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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  $0.7 \mu\text{g L}^{-1}$  in 10.0 mL of sample solution employing 8  $\mu\text{L}$  of 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (HmimNTf<sub>2</sub>) as the extraction solvent. The detection limit was found as  $0.004 \mu\text{g L}^{-1}$  with an enrichment factor of 200. The relative standard deviation (RSD) for seven replicate measurements of  $0.7 \mu\text{g L}^{-1}$  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.

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## 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  $3 \text{ mg L}^{-1}$  and single intake of water containing  $30 \text{ mg L}^{-1}$  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  $\mu\text{g}$  per liter level to several dozens of  $\mu\text{g}$  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  $1.3 \text{ mg L}^{-1}$  [5] and European proposals limit its content in fresh water to  $1 \text{ mg L}^{-1}$  and in sea water to  $2.64 \text{ mg L}^{-1}$  [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 ( $\text{LiNTf}_2$ ), 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<sup>-1</sup> solution of copper in 2% nitric acid, J.T.Baker). Solutions of  $\text{LiNTf}_2$ , HmimCl and DDTC were prepared in water at concentrations 0.2 g mL<sup>-1</sup>, 0.45 g mL<sup>-1</sup> and 0.11 g mL<sup>-1</sup>, 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%  $\text{HNO}_3$  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<sup>-1</sup>, 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%  $\text{HNO}_3$  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%  $\text{H}_2\text{O}_2$ . Then, 4 mL of 65%  $\text{HNO}_3$  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  $\mu\text{L}$  of DDTC solution was added. After 1 min 45  $\mu\text{L}$  of HmimCl solution was pipetted. Next 100  $\mu\text{L}$  of  $\text{LiNTf}_2$  solution was added to start metathesis reaction. As a result 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (HmimNTf<sub>2</sub>) was formed. Five minutes later the mixture was centrifuged for 5 min at 5000 rpm and HmimNTf<sub>2</sub> containing copper-DDTC complex settled on the bottom of the tube. The bulk water phase was removed and the ionic liquid phase (about 8  $\mu\text{L}$ ) was dissolved in 40  $\mu\text{L}$  of ethanol. In order to determine the analyte in the dissolved ionic liquid phase, 10  $\mu\text{L}$  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 micro-extraction 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

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