Talanta 129 (2014) 254–262

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Generation of volatile copper species after *in situ* ionic liquid formation dispersive liquid–liquid microextraction prior to atomic absorption spectrometric detection

Ewa Stanisz*, Agnieszka Zgoła-Grześkowiak, Henryk Matusiewicz[1]

Poznan University of Technology, Faculty of Chemical Technology, Piotrowo 3, 60-965 Poznań, Poland

ARTICLE INFO

Article history:
Received 28 February 2014
Received in revised form
17 May 2014
Accepted 23 May 2014
Available online 2 June 2014

Keywords:
In situ solvent formation
Ionic liquids
Volatile copper species generation
Photo-induced generation
Enhancement effect
Soil

ABSTRACT

The new procedure using *in situ* synthesis of ionic liquid extractant for dispersive liquid–liquid microextraction (*in situ* IL DLLME) combined with generation of volatile species prior to electrothermal atomic absorption spectrometry (ET AAS) for the determination of copper in soil samples was developed. Analytical signals were obtained without the back-extraction of copper from the IL phase prior to its determination. Under optimal conditions, the extraction in 10 mL of sample solution employing 8 μL of 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($HmimNTf_2$) (as the extraction solvent) was conducted. The ionic liquid served as two-task reagent: the efficient extractant and enhancement substance for generation step. The chemical generation of volatile species was performed by reduction of acidified copper solution (HCl 0.8 mol L^{-1}) with $NaBH_4$ (1.5%). Some essential parameters of the chemical generation such as $NaBH_4$ and HCl concentrations, the kind and concentration of ionic liquid, carrier gas (Ar) flow rate, reaction and trapping time as well as pyrolysis and atomization temperatures were studied. For photogeneration the effect of the parameters such as the kind and concentration of low molecular weight organic acids and ionic liquid, carrier gas (Ar) flow rate, UV irradiation and ultrasonication time on the analytical signals were studied. The detection limit was found as 1.8 ng mL^{-1} and the relative standard deviation (RSD) for seven replicate measurements of 100 μg mL^{-1} in sample solution was 7%. The accuracy of the proposed method was evaluated by analysis of the certified reference materials. 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 soil and sediment samples.

1. Introduction

Copper is known as a necessary micronutrient for plants, animals and humans [1]. It is a vital part of several enzymes (for example, ferroxidases, cytochrome *c* oxidase, superoxide dismutase, tyrosinase, lysyl oxidase, and dopamine beta hydroxylase) [2,3].

In human populations absorption of copper is highly variable and dependent upon the age, diet, metal amount ingested, its chemical form and the composition of other dietary components such as zinc, as well as the environmental matrix in which it is contained. Ingestion of a large amount of copper salts causes gastrointestinal disturbances, the first symptom to occur is nausea, which can be observed from approximately 4 mg L^{-1} of copper in drinking water. In severe cases, harmful effects especially hemolysis, liver and kidney damage, can occur [2,3].

In different types of uncontaminated soil the global copper contents are reported to range between 2 and 250 mg kg^{-1} with an average value of 30–40 mg kg^{-1} [2,4]. Generally copper is accumulated in the upper few centimeters of soil, but it also has tendency to be adsorbed by organic compounds, carbonates, clay minerals and oxyhydroxidies of manganese and iron in deeper soil layers [4,5]. Contents of copper are closely associated with soil texture and usually are the lowest in light sandy soils and the highest in loamy soils. The concentration of copper in plant tissues seems to be a function of its level in soil and the nutrient solution. The pattern of this relationship, however, differs among plant species and plant parts [4].

Contamination of soil by copper compounds results from utilization of Cu-containing material such as fertilizers, sprays, and agricultural or municipal wastes as well as industrial emissions [4]. Anthropogenic sources of copper come mainly from

---

* Corresponding author. Tel.: +48 61 6652005; fax: +48 61 6652571.
E-mail address: ewa.stanisz@put.poznan.pl (E. Stanisz).

[1] Contributed equally to this work.

http://dx.doi.org/10.1016/j.talanta.2014.05.048
0039-9140/© 2014 Elsevier B.V. All rights reserved.

mining and smelting operations [1]. Soils that are situated in the neighborhood of non-ferrous metal smelters exhibit considerable amounts of heavy metals [6,7]. In the case of copper mills, the environment is usually contaminated, primarily by high quantities of copper and lead [4,8].

The amount of accumulated metals, mainly in top layers of the soil, is dependent upon the distance from shaft furnace chimneys, wind direction and physico-chemical properties of soil. The presence of high copper and lead concentrations in soils poses an increased hazard of their migration into ground and underground water, thus transferring into the biomass of plants growing in these soils [8].

For the routine determination of copper in water, wastewater, acid-digested materials (soil, sediments, plants and animal tissues) and soil–water extracts [1] atomic absorption spectrometry (FAAS, GF AAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) are widely used.

Atomic absorption and emission spectrometry with chemical vapor generation (CVG) of volatile species of copper are also utilized for detection [9–16]. Recently, many attempts have been made to explore the enhancement reagents in order to improve efficiency of the generation of volatile copper species. Several reagents have been found to enhance the CVG of this metal, such as 1,10-phenanthroline [12,16], room temperature ionic liquids (RTILs) [15] and organic acids as the reaction medium [10]. For GF AAS *in situ* furnace trapping procedure is particularly attractive for the determination of very low concentrations of elements that form volatile species [17]. Preconcentration is easily achieved, the generation of volatile analytes and their introduction into an atomizer offers many significant advantages over conventional solution phase pneumatic nebulization of samples [11].

The disadvantages of CVG such as the requirement for preparation of chemical reductants ($NaBH_4$, $SnCl_2$), relatively large waste production, the possibility of contamination from reagents, and large amounts of gaseous byproducts result in the attempt to find new procedures for volatile species generation. For this purpose research into the use of UV radiation [18–21] and ultrasound energy [22,23] to generate volatile analytes has been undertaken. The use of UV radiation in the presence of low molecular weight organic acids maintains the advantages of vapor generation while eliminating the need for the utilization of chemical reductants, further simplifying the system [24]. The method (named photochemical or UV-induced generation) is, therefore, a “greener” method than “traditional” CVG for the determination of many metals.

For copper extraction from analytical samples several varieties of sample preparation techniques such as solid-phase extraction [25,26] and dispersive liquid–liquid microextraction (DLLME) [27–30] have been developed. The DLLME technique shortens sample preparation and can be used for metal and organic analytes [31]. In this technique mostly volatile organic compounds (VOCs) are used as extraction solvents. Most DLLME procedures require also the use of dispersion solvents (*e.g.* methanol, acetonitrile) to enable the dissipation of extraction solvents in water samples and the formation of a cloudy solution. Some researchers proposed using ultrasound for better dispersing the extraction solvent [32,33].

Nowadays, there is a worldwide tendency to use ionic liquids instead of VOCs used in many analytical procedures because ionic liquids are regarded as green solvents. Many extraction methods are now based on the use of ionic liquids. These include single step in-syringe system for liquid microextraction (SSLME) [34], cold induced aggregation microextraction (CIAME) [35], ionic liquid-based headspace microextraction [36], ionic liquid-based single-drop microextraction [37,38] and dispersive liquid–liquid microextraction [39].

The newest version of DLLME – *in situ* IL DLLME is an alternative to the former techniques. The extraction solvent (ionic liquid) is formed *in situ* in a relatively fast chemical reaction within a sample solution and no dispersion solvent is used [40–42].

This work was undertaken to study the effects of ionic liquids on the generation of volatile copper species. The ionic liquid (1-hexyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl]imide ($HmimNTf_2$)) [43] was used as the extraction solvent and reagent affecting the efficiency of the generation. Optimum conditions for chemical and UV-induced generation procedures in the presence of ionic liquid were investigated.

2. Materials and methods

2.1. Instrumentation

All measurements were performed with an AAS 5EA spectrometer (Analytik, 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, Victoria, Australia) was used as the radiation source. The software did not include procedure for copper volatile species generation, the conditions were optimized using arsenic procedure for construction of a working file and the appropriate wavelength and lamp current were set at the optimum values for copper.

HS 5 chemical vapor generation system (Analytik), which can operate alternatively in batch or continuous flow mode as well as photochemical generator were coupled to the electrothermal atomizer *via* an AS 51 autosampler for introduction of the volatile copper species into the graphite tube. The standard PTFE capillary was disconnected from the autosampler arm and replaced by a titanium capillary (1.0 mm i.d.) with a PTFE-tube transfer line (1.15 mm i.d., $l=0.5$ m) to transport the vapor from the commercial batch system/laboratory made UV reactor into the graphite tube. This modification permitted injection of the volatile products into the preheated graphite tube (250 °C) and their trapping *in situ* on the Ir coated graphite atomizer. The optimum distance between the titanium capillary tip and the inner surface of the heated tube was 1.0 mm.

The batch reactor used for copper volatile species generation utilizing UV source was detailed in previous works [44,45] and is therefore briefly summarized here. Laboratory made reactor was designed to perform photogeneration of copper in sample solution. The system consisted of a miniaturized quartz reactor sealed up with silicone stopper (Merck, Darmstadt, Germany). Samples were irradiated in the reactor with a 15 W low pressure UV lamp TNN 15/32 (Heraeus, Hanau, Germany) providing light of mainly 254 nm wavelength. The 2 mm diameter microtip of ultrasonic homogenizer (70 W, 20 kHz Sonopuls HD 70, VC-100 from Bandelin, Berlin, Germany) was inserted into the reactor (sample) for the efficient phase separation after generation of volatile products. The volatile forms of copper generated upon UV radiation were transported into the AAS graphite tube in the way describe above.

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 of 500–6000 rpm, was employed for phase separation after extraction procedure.

A UniClever focused microwave sample preparation system (Plazmatronika, Wrocław, Poland) operating at 2450 MHz and 300 W maximum output was used to CRMs and real samples microwave-assisted dissolution. 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), 1-butyl-3-methylimidazolium chloride (BmimCl), 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$), sodium diethyldithiocarbamate (DDTC) and solution of Ir (1000 mg L^{-1} in 10% HCl) 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 generation procedures. Acetic acid (99–100%, J.T. Baker), formic acid (for synthesis $\geq$99%) and propionic acid (for analysis, 89–91%) both from Merck were used for UV-induced generation.

A sodium tetrahydroborate (J.T. Baker) solution was prepared daily in water containing *ca.* 0.2% (w/v) sodium hydroxide (Suprapur, Merck).

Working standard solutions were obtained by appropriate dilution of the stock standard solution (1000 mg L^{-1} solution of copper in 0.5 mol L^{-1} nitric acid, Merck). 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). Hydrogen peroxide 30% and 40% HF of the highest quality (Suprapur, Merck) were used for microwave-assisted dissolution of CRMs and real samples.

High purity water: deionized and doubly distilled water (quartz apparatus, Bi18, Heraeus) was also used throughout the experiments.

2.3. Certified reference materials and real samples

Accuracy of the analytical procedure was verified with the use of the certified reference materials: SRM 2709 San Joaquin Soil (Baseline Trace Element Concentrations) and SRM 2711 Montana Soil (Moderately Elevated Trace Element Concentrations) both from the National Institute of Standards and Technology (NIST); SRM 2704 (Buffalo River Sediment) from National Bureau of Standards (NBS) and RM 433 (Trace Elements and Methylmercury in Marine Sediment) from International Atomic Energy Agency (IAEA).

Real soil samples (nos. 1–8) were collected in the vicinity of the Legnica Copper Smelter (southwest Poland, Silesia). The copper smelting plant in Legnica was opened in 1953 and in the past was indicated as a source of high metal-containing dust emission, which was considerably reduced in the 1980s and 1990s. Table 1 shows description of the soil samples collected from the vicinity of the smelter (nos. 1–8). For comparison, copper was also determined in soil samples from a suburb of Poznań (nos. 9–10) and in lake sediment samples from Malta Lake in Poznań (nos. 11–12). It was assumed that these samples were not exposed to anthropogenic copper contamination.

2.4. Analytical procedures

2.4.1. Sampling strategy and microwave-assisted dissolution of CRMs and real soil samples

Soil/sediment samples were collected from the outer surface (10–20 cm) after removing surface contamination. Use of metal tools was avoided and a plastic spatula was used for sample collection. The soil/sediment samples were collected according to similar procedure. The samples were dried thoroughly, ground in an agate mortar, sieved through a <2 mm sieve and then, digested.

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

2.4.2. Extraction and AAS determination procedures

Ten milliliters of diluted sample solution (after microwave-assisted dissolution) was poured into a centrifuge tube. The pH of the sample was adjusted to neutral. Then, 100 μL of DDTC (0.11 g L^{-1}) solution was added and after 1 min 45 μL of HmimCl (0.45 g L^{-1}) solution was pipetted. Next 100 μL of $LiNTf_2$ (0.2 g L^{-1}) 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 (*ca.* 8 μL) was dissolved in 50 μL of ethanol [43].

Before generation procedures and AAS detection the graphite tube was coated with iridium. It was chosen as the permanent modifier for *in situ* trapping the copper volatile species. The Ir coating was conducted thermally by pipetting 40 μL of a 1000 mg L^{-1} Ir stock solution. The tube was subjected to the temperature program in order to reduce the salt to the metal and produce a reactive surface layer. The modifier solution was gently dried at 90 °C then at 110 °C and in the final step of drying at 250 °C. Following this, a reduction step at 2200 °C was applied for 5 s. This procedure was repeated five times so the inner surface of the bottom part of the tube was covered homogeneously by 200 μg of the metal. This coating needed to be applied only once during the lifetime of the tube.

In order to generate volatile species of copper the dissolved ionic liquid phase ($HmimNTf_2$) was placed in the batch reactor vessel. Due to the fact that no satisfactory results were obtained for photochemical generation procedure, the real samples were analyzed after *in situ* DLLME with the use of chemical generation coupled to GF AAS.

For the chemical generation after extraction, ionic liquid phase was dissolved in 50 μL of ethanol, than HCl (0.8 mol L^{-1} in sample solution) was added and the volume was made up to 2 mL with water.

For the photogeneration, after dissolution of ionic liquid phase with ethanol (50 μL), acetic acid was added (50% v/v in sample solution) and the volume was made up to 500 μL with water. The conditions for generation procedures (chemical and UV-induced) are presented in Table 2.

Calibration was performed by the standard calibration technique using standards with addition of DDTC and ionic liquid. The detailed graphite furnace temperature program used for the copper determination in real samples is shown in Table 2.

2.4.3. Generation of volatile copper species

2.4.3.1. Chemical generation. In the case of analysis without extraction step (during optimization), IL was added to the sample solution containing copper in the reactor vessel.

For chemical generation procedure after extraction step, the copper determination was performed by the generation of copper species extracted in IL phase with 1.5% (w/v) $NaBH_4$ as a reducing agent. Sample solution (2 mL with 8 μL IL, diluted after extraction with 50 μL of ethanol, *ca.* 99%) was placed in the reaction flask for the generation. Copper species were generated in 0.8 mol L^{-1} HCl

Table 1
Description of the soil samples collected from the vicinity of the Legnica Copper Smelter.

Sample number	Type of land	Location of the sampling point
1	Farmland	Approximately 170 m to the west of the Legnica Copper Smelter, N 51°17′98″, E 16°09′81″
2	Copse	Approximately 800 m to the northeast of the Legnica Copper Smelter, N 51°19′66″, E 16°12′67″
3	Allotments	Approx. 1500 m to the northeast of the Legnica Copper Smelter, N 51°19′96″, E 16°13′40″
4	Wasteland	Approximately 800 m to the northeast of the Legnica Copper Smelter, N 51°19′29″, E 16°13′93″
5	Allotments	Approximately 1750 m to the northeast of the Legnica Copper Smelter, N 51°19’41”, E 16°15’17”
6	Farmland	Approx. 1700 m to the east of the Legnica Copper Smelter, N 51°18′31″, E 16°14′70″
7	Wasteland	Approximately 400 m to the east of the Legnica Copper Smelter, N 51°18′30″, E 16°12′94″
8	Allotments	Approximately 2300 m to the east of the Legnica Copper Smelter, N 51°18′47″, E 16°15′42″
9	Garden	Countryside nearby Poznan, N 52°26′23″, E 16°45′07″
10	Farmland	Countryside nearby Poznan, N 52°26′03″, E 16°43′54″
11	Lake sediment	Poznan, eastern part of the lake bottom, sample taken after draining the water, N 52°24′01″, E 16°59′11″
12	Lake sediment	Poznan, western part of the lake bottom, sample taken after draining the water, N 52°24′26″, E 16°57′27″

Table 2
Optimized experimental conditions for chemical and UV-induced generation of volatile copper species after *in situ* IL DLLME prior to AAS determination (parameters for microwave-assisted dissolution and *in situ* IL DLLME are also presented).

Microwave-assisted dissolution	
Sample mass (mg)	*ca.* 300
Reagents	65% HNO_3, 30% H_2O_2, 40% HF
Reagents volume (mL)	4, 1, 2
Final volume (mL)	20
MW power (W)/dissolution time (min)	300/20
in situ IL DLLME	
Sample volume (mL)	10
HmimCl (first component) (mg)	20
$LiNTf_2$ (second component) (mg)	20
$HmimNTf_2$ (extractant, product of the *in situ* synthesis) (μL)	*ca.* 8
pH of sample solution	7
Dissolving solution: concentration (%)/volume (μL)	Ethanol: *ca.* 99/50
Chemical generation	
Sample volume (mL)	2
Reduction agent, concentration (%)	$NaBH_4$, 1.5
Acid solution, HCl (mol L^{-1})	0.8
$HmimNTf_2$ (enhancement reagent (mmol L^{-1}))	10
Ar flow (L min^{-1})	0.2
UV-induced generation	
Sample volume (μL)	500
Acetic acid concentration (%, v/v)	50
Ultraviolet time (s)	40
Sonication time (s)	5
US microtip diameter (mm)	2
Ar flow (L min^{-1})	0.15
AAS detection	
Wavelength/spectral band width (nm)	324.8/0.8
Lamp current (mA)	3.0
Furnace program steps	
Drying	65 °C, ramp 10 °C s^{-1}, hold 5 s
Drying/trapping	250 °C, ramp 50 °C s^{-1}, hold 30 s
Pyrolysis	800 °C, ramp 200 °C s^{-1}, hold 4 s
Atomization	2000 °C, ramp 2500 °C s^{-1}, hold 4 s
Cleanout	2150 °C, ramp 1000 °C s^{-1}, hold 3 s
Measurement mode	Peak area

medium and transferred to the graphite tube preheated to 250 °C by an Ar stream (0.2 L min^{-1}). The copper concentration in the sample was determined by standard calibration technique. The Cu^{2+} standard solutions were prepared with addition of DDTC and $HmimNTf_2$ (8 μL, dissolved in ethanol). Peak area absorbance was taken for quantification. Experimental conditions for chemical generation of copper coupled to AAS are presented in Table 2.

2.4.3.2. Photogeneration. During optimization step IL was added to the sample solution containing copper in the quartz reactor vessel.

For photogeneration procedure after extraction step, copper extracted in IL phase ($HmimNTf_2$, 8 μL) was dissolved in 50 μL of ethanol (*ca.* 99%). After that acetic acid was added (50% v/v in sample solution); the final volume of the sample solution was 500 μL. Then the 2 mm diameter microtip was passed through the silicon cap and immersed into the solution at a depth of *ca.* 2 mm. The sample was sequentially subjected to 40 s of UV irradiation and 5 s of US irradiation. The volatile copper species were transferred to the preheated graphite tube by an Ar stream (0.15 L min^{-1}).

The determination was performed by the generation of volatile copper species in 50% v/v acetic acid (in sample solution, 500 μL) in the presence of UV radiation. The ultrasound was used for separation of gas phase (volatile copper) from sample solution after UV irradiation [23]; the volatile species were detected by AAS.

Peak area absorbance was taken for quantification. Experimental conditions for photo-induced generation of copper coupled to AAS are presented in Table 2.

3. Results and discussion

The parameters of chemical and UV-induced generation of volatile copper species 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. In order to investigate the chemical generation of Cu after *in situ* DLLME the following parameters were studied: HCl concentration in sample solution, $NaBH_4$ concentration, the kind and concentration of ionic liquid, carrier gas (Ar) flow rate, reaction and trapping time as well as pyrolysis and atomization temperatures.

The kind and concentration of low molecular weight organic acids and ionic liquid, carrier gas (Ar) flow rate, UV irradiation and ultrasonication time were investigated for UV generation system. The furnace parameters optimized for chemical generation were used for further UV generation. All experiments were performed after *in situ* DLLME from 10 mL of copper water standard solution (20 ng mL^{-1} for chemical and 100 ng mL^{-1} for UV-induced generation) using peak area measurements.

3.1. *in situ* IL DLLME

The main conditions of *in situ* IL DLLME were optimized in the previous work [43], therefore during this study microextraction procedure was used without modifications (Table 2). 5 mmol L^{-1} of DDTC was chosen as the optimal concentration of complexing agent, ensuring maximal absorbance as well as 1 min of reaction time leading to Cu–DDTC complex formation at pH 7. As the extraction solvent 8 μL of $HmimNTf_2$ was used. It was a product of the *in situ* synthesis in sample solution between HmimCl and $LiNTf_2$.

3.2. *Chemical volatile copper species generation and AAS detection*

HCl was chosen as a reagent providing appropriate pH for copper generation [9,11,17]. The effect of the HCl concentration in the sample solution on the analytical signals was investigated. The results are presented in Fig. 1. The optimum HCl concentration was 0.8 mol L^{-1}. No change was observed for HCl concentrations ranging from 0.8 to 1 mol L^{-1}. Concerning the influence of the $NaBH_4$ concentration, maximum absorbance was achieved at a concentration of 1.5% w/v (Fig. 1). The use of concentrations higher than 1.5% resulted in the production of too large quantities of H_2, causing the significant signal instability. The pump in the HS 5 system delivered the reductant solution in four selectable speed stages providing rates between 5 mL min^{-1} and 10 mL min^{-1}. During the study the speed 5 mL min^{-1} was chosen for all experiments.

One of the basic parameters affecting the efficiency of generation was the time required for the reaction between reductant and the metal in sample solution. The reaction time was strongly related with the trapping time (in the preheated graphite tube), therefore both parameters were considered together (Fig. 2). The increase of the analytical signals was observed between 5 and 30 s of reaction/trapping time. The longer time did not increase the analytical signals. The highest absorbance was achieved for 30 s, and that was the time needed for the efficient generation and transport of the volatile copper species to the graphite tube at the chosen carrier gas flow rate. The obtained analytical signal strongly depended on the trapping temperature. For temperature equal to 250 °C the highest absorbance was noted, that proved that this temperature was sufficient for trapping the copper species on the graphite surface coated with Ir.

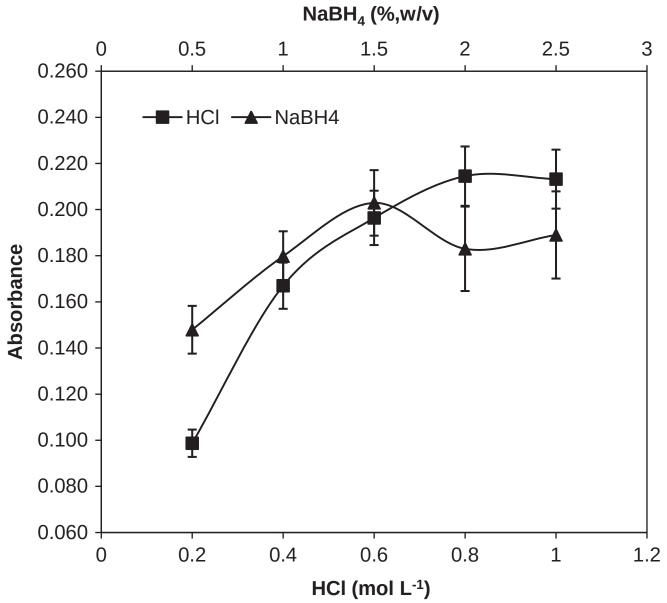

Fig. 1. Effect of $NaBH_4$ concentration and HCl concentration in sample solution on the absorbance during chemical generation of volatile copper species. Conditions: Cu solution 100 ng mL^{-1}, trapping time 25 s, trapping temperature 200 °C, $BmimBH_4$ 15 mmol L^{-1}. The error bar is the standard deviation (SD, $n=3$).

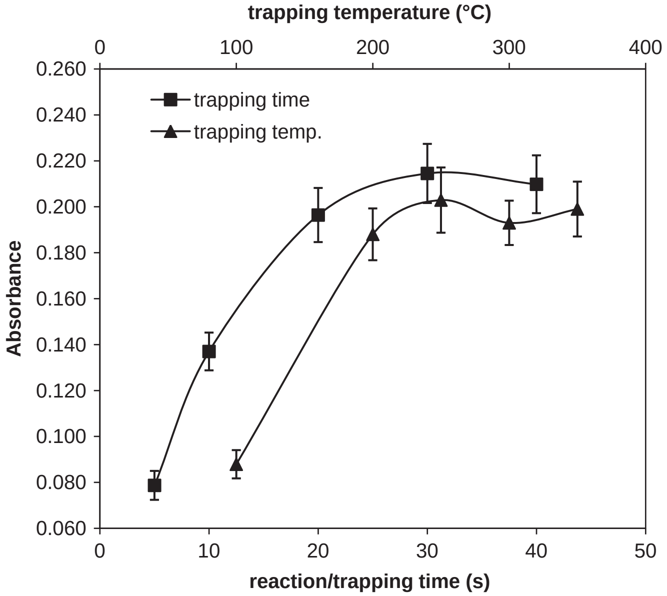

Fig. 2. Effect of reaction/trapping time and trapping temperature on the absorbance during chemical generation of volatile copper species. Conditions: Cu solution 100 ng mL^{-1}, $NaBH_4$ 1.5%, HCl 0.8 mol L^{-1}, $BmimBH_4$ 15 mmol L^{-1}. The error bar is the standard deviation (SD, $n=3$).

A temperature of 800 °C was selected as the pyrolysis temperature as well as temperature of 2000 °C was chosen for the atomization step.

The carrier/purge gas flow rates were studied at the range of 0.1–0.8 L min^{-1}. The argon flow rate of 0.2 L min^{-1} was sufficient for transport of volatile copper forms from the batch reactor to the preheated graphite tube. Flow rates higher than 0.2 L min^{-1} did not cause an increase of the analytical signals.

3.3. Effect of ionic liquids on the chemical generation of copper

The methods for improving the efficiency of copper generation as well as other metals were evaluated by Zhang et al. [15,46,47]. Only once the influence of ionic liquid N-butylpyridinium tetrafluoroborate was studied for generation of volatile species of copper after reduction with KBH_4 [15]. The addition of ionic liquid allowed to achieved *ca.* fivefold improvement in the generation efficiency. The authors used ionic liquid as an additional reagent. In this research were investigated both addition of ionic liquids to the sample solution before generation and ionic liquids used as copper extractant during *in situ* IL DLLME procedure before generation. The ILs in the study were categorized into two groups: ILs that were synthesized as extractant within extraction step: $HmimNTf_2$ and $BmimNTf_2$ as well as ILs that were added to the sample solution before generation procedure (without extraction step): $BmimBF_4$ and BmimCl. As $HmimNTf_2$ and $BmimNTf_2$ were the products of *in situ* metathesis formation, the amount of ionic liquid was connected with optimized procedure of extraction (*ca.* 8 μL) [43]. Therefore, to study the effect of different amounts of ILs on the analytical signals, the suitable additions of ILs were performed. Very poor signals were obtained without addition of the ionic liquids. The influence of ILs concentrations on the absorbance is shown in Fig. 3. All the tested ILs resulted in an improvement in analytical signals to some extent, depending on the concentration, nature and role of ILs. The concentration of ILs in sample solutions were studied in the range of 0.5–40 mmol L^{-1}. The maximum improvements in analytical signals were obtained with $BmimBF_4$ and $HmimNTf_2$ (*ca.* 11 and 10 times, respectively) (Fig. 3) for the concentrations of 30 and 10 mmol L^{-1}, respectively.

$HmimNTf_2$ was used during *in situ* IL DLLME CVG AAS procedure as two task reagent. First, it was used as the efficient extractant for copper, and secondly as the enhancement reagent improving the efficiency of the generation of volatile copper species. Explanation of the positive effect of ionic liquids on the chemical generation is quite difficult. It is assumed that the reaction of the transition and noble metals with tetrahydroborate(III) in aqueous solution generates unidentified volatile species. In addition to the metal hydride and free metal atoms, the volatile species may consist of metal nanoparticles [14,47]. It is well known that the final products are the reduced metals or metal borides, depending on the metal and on the experimental parameters. This reaction is widely employed for the preparation of nanoparticles of metals or metal borides [48,49]. Therefore, ionic liquids present in sample solution can reduce the loss of the volatile products of metal reduction by inhibiting further coalescence of the nanoparticles and facilitating the release of the volatile species from the solution. The stabilization process against aggregation into large particles or even deposition can be achieved by the fact that ionic liquids can create an electrostatic and steric bulk stabilization of the metal nanoparticles. For this reason some of the ILs are used for this purpose in the synthesis of the nanoparticles [47,50–53].

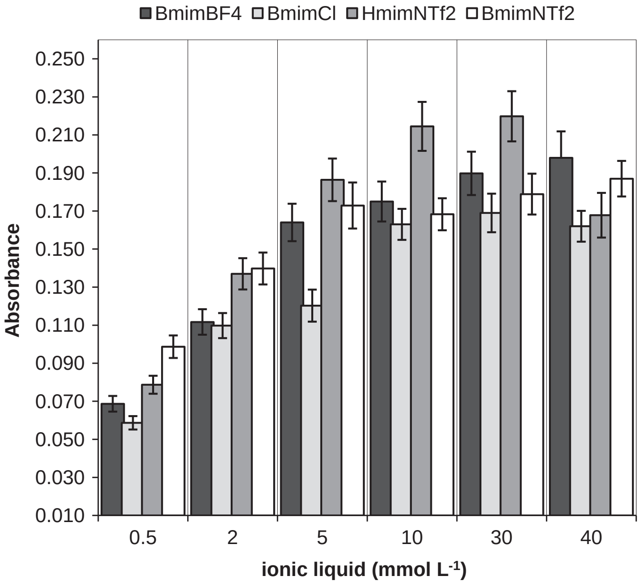

Fig. 3. Effect of ionic liquids concentration on the absorbance during chemical generation of volatile copper species. Conditions: Cu solution 100 ng mL^{-1}, $NaBH_4$ 1.5%, HCl 0.8 mol L^{-1}, trapping time 25 s, trapping temperature 250 °C. The error bar is the standard deviation (SD, $n=3$).

3.4. Effect of ionic liquids on the photochemical volatile copper species generation

Prior to studying of photogeneration of copper, chemical vapor generation was undertaken to optimize the graphite furnace program. For this purpose, experimental parameters established in earlier sections were adopted for use. All subsequent measurements were conducted with the use of the trapping of volatile species on the surface of preheated graphite tube.

Experiments performed with solutions containing 500 ng mL^{-1} of Cu^{2+} in acetic, formic and propionic acids generated very poor absorbance signals. The concentrations of acids were in the range of 10–70% (v/v). Only for 50% acetic acid the analytical signals were about five times higher than signals obtained for analytical blanks. No response from copper was observed for other organic acids over the range of studied concentrations. The ultraviolet irradiation time for efficient photogeneration of copper was optimized in the range of 10–50 s. Very low signals (but the highest) were detected for 40 s of irradiation time. For degasification of solution after UV irradiation ultrasound sonication was performed (5 s) [23,44,45]. The influence of pH on photogeneration efficiency was earlier presented by Sturgeon et al. [17,54]. Thus additional experiments were undertaken to study the effect of pH (in the range 1–5) on generation efficiency in acetic acid solutions. However, no significant effect was observed. This contrasts with the earlier report by Sturgeon et al. [17,54] who noted the influence of pH on the photogeneration of Cd [17] from acetic acid solution and Fe [54] from formic acid.

As the last factor influencing the UV-induced generation of volatile copper species, concentrations of chosen ionic liquids ($BmimBF_4$ and $HmimNTf_2$) were tested in the range of 5–40 mmol L^{-1} in sample solution. In the literature the effect of ILs on the analytical signal achieved during photogeneration of metals has not been studied yet. However, as in the case of pH, the presence of ionic liquids in solution did not affect the efficiency of generation. Despite optimizing the UV system it was impossible to obtain the reproducible analytical signals. Relative standard deviations (RSD) as high as 25% characterized the signals obtained in 50% acetic acid solution. Future analytical applications for real samples will require extensive improvement in the experimental conditions for this system. Thus, analytical figures of merit and analysis of real samples were conducted with the use of chemical copper generation after *in situ* IL DLLME.

3.5. Analytical figures of merit

Figures of merit of the proposed *in situ* IL DLLME prior to chemical generation coupled to AAS for copper determination were evaluated under the optimum experimental conditions (Table 2). The calibration curve for Cu^{2+} was constructed in the concentration range from 20 to 150 ng mL^{-1} with a correlation coefficient of 0.9957. The Cu^{2+} standard solutions were prepared with addition of DDTC and IL dissolved in ethanol. The limit of detection (LOD), calculated as the concentration of absolute amount of copper yielding an absorbance equivalent to three times the standard deviation of the blank signal ($n=11$), was 1.8 ng mL^{-1}. RSD for eleven-replicate measurement of sample solution containing 100 ng mL^{-1} Cu^{2+} was 7%.

Due to the fact that the minimum volume of sample solution for the CVG system was 2 mL and for UV-induced generation 500 μL, enrichment factors were not calculated. The goal of the study was to present the influence of ionic liquids on chemical an UV-induced generation of copper.

In comparison to other generation procedures, reported in the literature for copper determination based on spectroscopic determination, the proposed method requires lower or equal volume of sample and reagents, reducing the production of wastes in the laboratory (Table 3). In addition, our method presents a lower or comparable limit of detection as well as satisfactory precision with respect to other works using generation technique in the detection step. It is the first time when *in situ* IL DLLME before chemical generation of volatile copper species combines the use of ionic liquid as extractant, and at the same time, as an enhancement reagent for generation step.

After *in situ* extraction step copper was determined by chemical generation coupled to GF AAS, directly from organic phase after dissolution in ethanol (without the back-extraction of the analyte from the IL phase into an aqueous media prior to the generation).

3.6. *Accuracy verification and copper determination in real samples*

The accuracy of the proposed method was evaluated by analysis of the three certified reference materials: SRM 2709, SRM 2711, SRM 2704 and one reference material RM 433. The copper recoveries were in the range of 95–103% which is considered satisfactory for the certified concentration of the element (Table 4). The results were in good agreement with the *t*-test at a 95% confidence level of the certified values in the investigated reference materials. The precision expressed as RSD was in the range of 5–7%.

The certified reference materials used in the research had a matrix containing high concentrations of other elements (*e.g.* Al, Ag, Ba, *Ca*, Cr, Fe, Mg, Mn, Ni, Pb, Si, Zn), sometimes in the range from μg g^{-1} to %. The obtained recoveries and analytical signals of copper in the presence of the elements proved that the interferences from foreign ions can be ignored. Due to the satisfactory results, the additional study in terms of matrix influence was not carried out. It was confirmed that the developed methodology for copper isolation/preconcentration and chemical generation was applicable to the analysis of soil and sediment materials with complex matrices.

The applicability of the developed method was assessed by isolation/preconcentration and determination of copper in real soil samples (Tables 1 and 5). The samples were digested according to the procedure described in Section 2.4.1. and the element was preconcentrated and determined according to the procedures described in Sections 2.4.2 and 2.4.3 (Table 2).

The results presented in Table 5 show considerable differences between copper content in soil samples collected in the vicinity of the Legnica Copper Smelter (nos. 1–8) and four other samples from the area of Poznan (nos. 9–12). Concentrations of copper in the samples from Legnica were in a range of 44–1104 μg g^{-1} with mean value of 386 μg g^{-1}. The determined metal amount in samples from the vicinity of Poznan was in a range of 6.5–21.7 μg g^{-1} with mean value of 16.3 μg g^{-1}. The results showed that the Legnica soil contains higher amounts of copper than samples from Poznan. The found values were compared with those obtained for the samples collected in the same points by The Regional Inspectorate of Environmental Protection in 2007.

The determined copper amounts in samples 1, 2 and 4–8 exceeded the acceptable copper concentration in the soil. All analyzed soil samples belonged to the soil class B. According to the Polish legislation acceptable concentration of copper in this class at a depth of 0–0.3 m is 150 μg g^{-1}.

Table 4
Accuracy verification of the method for copper determination in selected certified reference materials by *in situ* DLLME coupled to CVG AAS using the optimized parameters. Recovery and relative standard deviation (RSD) values also are shown. Obtained values: average value ± standard deviation ($n=5$).

Reference material	Determined			Certified
	Cu (μg g^{-1})	Recovery (%)	RSD (%)	Cu (μg g^{-1})
SRM 2709	32.9 ± 2.2	95	7	34.6 ± 0.7
SRM 2711	109 ± 7	96	6	114 ± 2
SRM 2704	101.2 ± 5.1	103	5	98.6 ± 5.0
RM 433	29.3 ± 1.7	95	6	30.8 ± 2.6

Table 3
Comparison of *in situ* IL DLLME coupled to chemical generation and other techniques for the copper volatile species generation (the table also shows the type of enhancement reagent).

Generation technique	Detection technique	Sample	Enhancement reagent	RSD (%)	LOD (ng mL^{-1})	Ref.
$NaBH_4$ (2%; 0.6 mol L^{-1} HCl)	QTA AAS	Aqueous standard solution	–	9	8 ng[d]	[9]
$NaBH_4$ (1.2%; 1.0 mol L^{-1} HCl or 0.3 mol L^{-1} HNO_3)	ICP-AES	Lobster tissue, marine sediment	–	9.7[b]/8.6[c]	–[e]	[11]
$NaBH_4$ (1%; 0.6 mol L^{-1} HCl)	GF AAS	Aqueous standard solution	–	11	28	[17]
$NaBH_4$ (1.0%; 1% HCOOH)	Flow injection GF AAS	Water, biological tissue	0.0005% (w/v) 1,10-phenanthroline	4	0.1	[55]
$NaBH_4$ (0.1%; 0.1 mol L^{-1} CH_3COOH)	Flow injection ICP-OES	Human hair, steel alloy	–	1.6	0.4	[56]
KBH_4 (15 g L^{-1}; 0.3 mol L^{-1} HNO_3)	Flow injection AFS	Tea, peach leaves, ores	N bupyBF_4[a]	4.4	19	[15]
$NaBH_4$ (0.3%; 0.1 mol L^{-1} HNO_3)	Flow injection AAS	River, tap, mineral water	0.00048% (w/v) 1,10-phenanthroline	2.6	1.8	[16]
$NaBH_4$ (1.5%; 0.8 mol L^{-1} HCl)	GF AAS	Soil, sediments	HmimNTf_2	8	1.8	This work

[a] N-butylpyridinium tetrafluoroborate.
[b] For 100 ng Cu^{2+} mL^{-1}.
[c] For 1 μg Cu^{2+} mL^{-1}.
[d] For 10 μL of sample solution.
[e] Not given.

Table 5
Concentration of copper ($\mu g\, g^{-1}$) in real soil samples determined after *in situ* DLLME CVG AAS. Obtained values: average value ± standard deviation for $n=5$.

Sample number	Determined Cu ($\mu g\, g^{-1}$)	RSD (%)	Ref[a] ($\mu g\, g^{-1}$)
1	213 ± 15	7	196
2	290 ± 13	4	141
3	44 ± 3	7	216
4	296 ± 21	7	245
5	234 ± 12	5	279
6	1104 ± 60	5	480
7	440 ± 28	6	1075
8	465 ± 22	5	617
9	19.7 ± 1.1	6	–
10	6.5 ± 0.4	6	–
11	21.7 ± 1.1	5	–
12	17.1 ± 0.8	5	–

[a] The report of the Regional Inspectorate of Environmental Protection (Wrocław) [57].

It is difficult to explain the result obtained for the sample no. 3. Determined concentration was equal to 44 ± 3 $\mu g\, g^{-1}$ and was much lower than in other samples. It is suspected that some plants able to accumulate copper from the soil emerged in a studied area (allotments). During the study the greatest concentration of copper was found in the soil located east of the smelter (samples 6, 7 and 8) that was consistent with the direction of the wind in the area. The determined concentration of copper in these samples exceeded the permitted concentration of 150 $mg\, kg^{-1}$. In the soil samples from the vicinity of Poznan (nos. 9–10) the detected metal amount was close to those naturally occurring in the Polish soil. The mean content of copper in agricultural surface soils and forest soils of Poland is estimated at 6.5 $\mu g\, g^{-1}$, which is due to the predomination of light sandy acid soils [4]. However, the variations in the copper distribution are remarkable that is connected with the parent materials and to the impact of industrial and/or agricultural pollution [4]. The copper content of sediments was also low. The samples from Malta Lake (nos. 11–12) contained 21.7 and 17.1 $\mu g\, g^{-1}$ of the determined metal.

4. Conclusion

in situ synthesis of ionic liquid extractant ($HmimNTf_2$) for dispersive liquid–liquid microextraction combined with generation of volatile species prior to electrothermal atomic absorption spectrometry for the determination of copper in environmental samples was demonstrated. The extraction technique can be employed for isolation and preconcentration of copper from soil and sediment samples. The extraction solvent is formed *in situ* in relatively fast chemical reaction in a sample solution and no dispersion solvent is needed. The analytical methodology enables direct analysis (from organic phase, without back-extraction) and subsequent determination of copper by chemical generation coupled to ET AAS. The product of *in situ* reaction has the potential to replace traditional VOCs in DLLME procedures for copper preconcentration due to its low vapor pressure and nonflammable properties. The presence of ionic liquid (as the extractant for metal) in sample solution during chemical generation offers a great possibility as the reagent positively affected the efficiency of chemical generation. Despite optimizing the photogeneration procedure it was impossible to obtain the reproducible analytical signals. Relative standard deviations as high as 25% characterized the signals obtained in 50% acetic acid solution. Future analytical efforts for extensive improvement in the experimental conditions of the procedure are required. Thus, analysis of real samples with complex matrices was conducted with the use of chemical copper species generation after *in situ* IL DLLME. The results obtained for the samples from an industrial area showed high contamination and were similar to those previously reported for that region. Copper concentration in the samples taken nearby Poznan from an agricultural area was low and similar to mean content of copper in Polish soils.

Acknowledgments

The study was financially supported by the National Science Centre (NCN), Poland (Grant no. UMO-2012/06/A/ST4/00382).

References

[1] J.F. Artiola, Speciation of copper, in: R. Cornelis, J. Caruso, H. Crews, K. Heumann (Eds.), Handbook of Elemental Speciation II – Species in the Environment, Food, Medicine and Occupational Health, John Wiley & Sons, Ltd., 2005, pp. 174–186 (chapter 2.8).

[2] D.G. Ellingsen, N. Horn, J. Aaseth, Copper, in: G.F. Nordberg, B.A. Fowler, M. Nordberg, L.T. Friberg (Eds.), Handbook on the Toxicology of Metals, third ed.,Academic Press, Inc., 2007, pp. 529–546 (chapter 26).

[3] National Research Council; Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium and Zinc, National Academy Press, Washington, D.C., 2001, chapter 7: Copper, pp. 224–257.

[4] A. Kabata-Pendias, H. Pendias, Trace Elements in Soils and Plants, third ed., CRC Press, Boca Raton, 2001.

[5] A. Kabata-Pendias, A.B. Mukherjee, Trace Elements from Soil to Human, Springer-Verlag, Berlin Heidelberg, 2007.

[6] S. Kuo, P.E. Heilman, A.S. Baker, Soil Sci. 135 (1983) 101–109.

[7] L. Pilc, J. Rosada, J. Siepak, Pol. J. Environ. Stud. 8 (1999) 107–110.

[8] A. Mocek, W. Spychalski, A. Dobek, A. Mocek-Płóciniak, Pol. J. Environ. Stud. 21 (2012) 159–164.

[9] A.S. Luna, R.E. Sturgeon, R.C. de Campos, Anal. Chem. 72 (2000) 3523–3531.

[10] S. Xu, R.E. Sturgeon, Y. Guo, W. Zhang, H. Zhao, Ann. Chim. 95 (2005) 491–499.

[11] R.E. Sturgeon, J. Liu, V.J. Boyko, V.T. Luong, Anal. Chem. 68 (1996) 1883–1887.

[12] H.Y. Zhou, S.K. Xu, Z.L. Fang, Spectrosc. Spectral Anal. (in Chinese) 20 (2000) 525–528.

[13] X. Duan, R.L. McLaughlin, I.D. Brindle, A. Conn, J. Anal. At. Spectrom. 17 (2002) 227–231.

[14] Y.L. Feng, R.E. Sturgeon, J.W. Lam, A. D'Ulivo, J. Anal. At. Spectrom. 20 (2005) 255–265.

[15] C. Zhang, Y. Li, X.-Y. Cui, Y. Jiang, X.-P. Yan, J. Anal. At. Spectrom. 23 (2008) 1372–1377.

[16] S. Xu, H. Zhou, X. Du, D. Zhu, Chem. J. Internet CJI 3 (2001) 29–36.

[17] A.S. Luna, H.B. Pereira, I. Takase, R. Araújo Gonçalves, R.E. Sturgeon, R. Calixto de Campos, Spectrochim. Acta Part B 57 (2002) 2047–2056.

[18] X. Guo, R.E. Sturgeon, Z. Mester, G.J. Gardner, Anal. Chem. 75 (2003) 2092–2099.

[19] X. Guo, R.E. Sturgeon, Z. Mester, G.J. Gardner, Anal. Chem. 76 (2004) 2401–2405.

[20] C. Zheng, Y. Li, Y. He, Q. Ma, X. Hou, J. Anal. At. Spectrom. 20 (2005) 746–750.

[21] R.F. Bendl, J.T. Madden, A.L. Regan, N. Fitzgerald, Talanta 68 (2006) 1366–1370.

[22] S. Gil, I. Lavilla, C. Bendicho, Anal. Chem. 78 (2006) 6260–6264.

[23] A. López-Rouco, E. Stanisz, H. Matusiewicz, I. Lavilla, C. Bendicho, J. Anal. At. Spectrom. 23 (2008) 1026–1029.

[24] P. Wu, L. He, C. Zheng, X. Hou, R.E. Sturgeon, J. Anal. At. Spectrom. 25 (2010) 1217–1246.

[25] Y. Yamini., A. Tamaddon, Talanta 49 (1999) 119–124.

[26] M. Soylak, L. Elci, M. Dogan, J. Trace Microprobe Tech. 19 (2001) 329–344.

[27] R. Khani, F. Shemirani, B. Majidi, Desalination 266 (2011) 238–243.

[28] M.A. Farajzadeh, M. Bahram, B.G. Mehr, J.Å. Jonsson, Talanta 75 (2008) 832–840.

[29] S.Z. Mohammadi, D. Afzali, Y.M. Baghelani, Anal. Chim. Acta 653 (2008) 173–177.

[30] Z.A. Alothman, M. Habila, E. Yilmaz, M. Soylak, J. AOAC Int. 96 (2013) 1425–1429.

[31] A. Zgoła-Grześkowiak, T. Grześkowiak, TrAC Trends Anal. Chem. 30 (2011) 1382–1399.

[32] H. Chen, P. Du, J. Chen, S.H. HuSh. LiH. Liu, Talanta 81 (2010) 176–179.

[33] S.H. Li, S.H. Cai, W. Hu, H. Chen, H. Liu, Spectrochim. Acta Part B 64 (2009) 666–671.

[34] F. Shah, M. Soylak, T.G. Kazi, H.I. Afridi, J. Anal. At. Spectrom. 27 (2012) 1960–1965.

[35] M. Baghdadi, F. Shemirani, Anal. Chim. Acta 613 (2008) 56–63.

[36] C.L. Ye, Q.X. Zhou, X.M. Wang, Anal. Chim. Acta 572 (2006) 165–171.

[37] H.E. Aguilera, R. Lucena, S. Cárdenas, M. Valcárcel, J. Chromatogr. A 1201 (2008) 106–111.

[38] L.B. Xia, X. Li, Y.L. Wu, B. Hu, R. Chen, Spectrochim. Acta Part B 63 (2008) 1290–1296.

[39] M. Gharehbaghi, F. Shemirani, M. Baghdadi, Int. J. Environ. Anal. Chem. 89 (2009) 21–33.
[40] M. Baghdadi, F. Shemirani, Anal. Chim. Acta 634 (2009) 186–191.
[41] S. Mahpishanian, F. Shemirani, Talanta 82 (2010) 471–476.
[42] B. Majidi, F. Shemirani, Biol. Trace Elem. Res. 143 (2011) 579–590.
[43] E. Stanisz, A. Zgoła-Grześkowiak, Talanta 115 (2013) 178–183.
[44] H. Matusiewicz, E. Stanisz, Microchem. J. 95 (2010) 268–273.
[45] H. Matusiewicz, E. Stanisz, J. Braz, Chem. Soc. 23 (2012) 247–257.
[46] C. Zhang, Y. Li, P. Wu, X.-P. Yan, Anal. Chim. Acta 652 (2009) 143–147.
[47] C. Zhang, Y. Li, P. Wu, Y. Jiang, Q. Liu, X.-P. Yan, Anal. Chim. Acta 650 (2009) 59–64.
[48] G.N. Glavee, K.J. Klabunde, C.M. Sorensen, G.C. Hadjipanayis, Inorg. Chem. 32 (1993) 474–477.
[49] G.N. Glavee, K.J. Klabunde, C.M. Sorensen, G.C. Hadjipanayis, Inorg. Chem. 34 (1995) 28–35.
[50] C.W. Scheeren, G. Machado, J. Dupont, P.F.P. Fichtner, S.R. Texeira, Inorg. Chem. 42 (2003) 4738–4742.
[51] X.-D. Mu, J.-Q. Meng, Z.-C. Li, Y. Kou, J. Am. Chem. Soc. 127 (2005) 9694–9695.
[52] G.S. Fonseca, A.P. Umpierre, P.F.P. Fichtner, S.R. Teixeira, J. Dupont, Chem. Eur. J. 9 (2003) 3263–3269.
[53] E.T. Silveira, A.P. Umpierre, L.M. Rossi, G. Machado, J. Morais, G.V. Soares, I.J. R. Baumvol, S.R. Teixeira, P.F.P. Fichtner, J. Dupont, Chem. Eur. J. 10 (2004) 3734–3740.
[54] C. Zheng, R.E. Sturgeon, C.S. Brophy, S. He, X. Hou, Anal. Chem. 82 (2010) 2996–3001.
[55] C. Zheng, R.E. Sturgeon, X. Hou, J. Anal. At. Spectrom. 25 (2010) 1159–1165.
[56] S. Xu, R.E. Sturgeon, Y. Guo, W. Zhang, H. Zhao, Ann. Chim. 95 (2005) 491–499.
[57] The report of the Regional Inspectorate of Environmental Protection (2008, Wrocław, Poland) (pp. 51–54, in Polish). Available from: ⟨http://www.wroclaw.pios.gov.pl/pliki/gleby/ocena_2007.pdf⟩.