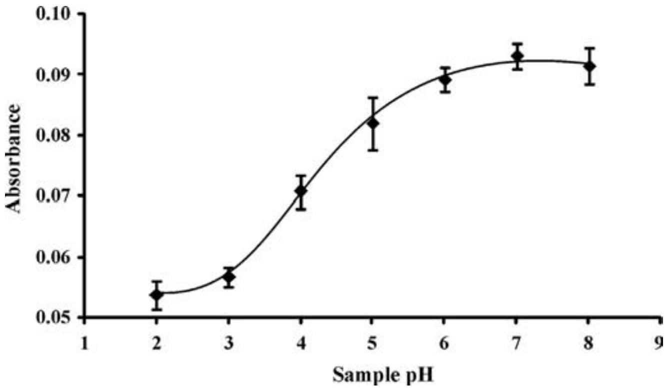

Fig. 1. Effect of the sample pH on the absorbance. Conditions: sample volume: 10 mL, $LiNTf_2$: 30 mg, HmimCl: 30 mg, DDTC concentration: 5.0×10^{-3} mol L^{-1}, reaction time: 2 min, 0.7 μg Cu (II) L^{-1}. The error bar is the standard deviation (SD, $n=3$).

10 mL of copper water standard solution (0.7 ng mL^{-1}) using peak height measurements.

3.1. Effect of pH

Formation of metal complexes is strongly dependent on pH of the water phase. Therefore, influence of pH on the extraction of copper was studied in the first step of the optimization. The effect of pH was studied in the range of 2–8. The results presented in Fig. 1 show increase of absorbance from pH 2 to pH 7. Lower extraction efficiency obtained for more acidic media can be connected with competition of copper ions with protons for the reaction with DDTC [26]. At low pH the protonated DDTC can also be easily extracted to the ionic liquid leaving limited amount of its deprotonated form for formation of Cu-DDTC complex similarly to Cu-dithizone pair described by Wei et al. [27]. On the other hand, higher pH leads to enlarged concentration of Cu-DDTC complex that can be easily extracted into the ionic liquid phase. It should be also noted that DDTC is unstable in acidic media rapidly decomposing below pH 5 to diethylamine and carbon disulfide [28].

Mean absorbance obtained for pH 8 is slightly lower than this noted for pH 7. However, statistical evaluation of these results with the *t*-test gives the *p*-value equal to 0.436. Thus, it can be concluded that there is no statistical difference between the two means obtained at pH 7 and pH 8. The extraction conditions are stable in this range. Therefore, pH 7 was used in further studies.

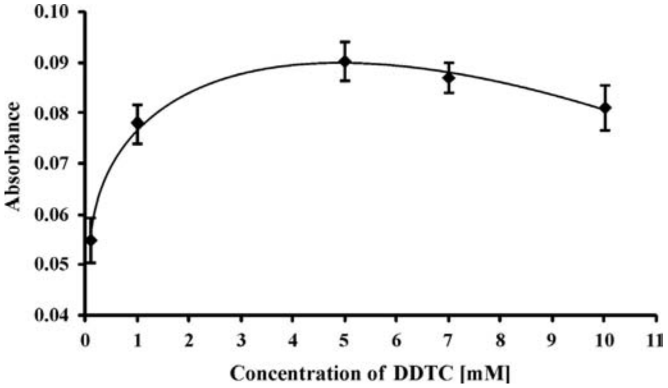

Fig. 2. Effect of DDTC concentration on the absorbance. Conditions: sample volume: 10 mL, $LiNTf_2$: 30 mg, HmimCl: 30 mg, reaction time: 2 min, pH=7, 0.7 μg Cu (II) L^{-1}. The error bar is the standard deviation (SD, $n=3$).

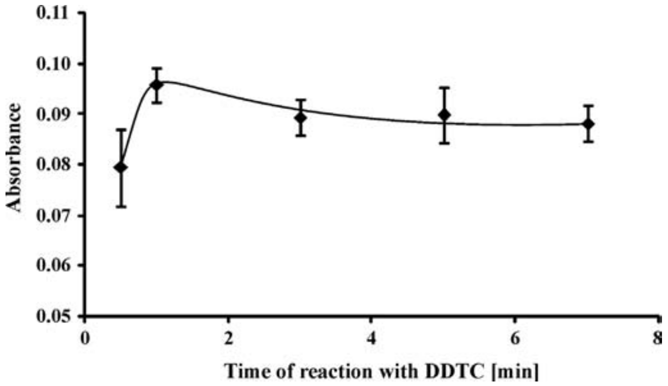

Fig. 3. Effect of reaction time with DDTC on the absorbance. Conditions: sample volume: 10 mL, $LiNTf_2$: 30 mg, HmimCl: 30 mg, DDTC concentration: 5.0×10^{-3} mol L^{-1}, pH=7, 0.7 μg Cu (II) L^{-1}. The error bar is the standard deviation (SD, $n=3$).

3.2. Effect of DDTC concentration and complexation time

The copper extraction depends on the formation of Cu-DDTC complex, therefore, the effect of DDTC concentration was studied in the range of 0.1–10 mM. The absorbance increased with increase of DDTC concentration up to 5 mM and decreased for higher concentrations (Fig. 2). Increase of absorbance observed up to 5 mM DDTC can be connected with better complexation of copper for higher amount of DDTC. Lower absorbance noted for higher concentration of DDTC is difficult to explain. Therefore, 5 mM of DDTC was chosen as the optimal concentration ensuring maximal absorbance.

Influence of time measured from injection of DDTC solution to injection of HmimCl solution was studied. The range of 0.5–7 min was tested and maximum absorbance was found for 1 min (Fig. 3). Therefore, 1 min of reaction time leading to complex formation was selected for further experiments.

3.3. Effect of amount of added HmimCl and $LiNTf_2$

Influence of amount of HmimCl added to the water phase was tested in a range of 10–50 mg. The highest absorbance was found for 20 mg (Fig. 4). Higher amount of HmimCl led to decreased concentration of copper which can be connected with higher volume of $HmimNTf_2$ formed. Lower amount of HmimCl also resulted in decreased recovery. This can be explained by incomplete extraction into small $HmimNTf_2$ drop or analyte loss.

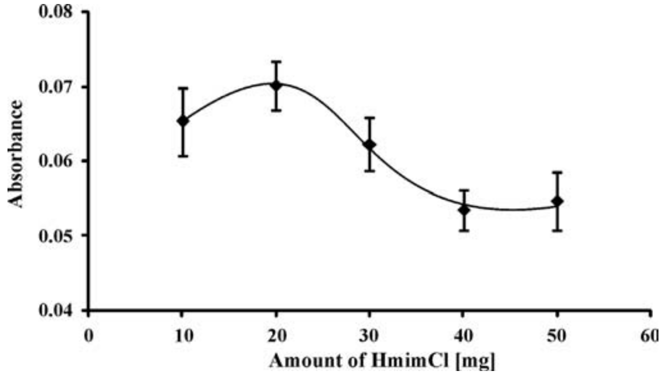

Fig. 4. Effect of HmimCl amount on the absorbance. Conditions: sample volume: 10 mL, $LiNTf_2$: 30 mg, DDTC concentration: 5.0×10^{-3} mol L^{-1}, reaction time: 1 min, pH=7, 0.7 μg Cu (II) L^{-1}. The error bar is the standard deviation (SD, $n=3$).

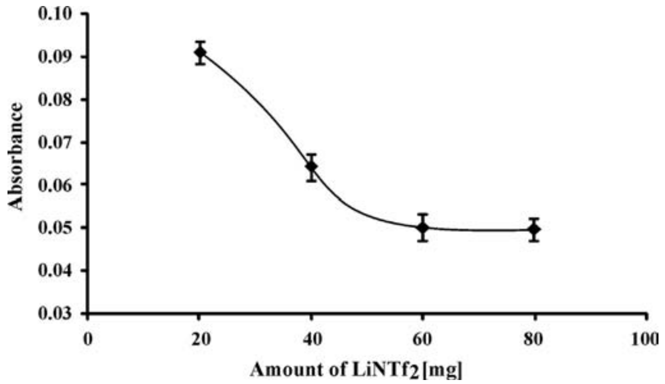

Fig. 5. Effect of $LiNTf_2$ amount on the absorbance. Conditions: sample volume: 10 mL, HmimCl: 20 mg, DDTC concentration: 5.0×10^{-3} mol L^{-1}, reaction time: 1 min, pH=7, 0.7 μg Cu (II) L^{-1}. The error bar is the standard deviation (SD, $n=3$).

Influence of amount of $LiNTf_2$ added to the water phase was tested in a range of 20–80 mg. The results presented in Fig. 5 show increase of absorbance for lower volumes of $LiNTf_2$. The highest absorbance was found for 20 mg. However, lower amount of this reagent could not be used in the extraction. No visible $HmimNTf_2$ drop could be found for 10 mg of added $LiNTf_2$.

3.4. Study of ET AAS conditions

The high viscosity of the obtained ionic liquid phase ($HmimNTf_2$) made it difficult for direct injection into the graphite tube. Therefore, ionic liquid phase (8 μL) was dissolved with ethanol prior to ET AAS determination. The total dissolution of the IL phase was observed for 40 μL of ethanol, while lower volumes resulted in unsatisfactory repeatability of injections and analytical signals. The final concentration of the ionic liquid was 17% (v/v). For that dissolution of organic phase increased background signal was observed due to matrix effects. Since the deuterium background correction is more accurate when background absorbance is minimal different temperatures and hold times were investigated in the last drying, pyrolysis and atomization steps to increase matrix elimination and obtain minimal background signal in the atomization step (Fig. 6). The rest of the operating conditions of graphite furnace program were those recommended by the manufacturer. There was no need to use any modifiers to accelerate the pyrolysis and volatilization of organic phase in the graphite furnace.

A temperature of 400 °C was selected as the working third drying temperature. To establish the effect of third draying hold time on the absorbance, the hold time in the range of 5–30 s was investigated. With increasing time, the absorbance increased up to 20 s and then stayed approximately constant. A hold time of 20 s for third drying step with a ramp of temperature 50 °C s^{-1} was chosen. The most important was to select an appropriate pyrolysis temperature for removing organic matter, resulting from the presence of the ionic liquid phase while, preventing the loss of copper prior to atomization step. The influence of pyrolysis temperature on the absorbance was studied within a range of 700–1300 °C. For temperatures lower than 700 °C it was impossible to achieve any analytical signals due to incomplete pyrolysis of ionic liquid in the graphite tube. The maximum absorbance was achieved for 1100 °C and it was selected as the working pyrolysis temperature. No significant improvements were observed for pyrolysis time longer than 20 s. A ramp of temperature 500 °C s^{-1} was chosen as it allowed slow elimination of organic matrix and analyte loss was avoided. After optimization of pyrolysis conditions the effect of atomization temperature on copper signal was studied within the range of 1600–2300 °C. The maximum signal was obtained at about 2100 °C and stayed constant up to 2200 °C. Complete vaporization and atomization of copper have been achieved in the graphite tube with minimal influence of organic matrix. An atomization hold time and ramp of 3 s and 1900 °C s^{-1} were selected, respectively.

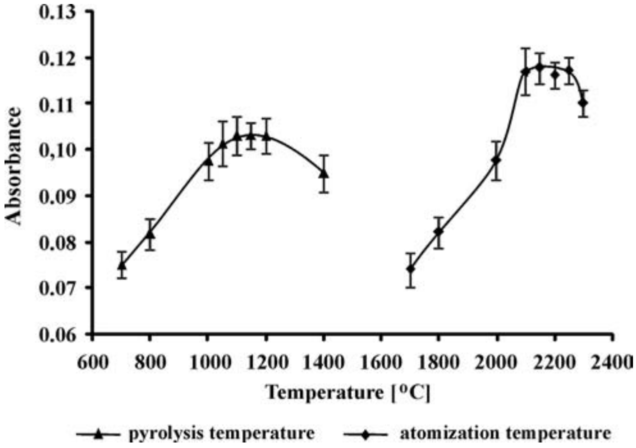

Fig. 6. Pyrolysis and atomization temperature curves for copper obtained by injection of 10 μL of ionic liquid ethanol solution. Atomization temperature for pyrolysis optimization was 2000 °C. Pyrolysis temperature for atomization optimization was 1100 °C. The concentration of copper in sample solution was 0.7 μg L^{-1}. The error bar is the standard deviation (SD, $n=3$).

3.5. Effect of other ions

In the presented study DDTC was used in the sample solution as a complexing agent for copper. It can also react with other metal ions to form corresponding complexes and may interfere in the extraction of analyte. Thus, the effect of coexisting metal ions (commonly determined in natural water) on the extraction of copper was investigated. The effect of 100 mg L^{-1} concentrations of Ca(II), Cd(II), Co(II), Cr(IV), Fe(III), Ni(II), Mg(II), Mn(IV), Pb(II) and Zn(II) present in a 0.7 μg L^{-1} solution of Cu(II) was examined. It was found that none of the chosen metal ions influence the analytical signals of copper. Despite the extraction of some metal ions with copper (in some cases color formation was observed), high selectivity of ET AAS enabled to determine ultratrace copper in SRMs and real water samples with complex matrices. The recoveries of copper in the presence of these concomitants did not produce a relative standard deviation of more than 5% in the absorbance of the analyte.

In natural water the copper ions can be complexed by humic matter. The formation of the complex depends obviously on the parameters, such as pH, concentration of complexing agent and other components, hence, it depends strongly on the type of the natural water, i.e., sea water, fresh water, humic-rich waters, etc. Thus, in analytical samples humic acid can compete with DDTC to form a complex with copper and may lead to interference [29–31]. For this reason, the effect of humic acid on the extraction efficiency was investigated. The results proved that the interference of humic acid with the formation and extraction of the copper-DDTC complex is negligible for the humic acid concentration 100 mg L^{-1} in water sample in the presence of DDTC. This is probably due to the large formation constant of the copper-DDTC complex.

3.6. *Analytical figures of merit*

The analytical characteristics of the proposed *in situ* IL DLLME ET AAS method were investigated under the optimized experimental conditions. The relative standard deviation (RSD) for seven replicate measurements of 0.7 μg L^{-1} in sample solution was 4%. The detection limit (LOD), calculated as the concentration of the analyte yielding a signal equivalent to three times the standard deviation of the blank value ($n=7$), was 4 ng L^{-1} for 10 mL of sample solution. The calibration curves were prepared under the optimized conditions with standard copper-IL-ethanol solutions containing 17% (v/v) $HmimNTf_2$ and 5 mM DDTC. An acceptable correlation coefficient was found 0.9968. The calibration curve was investigated up to 200 μg L^{-1} and was linear in the tested range. Enrichment factor was calculated using the ratio of the analyte concentration in the ionic liquid phase (C_{IL}) to the initial concentration of analyte (C_0) within the sample solution: $EF=C_{IL}/C_0$ [32] and was obtained as high as 200.

3.7. *Accuracy verification*

The accuracy of the proposed method was evaluated by analyzing certified reference materials with different complex matrices: SRM 1643e (water), DOLT-2 (liver), SRM 2709 (soil) and SRM 2704 (river sediment). The materials were analyzed according to the optimized *in situ* IL DLLME ET AAS method. The results were compared with the certified value using a *t*-test at 95% confidence limits (Table 2). Recovery values of copper were between 101 and 107%. Obtained results show that the proposed method can be applied for the preconcentration and determination of copper in water and environmental samples with complex matrices. The precision expressed as relative standard deviation (RSD, %) was in the range 3–8% for the reference materials. The sample preparation technique did not influence the analytical results.

Table 2
Accuracy verification of *in situ* IL DLLME ET AAS method for copper determination in selected standard reference materials in optimized conditions. Obtained values: average value ± standard deviation for $n=5$.

Reference material code	Certified	Determined	
	Cu (μg g^{-1})	Cu (μg g^{-1})	Recovery (%)
SRM 1643e	22.76[a] ± 0.31	22.99[a] ± 0.67	101
SRM 2709	34.6 ± 0.7	37.1 ± 2.9	107
SRM 2704	98.6 ± 5.0	101.5 ± 6.9	103
DOLT-2	25.8 ± 1.1	26.8 ± 1.1	104

[a] μg L^{-1}

Table 3
Concentration of copper in real water samples. Obtained values: average value ± standard deviation for $n=5$.

Sample number	Sample type	Cu (μg L^{-1})
1	tap water	29.44 ± 0.71
2		68.80 ± 2.97
3		6.24 ± 0.21
4		1.32 ± 0.05
5		0.35 ± 0.02
6		1.55 ± 0.07
7		0.51 ± 0.03
8		22.90 ± 0.80
9		7.44 ± 0.33
10		25.66 ± 0.68
11		8.97 ± 0.30
12	lake water	1.00 ± 0.07
13		255.6[a] ± 21.0
14		1.89 ± 0.12
15		0.64 ± 0.04
16		21.2[a] ± 2.0
17	mineral water	89.3[a] ± 7.0
18		138.3[a] ± 9.1
19		104.9[a] ± 6.0
20		0.320 ± 0.018

[a] ng L^{-1}

3.8. *Analysis of real samples*

Three types of water samples were analyzed: tap, mineral and lake water. The results presented in Table 3 show considerable differences between tap water and the two other sources of water. Concentrations of copper in the samples of tap water were in a range of 0.35–68.80 μg L^{-1} with mean value 15.74 μg L^{-1}. The presence of copper in tap water can be caused by corrosion of household plumbing systems, erosion of natural deposits as well as fittings. Its amount depends on the types of pipes and amounts of minerals in the water, how long the water stays in the pipes, and the acidity of water and its temperature [5]. However, none of the tested tap water samples contained copper above the limit 1.3 mg L^{-1} given by US legislation [5]. Thus, water from all these sources can be considered safe for humans, although contaminated in comparison to lake water.

Water from the tested lakes contained from 0.09 to 1.89 μg L^{-1} of copper with mean value 0.76 μg L^{-1}. One tested sample contained copper above European limit 1 μg L^{-1} [6]. This sample was taken from Lake Malta which receives water from a small river highly polluted by illegal discharge of sewage from local houses and small firms. Two other lakes containing 1.00 and 0.64 μg L^{-1} of copper are also situated close to human residential areas. The two samples from lakes located away from human presence contained low levels of copper i.e. 89 and 256 ng L^{-1}. In this context high levels of copper in environmental samples can be used as a measure of their anthropogenic contamination.

Tested mineral water samples contained low amounts of copper at level comparable to water from uncontaminated lakes. Even highly mineralized mineral water (sample 20) contained only 0.320 μg L^{-1} of copper—over a thousand times less than safety level for human beings [5]. Low copper content in comparison to tap water means also that copper plumbing was not used in the production process of mineral water and that the tested mineral waters are not just bottled tap waters.

3.9. *Comparison with other methods*

A comparison of the proposed method with reported extraction and preconcentration methods for copper determination is given in Table 4. As can be seen, presented *in situ* IL DLLME procedure

Table 4
Comparison of the proposed method with other analytical procedures for determination of copper.

Sample preparation method	Analytical measurement	Sample volume (mL)	EF	Estimated sample preparation time (min)	LOD ($\mu g\ L^{-1}$)	Ref.
IL DLLME	FAAS	10	136.6	7	0.45	[10]
DLLME	FAAS	5	42–48	10	3	[14]
PEP	GFAAS	2	1–4	10	3.6	[33]
FI-SPE	FAAS	13.2–26.4	21–43	2–4	0.93	[34]
CPE	GFAAS	5	10	30	0.05	[35]
CPE	FAAS	50	64.3	45	0.27	[36]
LLE	GFAAS	3.3	5.4	10	0.10	[37]
in situ IL DLLME	GFAAS	10	200	7	0.004	this study

EF—enrichment factor,
PEP—polymer extraction–precipitation,
FI-SPE—flow injection on-line SPE preconcentration,
CPE—cloud point extraction.

shows a low detection limit (0.004 $\mu g\ L^{-1}$) for 10 mL of sample and high enrichment factor (200) in relatively short time (7 min) of extraction. The method is free of volatile extraction organic solvent by using the ionic liquid as the green extraction solvent. The copper in the complex form could be determined by ET AAS directly from organic phase (ionic liquid and ethanol) without the back-extraction of the analyte from the IL phase into another aqueous media.

4. Conclusions

The *in situ* metathesis ionic liquid formation for dispersive liquid–liquid microextraction of copper as DDTC complex was demonstrated. This technique can be employed for isolation and preconcentration of copper from water and environmental samples. The product of *in situ* reaction is “environmentally friendly” because of its low volatile and nonflammable properties and has the potential to replace traditional VOCs in DLLME procedures for copper preconcentration.

Direct analysis (from organic phase, without back-extraction) and subsequent determination of copper by ET AAS was demonstrated even in the presence of the complex organic matrix of the ionic liquid. Also the effect of complex matrices presented in the samples was tolerable by the proposed method. A low limit of detection and good precisions were achieved for analyte. With using the *in situ* metathesis ionic liquid formation, the amount of the organic (ionic liquid) phase was minimized and the enrichment factor of the microextraction technique was improved. Therefore, a simple, rapid as well as “environmentally friendly” analytical method was achieved.

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References

[1] Toxicological Profile for Copper, Agency for Toxic Substances and Disease Registry U.S. Public Health Service, 1990.
[2] J.M. Besser and K.J. Leib, Toxicity of metals in water and sediments to aquatic biota, In: S.T. Church, P. van Guerard, S.E. Finger, (Eds.), Integrated Investigations of Environmental Effects of Historical Mining in the Animas River Watershed, San Juan County, Colorado, 2007, U.S. Geological Survey, Professional Paper 1651.
[3] L. Bat, M. Akbulut, M. Çulha, A. Gündoğu, H.H. Satilmiş, Turk. J. Zool. 24 (2000) 409–415.
[4] N.M. Franklin, J.L. Stauber, S.J. Markich, R.P. Lim, Aquat. Toxicol. 48 (2000) 275–289.
[5] National Primary Drinking Water Regulations, US Environmental Protection Agency, EPA 816-F-09-004, 2009.
[6] Proposals for Further Environmental Quality Standards for Specific Pollutants, UK Technical Advisory Group on the Water Framework Directive, 2012.
[7] Y. Yamini, A. Tamaddon, Talanta 49 (1999) 119–124.
[8] S.L.C. Ferreira, J.R. Ferreira, A.F. Dantas, V.A. Lemos, N.M.L. Araújo, A.C. Spinola Costa, Talanta 50 (2000) 1253–1259.
[9] S. Chanthai, N. Suwamart, Ch. Ruangviriyachai, E-J. Chem. 8 (2011) 1280–1292.
[10] R. Khani, F. Shemirani, B. Majidi, Desalination 266 (2011) 238–243.
[11] X. Wen, Q. Yang, Z. Yan, Q. Deng, Microchem. J. 97 (2011) 249–254.
[12] H. Sereshti, V. Khojeh, S. Samadi, Talanta 83 (2011) 885–890.
[13] M.A. Farajzadeh, M. Bahram, M.R. Vardast, CLEAN-Soil, Air, Water 38 (2010) 466–477.
[14] M.A. Farajzadeh, M. Bahram, B.G. Mehr, J.A. Jönsson, Talanta 75 (2008) 832–840.
[15] S.Z. Mohammadi, D. Afzali, Y.M. Baghelani, Anal. Chim. Acta 653 (2008) 173–177.
[16] A. Zgoła-Grześkowiak, T. Grześkowiak, TRAC-Trends Anal. Chem. 30 (2011) 1382–1399.
[17] H. Chen, P. Du, J. Chen, Sh. Hu, Sh. Li, H. Liu, Talanta 81 (2010) 176–179.
[18] Sh. Li, Sh. Cai, W. Hu, H. Chen, H. Liu, Spectrochim. Acta Part B 64 (2009) 666–671.
[19] E. Molaakbari, A. Mostafavi, D. Afzali, J. Hazard. Mater. 185 (2011) 647–652.
[20] Q. Zhou, X. Zhang, G. Xie, Anal. Methods 3 (2011) 356–361.
[21] F. Kamarei, H. Ebrahimzadeh, Y. Yamini, Talanta 83 (2010) 36–41.
[22] H.-F. Zhang, Y.-P. Shi, Talanta 82 (2010) 1010–1016.
[23] M. Baghdadi, F. Shemirani, Anal. Chim. Acta 634 (2009) 186–191.
[24] S.R. Yousefi, F. Shemirani, Anal. Chim. Acta 669 (2010) 25–31.
[25] Sh. Mahpishanian, F. Shemirani, Talanta 82 (2010) 471–476.
[26] M. Amirkavei, Sh. Dadfarnia, A.M. Haji Shabani, Quim. Nova 36 (2013) 63–68.
[27] G.-T. Wei, Z. Yang, Ch.-J. Chen, Anal. Chim. Acta 488 (2003) 183–192.
[28] Z. Fan, Z. Jiang, F. Yang, B. Hu, Anal. Chim. Acta 510 (2004) 45–51.
[29] S. Haixia, L. Zaijun, L. Ming, Microchim. Acta 159 (2007) 95–100.
[30] S.M. Ullrich, T.W. Tanton, S.A. Abdrashitova, Crit. Rev. Environ. Sci. Technol. 31 (2001) 241–293.
[31] K. Leopold, A. Zierhut, J. Huber, Anal. Bioanal. Chem. 403 (2012) 2419–2428.
[32] X. Jia, Y. Han, C. Wei, T. Duan, H. Chen, J. Anal. At. Spectrom. 26 (2011) 1380–1386.
[33] N. Tokman, S. Akman, C. Ozeroglu, Talanta 63 (2004) 699–703.
[34] R.J. Cassella, O.I.B. Magalhães, M.T. Couto, E.L.S. Lima, M.A.F.S. Neves, F.M. B. Coutinho, Talanta 67 (2005) 121–128.
[35] N.N. Meeravali, S.J. Kumar, Anal. Methods 4 (2012) 2435–2440.
[36] J. Chen, K.Ch. Teo, Anal. Chim. Acta 450 (2001) 215–222.
[37] J. Škrlíková, V. Andruch, I.S. Balogh, J. Posta, Y. Bazel, A. Hudák, V. Jalčoviková, L. Kocúrová, Anal. Methods 3 (2011) 2412–2415.