

**PRECONCENTRATION OF COPPER FROM NATURAL WATER SAMPLES USING LIGAND-LESS *IN SITU* SURFACTANT-BASED SOLID PHASE EXTRACTION PRIOR TO FAAS DETERMINATION**Sayed Zia Mohammadi<sup>a,\*</sup>, Daryoush Afzali<sup>b</sup>, Fatemeh Sabermahani<sup>a</sup> and Samira Afshari<sup>a</sup><sup>a</sup>Department of Chemistry, Payame Noor University, Tehran, Iran<sup>b</sup>Department of Chemistry, Graduate University of Advanced Technology, Kerman, Iran

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In the present work, a simple and rapid ligand-less, *in situ*, surfactant-based solid phase extraction for the preconcentration of copper in water samples was developed. In this method, a cationic surfactant (n-dodecyltrimethylammonium bromide) was dissolved in an aqueous sample followed by the addition of an appropriate ion-pairing agent ( $\text{ClO}_4^-$ ). Due to the interaction between the surfactant and ion-pairing agent, solid particles were formed and subsequently used for the adsorption of  $\text{Cu}(\text{OH})_2$  and  $\text{CuI}$ . After centrifugation, the sediment was dissolved in 1.0 mL of 1 mol L<sup>-1</sup>  $\text{HNO}_3$  in ethanol and aspirated directly into the flame atomic absorption spectrometer. In order to obtain the optimum conditions, several parameters affecting the performance of the LL-ISS-SPE, including the volumes of DTAB,  $\text{KClO}_4$ , and KI, pH, and potentially interfering ions, were optimized. It was found that KI and phosphate buffer solution (pH = 9) could extract more than 95% of copper ions. The amount of copper ions in the water samples varied from 3.2 to 4.8 ng mL<sup>-1</sup>, with relative standard deviations of 98.5%–103%. The determination of copper in water samples was linear over a concentration range of 0.5–200.0 ng mL<sup>-1</sup>. The limit of detection ( $3S_b/m$ ) was 0.1 ng mL<sup>-1</sup> with an enrichment factor of 38.7. The accuracy of the developed method was verified by the determination of copper in two certified reference materials, producing satisfactory results.

Keywords: ligand-less *in situ* surfactant-based solid phase extraction; preconcentration; copper determination.

**INTRODUCTION**

Copper is considered as an essential micronutrient for all high plants and animals and is required for good health. This element is needed by many living organisms at very low levels (nearly 40 ng mL<sup>-1</sup>) because it plays a role in trace quantities as a co-factor in some important enzymes.<sup>1,2</sup> However, high concentrations of copper are harmful, causing vomiting, nausea, diarrhea, liver or kidney damage, or even death.<sup>3</sup>

Due to the numerous applications of copper in industry<sup>2</sup> and its crucial role in biological systems,<sup>2</sup> its determination in different samples is important.

Flame atomic absorption spectrometry (FAAS) is the most common technique used for copper determination due to its relatively low cost, simple operation, and experimental rapidity. The direct determination of copper ions at trace levels in many environmental and biological samples, however, is limited due to insufficient sensitivity and matrix interference. In order to solve these important problems, separation-enrichment techniques such as liquid-liquid extraction,<sup>4,5</sup> membrane filtration,<sup>6,7</sup> microextraction methods,<sup>8,9</sup> cloud point extraction,<sup>10,11</sup> and solid phase extraction (SPE)<sup>12-14</sup> have been employed by researchers around the world.

Among preconcentration methods, SPE has several advantages including high preconcentration factor, low reagent consumption, the ease of solid phase regeneration, reusability of the adsorbent, ease of automation, environmental friendliness, ease of usage, time and cost savings, and the ability to be combined with different detection techniques.<sup>15</sup>

Recently, Shemirani and Yousefi<sup>16</sup> demonstrated a surfactant-based SPE method termed *in situ* surfactant-based solid phase extraction (ISS-SPE). In this procedure, a cationic surfactant containing an appropriate alkyl group was dissolved in the aqueous sample, and then a suitable ion-pairing agent was added. Due to the interaction between

the surfactant and the ion-pairing agent, very fine solid particles were formed. After centrifugation, the solid particles were sedimented at the bottom of the centrifuge tube. They were then dissolved in an organic solvent or leached with acid in order to recover the analyte.

In the present study, we developed a new mode of ISS-SPE termed ligand-less *in situ* surfactant-based solid phase extraction (LL-ISS-SPE) for the preconcentration of trace amounts of copper from aqueous samples without any chelating agent.

**EXPERIMENTAL****Instrumentation**

An atomic absorption spectrometer (SensAA GBC, Dandenong, Australia) equipped with deuterium background correction and an air-acetylene burner was used for absorbance measurements. A copper hollow cathode lamp was used as the light source at a wavelength of 324.8 nm. The operating parameters were set according to the manufacturer's recommendation. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal for copper. A pH meter (Metrohm 692, Herisau, Switzerland) and a tabletop centrifuge (K240, Centurion West Sussex, United Kingdom) were used.

**Reagents and solutions**

All solutions were prepared from analytical grade reagents, and the water used was from a Milli-Q purification system (Millipore, Bedford, MA, USA). Before use, all laboratory glassware was kept overnight in a 10% (v/v)  $\text{HNO}_3$  solution, rinsed with de-ionized water, and dried in an oven at 100 °C. A stock solution of copper at a concentration of 1000.0 mg L<sup>-1</sup> was purchased from Merck (Darmstadt, Germany). A solution of 0.02 mol L<sup>-1</sup>  $\text{KClO}_4$  (JHD, Guangdong Guanghua Chemical Factory Co., Shantou, Guangdong, China) was prepared by dissolving the appropriate amount of  $\text{KClO}_4$  in

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de-ionized water. A stock solution of n-dodecyltrimethylammonium bromide (DTAB; Sigma–Aldrich, Munich, Germany;  $0.2 \text{ mol L}^{-1}$ ) was prepared in de-ionized water and ethanol. One series of  $0.5 \text{ mol L}^{-1}$  solutions of  $\text{I}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{C}_2\text{O}_4^{2-}$  were prepared by respectively dissolving the appropriate amounts of KI, NaCl, KBr,  $\text{Na}_2\text{CO}_3$ , and  $\text{Na}_2\text{C}_2\text{O}_4$  (Merck) in de-ionized water. Solutions of various metal salts ( $1000 \text{ mg L}^{-1}$ ) were prepared to study the interference of anions and cations by dissolving the appropriate salt amounts in de-ionized water. Phosphate buffer solution ( $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ ) was prepared by mixing the appropriate volumes of  $0.2 \text{ mol L}^{-1}$  potassium dihydrogen phosphate and disodium hydrogen phosphate solutions to obtain a pH of 9.

### LL-ISS-SPE procedure

The sample solution (40 mL) was placed in a screw-cap glass test tube, and 1 mL phosphate buffer  $0.2 \text{ mol L}^{-1}$  and 1.5 mL  $0.5 \text{ mol L}^{-1}$  KI were added and mixed manually. Subsequently, 2 mL DTAB ( $0.2 \text{ mol L}^{-1}$ ) was added, the mixture was manually shaken, and 2 mL  $\text{KClO}_4$  ( $0.02 \text{ mol L}^{-1}$ ) was added. A cloudy suspension of solid particles (-dodecyltrimethylammonium perchlorate salt) dispersed in the solution was formed. The cloudy solution was centrifuged at 3200 rpm for 5 min, the aqueous phase was decanted, and any residual water was removed with a micro-syringe. The sediment was dissolved in 1.0 mL of  $1.0 \text{ mol L}^{-1}$   $\text{HNO}_3$  in ethanol, and the solution was aspirated directly into the flame of the atomic absorption spectrometer.

### Sample preparation

Water samples were collected in acid-leached polyethylene bottles. The only pretreatment was acidification to pH 2 with  $\text{HNO}_3$ , which was performed immediately after collection in order to prevent adsorption of the metal ions on the flask walls. River water samples were collected from two local rivers (Kohpayeh and Shahdad in Kerman, Iran), and wastewater samples were obtained from the Bahonar copper factory (Kerman, Iran) and the copper factory in Sarcheshmeh (Rafsanjan, Iran). A well water sample was collected from the university groundwater well (Kerman, Iran), and mineral water was purchased from a local supermarket. The samples were filtered through a cellulose membrane with a pore size of  $0.45 \mu\text{m}$  (Millipore) in order to prevent metal precipitation by colloidal-sized particulates suspended in water.

Two certified reference materials were analyzed: CRM TMDW-500 (High-Purity Standards, Inc.) and NIST CRM 1643e (National Institute of Standard and Technology, Trace elements in water). Each CRM (20 mL) was placed into a 50-mL volumetric flask, and the pH was adjusted to 9 with buffer solution. An aliquot of these sample solutions was taken, and Cu(II) ion was determined using the LL-ISS-SPE procedure.

### Variable optimization

In order to obtain the best conditions, several parameters affecting the performance of the LL-ISS-SPE such as volumes of DTAB,  $\text{KClO}_4$ , and KI, pH, and potentially interfering ions were optimized. All experiments were performed using 40 mL of an aqueous solution containing  $2.0 \mu\text{g}$  copper.

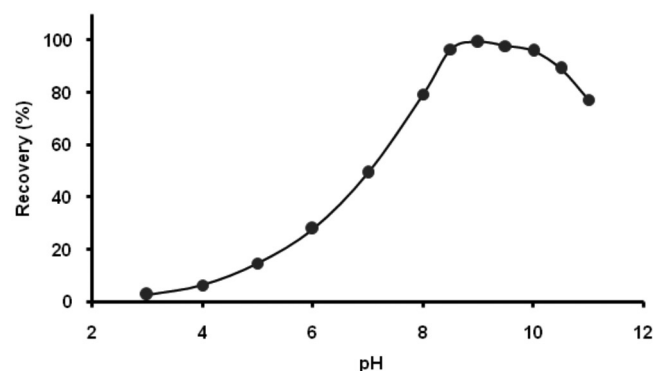
#### Selection of the appropriate anion

In the LL-ISS-SPE procedure, the cation should be reacted with an appropriate anion. Therefore, the selection of the anion is important for LL-ISS-SPE. Several experiments were performed

by the addition of 2 mL of various anions such as  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ , and  $\text{CO}_3^{2-}$  ( $0.5 \text{ mol L}^{-1}$ ) while keeping other variables constant (phosphate buffer pH = 9). The obtained recoveries for  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ , and  $\text{CO}_3^{2-}$  were 77.2%, 97.8%, 59.3% and 79.6%, respectively. Based on these results, KI was selected for the recovery of copper ion in all subsequent experiments.

#### Effect of pH on copper extraction

The pH values of the sample solutions were adjusted within the range of 3–11 using diluted HCl and NaOH, and the LL-ISS-SPE procedure was then applied to these solutions. As shown in Figure 1, the recovery of copper increased with increasing pH, and quantitative recoveries for Cu(II) ions were obtained in the pH range of 8.5–10. Above pH 10, the recovery of Cu(II) decreased with increasing pH. At higher pH values, Cu(II) ions may be in the form of  $\text{Cu}(\text{OH})_4^{2-}$ , decreasing the extraction of Cu(II) ion. Therefore, in subsequent studies, the pH was maintained at approximately 9.



**Figure 1.** Effect of pH on the recovery of copper ion. Conditions: Cu(II)  $0.05 \mu\text{g mL}^{-1}$ , 40 mL; Phosphate buffer  $0.2 \text{ mol L}^{-1}$ , 1 mL; KI  $0.5 \text{ mol L}^{-1}$ , 1.5 mL; DTAB  $0.2 \text{ mol L}^{-1}$ , 1.5 mL;  $\text{KClO}_4$   $0.02 \text{ mol L}^{-1}$ , 2 mL; Centrifuge time, 5 min; Centrifuge speed, 3000 rpm

After the optimum pH was identified (pH 9, phosphate buffer), the volume of buffer was also studied. The results showed that the addition of 0.5–4 mL of buffer ( $0.2 \text{ mol L}^{-1}$ ) did not have any effect on the extraction of copper. Therefore, 1 mL of  $0.2 \text{ mol L}^{-1}$  potassium dihydrogen phosphate and disodium hydrogen phosphate buffer were used in all subsequent experiments.

#### Effect of KI volume

The effect of KI volume on the recovery of copper was studied in the range of 0.5 to 3.0 mL while keeping other variables constant. The results showed that the extraction yield increased with KI volumes from 0.5 to 1.0 mL and then remained constant. When a small volume of KI was used, the amount of  $\text{I}^-$  was not sufficient for complete extraction. Therefore, 1.5 mL of  $0.5 \text{ mol L}^{-1}$  KI was chosen for the subsequent experiments.

#### Effect of surfactant concentration

In the LL-ISS-SPE procedure, the amount of surfactant not only affects the extraction efficiency, but also the amount of the sediment phase. Therefore, the effect of DTAB volume on the recovery of copper was studied. For this purpose, several experiments were carried out using different volumes of DTAB in the range of 0.5–3.0 mL. The results showed that the extraction yield of copper increased with increasing surfactant volume from 0.5 to 1.0 mL and then remained constant. When a small volume of surfactant was used, there was not enough sorbent for complete extraction. Therefore, 1.5 mL DTAB was chosen for the subsequent experiments.

### Effect of ion-pairing agent volume

The volume of ion-pairing agent is an important factor in the LL-ISS-SPE procedure. Increasing the amount of  $\text{KClO}_4$  is expected to form more solid sorbent and increase recovery. Therefore, the effect of  $\text{KClO}_4$  volume was investigated in the range of 0.5–3.0 mL. The results demonstrated that the recovery of copper increased with increasing  $\text{KClO}_4$  volume up to 1.5 mL and then remained constant. Therefore, 2 mL  $\text{KClO}_4$  ( $0.02 \text{ mol L}^{-1}$ ) was selected for the subsequent experiments.

### Effect of equilibrium time

In the LL-ISS-SPE procedure, the extraction time is defined as the time interval between the addition of the ion-pairing agent and the beginning of centrifugation. The effect of extraction time was examined in the range of 1 to 10 min. The obtained results showed that the extraction time has no significant influence on the extraction. The fast equilibrium is attributed to the very small size and high surface area of the sorbent particles.<sup>16</sup>

### Effect of centrifugation time and rate

The effect of centrifugation rate on the analytical signal was studied in the range of 500–3500 rpm. The analytical signal increased with increasing centrifugation rate from 500 to 2800 rpm and then remained constant. Therefore, a centrifugation rate of 3000 rpm was chosen in this study. The effect of centrifugation time on the analytical signal was also studied in the range of 3–15 min. The results showed that the analytical signal increased with increasing centrifugation time up to 5 min and then remained constant. Therefore, a centrifugation time of 5 min at 3000 rpm was selected for the entire procedure.

### Influence of interfering ions

One of the main problems in FAAS is the interference effect of the sample matrices. In order to assess the possible analytical applications of the LL-ISS-SPE procedure, the interference of several cations and anions were examined under optimized conditions. For this purpose, various amounts of foreign ions were added to a fixed amount of copper ions, and the LL-ISS-SPE procedure was carried out. A tolerable amount was defined as the maximum concentration found to cause a  $\pm 5\%$  change in the recovery of copper compared to the recovery for copper ion alone. Each experiment was repeated three times, and the averaged values are given in Table 1. The results showed that the tested anions and cations have no considerable effect on the determination of copper. Therefore, the LL-ISS-SPE procedure can be applied to the determination of copper ions in wastewater and water samples.

**Table 1.** Tolerance limit of interference ions

Interference ions	Salt	Interference/ copper ratio
$\text{PO}_4^{3-}$ , $\text{HPO}_4^{2-}$	$\text{Na}_3\text{PO}_4$ , $\text{Na}_2\text{HPO}_4$	>6000
$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$	$\text{Ca}(\text{NO}_3)_2$ , $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2500
$\text{Na}^+$	$\text{NaCl}$	>5500
$\text{Al}^{3+}$	$\text{AlCl}_3 \cdot 2\text{H}_2\text{O}$	450
$\text{Cd}^{2+}$	$\text{Cd}(\text{NO}_3)_2$	350
$\text{Ni}^{2+}$ , $\text{Co}^{2+}$	$\text{Ni}(\text{NO}_3)_2$ , $\text{Co}(\text{NO}_3)_2$	300
$\text{Fe}^{3+}$	$\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	400
$\text{Mn}^{2+}$ , $\text{Zn}^{2+}$	$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	300
$\text{Pb}^{2+}$	$\text{Pb}(\text{NO}_3)_2$	250

Conditions were the same as Figure 1.

## RESULTS AND DISCUSSION

In this study, LL-ISS-SPE was combined with FAAS to develop a method for the determination of trace amounts of copper ions. Due to the interaction between DTAB and  $\text{KClO}_4$ , solid particles were formed, and  $\text{Cu}(\text{OH})_2$  and  $\text{CuI}$  then adsorbed on surface of the solid particles. After centrifugation, the solid particles were sedimented at the bottom of the centrifuge tube, and the aqueous phase was decanted. Subsequently, the solid particles were dissolved in 1.0 mL of  $1.0 \text{ mol L}^{-1} \text{ HNO}_3$  in ethanol, and the solution was aspirated directly into the flame for AAS.

### Analytical performance

Under the optimized conditions, a calibration curve was constructed for the determination of copper according to the LL-ISS-SPE procedure. For a sample volume of 40.0 mL, the calibration curve exhibited linearity over the range of 0.5–200.0  $\text{ng mL}^{-1}$  with a correlation coefficient of 0.9995. The regression equation was  $A = 3.925C + 0.006$ , where  $A$  is the absorbance of the copper and  $C$  is the concentration of copper in the original solution ( $\mu\text{g mL}^{-1}$ ). The reproducibility of the procedure was evaluated by seven replicate measurements of 50.0  $\text{ng mL}^{-1}$  of copper. The relative standard deviation (RSD) was found to be  $\pm 2.2\%$ . The limit of detection (LOD) based on three times the standard deviation of the blank divided by the slope of the analytical curve ( $3S_b/m$ ) was 0.1  $\text{ng mL}^{-1}$ . The enrichment factor was calculated as the ratio of the analytical signal of copper obtained after and before extraction. The enrichment factor (EF) was 38.7 for the 40.0 mL sample solution.

### Accuracy of the LL-ISS-SPE procedure

The accuracy of the LL-ISS-SPE procedure was studied by the determination of copper in two certified reference materials, CRM TMDW-500 and NIST CRM 1643e, with copper concentrations of  $20.0 \pm 0.1$  and  $19.63 \pm 0.21 \text{ ng mL}^{-1}$ , respectively. Aliquots of these certified reference materials were subjected to the LL-ISS-SPE procedure for the preconcentration and determination of copper using the standard addition method. The determined concentrations of copper in CRM TMDW-500 and NIST CRM 1643e were  $20.7 \pm 0.6$  and  $18.9 \pm 0.4 \text{ ng mL}^{-1}$ , respectively. The t-test at a 95% confidence level showed that there is no significant difference between the obtained results of the proposed LL-ISS-SPE procedure and the certified amounts.

### Analysis of real samples

In order to test the possibility of applying the LL-ISS-SPE procedure to water samples with different matrices, further experiments were done on wastewater, river water and well water. In order to test the applicability of the proposed LL-ISS-SPE procedure for the preconcentration and determination of copper in the real samples, two wastewater, two river water, one tap water and one mineral water samples were analyzed. The recovery of copper from samples spiked with  $\text{Cu}(\text{II})$  standard solutions was also studied. The results (Table 2) showed that the added copper ions can be quantitatively recovered from the samples using the LL-ISS-SPE procedure. As can be seen, a good agreement between the added and detected copper concentrations in the water samples was obtained.

In addition to evaluating the accuracy of the proposed method, the results obtained with the LL-ISS-SPE procedure were compared with those from graphite furnace atomic absorption spectrometry (GF-AAS). A t-test at the 95% confidence level showed that there was no

**Table 2.** Determination of copper in water samples

Sample	Copper amount (ng mL <sup>-1</sup> )			Recovery (%)	
	Added	Found by LL-ISS-SPE procedure <sup>a</sup>	Found by GF-AAS	LL-ISS-SPE procedure	GF-AAS
Kohpayeh river (Kohpayeh, Kerman)	0.0	4.8±0.1	4.6±0.2	----	----
	20.0	25.3±0.9	25.2±1.3	102.5	103.0
Shahdad river (Shahdad, Kerman)	0.0	3.9±0.1	4.0±0.1	----	----
	20.0	23.5±0.7	24.3±1.0	98.0	101.5
Mineral water	0.0	3.3±0.1	3.3±0.1	----	----
	20.0	22.8±0.7	23.0±1.0	97.5	98.5
Tap water	0.0	4.6±0.2	5.0±0.2	----	----
	20.0	25.0±0.6	24.8±1.2	102.0	99.0
Wastewater (Copper factory, Sarchashmeh, Rafsanjan)	0.0	3.2±0.1	3.3±0.1	----	----
	20.0	23.9±1.0	23.5±0.9	103.5	101.0
Wastewater (Copper factory, Shahid Bahonar, Kerman)	0.0	4.3±0.2	4.0±0.1	----	----
	20.0	24.7±1.0	23.7±1.1	102.0	98.5

<sup>a</sup>Mean ± standard deviation (n = 4).

**Table 3.** Comparison of reported methods with the LL-ISS-SPE procedure

Enrichment method	Detection method	Linear range (ng mL <sup>-1</sup> )	EF	RSD%	LOD (ng mL <sup>-1</sup> )	Ref.
SPE	FAAS	3-120	41	2.0	0.56	17
SPE	FAAS	1-4000	----	2.4	1.0	18
SPE	FAAS	-----	55.5	1.1	1.67	19
SPE	FAAS	0.75-500	14	1.86	0.75	20
SPE	FAAS	16-100	16	3.3	3	21
SPE	FAAS	1-50	87	4	0.87	22
SPE	FAAS	0.2-75	----	2.5	0.05	23
LL-ISS-SPE	FAAS	0.5-200.0	38.7	2.2	0.1	This work

significant difference between the obtained results of the presented LL-ISS-SPE method and the GF-AAS method.

### Comparison of LL-ISS-SPE with the other reported methods for the preconcentration of copper

A comparison of the LL-ISS-SPE procedure with some of the other reported methods for copper determination using FAAS is given in Table 3.<sup>17-23</sup> The detection limit obtained using the LL-ISS-SPE procedure was comparable to or better than some of the other reported methods,<sup>17-22</sup> and its linear range was wider than some of the other reported methods.<sup>17,21-23</sup> The relative standard deviation of the proposed procedure was lower than some of the other reported methods.<sup>18,21-23</sup>

### CONCLUSIONS

A new mode of solid phase extraction (ligand-less in situ surfactant-based solid phase extraction) was developed for the extraction and preconcentration of copper from water samples. This method is fast, simple, inexpensive, and environment-friendly. The LL-ISS-SPE procedure possesses the following advantages over existing SPE methods: the sorbent was formed in the sample solution; the sorbent and support were the same; the cost of the method was low; the sorbent was a safe surfactant; and the small particle size and large surface area of the sorbent led to a short extraction time and a high extraction recovery. The LL-ISS-SPE procedure offers good accuracy, precision, and reproducibility, making it useful for the analysis of

copper in water samples with different compositions, including river water, wastewater, and well water samples.

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### REFERENCES

- Liang, P.; Yang, J.; *J. Food Compos. Anal.* **2010**, *23*, 95.
- Fathi, S. A. M.; Yafthian, M. R.; *J. Colloid Interface Sci.* **2009**, *334*, 167.
- Sahin, C. A.; Tokgoz, I.; Bektas, S.; *J. Hazard. Mater.* **2010**, *181*, 359.
- Lemos, L. R. D.; Boggione Santos, I. J.; Rodrigues, G. D.; Silva, L. H. M. D.; Silva, M. C. H. D.; *J. Hazard. Mater.* **2012**, *237*, 209.
- Teixeira Diniz, M. C.; Filho, O. F.; Rohwedder, J. J. R.; *Anal. Chim. Acta* **2004**, *525*, 281.
- Soylak, M.; Unsal, Y. E.; Kizil, N.; Aydin, A.; *Food Chem. Toxicol.* **2010**, *48*, 517.
- Hedberg, Y.; Herting, G.; Wallinder, I. O.; *Environ. Pollut.* **2011**, *159*, 1144.
- Amirkavei, M.; Dadfarnia, S.; Shabani, A. M. H.; *Quim. Nova*, **2013**, *36*, 63.
- Mohammadi, S. Z.; Afzali, D.; Baghelani, Y. M.; *Anal. Chim. Acta* **2009**, *653*, 173.
- Shokrollahi, A.; Ghaedi, M.; Gharaghani, S.; Fathi, M. R.; Soyylak, M.; *Quim. Nova*, **2008**, *31*, 70.
- Ramazan, G.; Nail, A.; *Quim. Nova* **2013**, *36*, 1146.

12. Ganjali, Pourjavid, M. R.; Haji-agma Babaei, L.; Salavati-Niasari, M.; *Quim. Nova*, **2004**, *27*, 213.
13. Elvan, H.; Ozdes, D.; Duran, C.; Sahin, D.; Tufekci, M.; Bahadir, Z.; *Quim. Nova*, **2013**, *36*, 831.
14. Shokrollahi, A.; Montazerzohori, M.; Mehrpour, T.; Tavallali, H.; Zare Khafri, B.; Montaseri, Z.; *Quim. Nova*, **2013**, *36*, 1354.
15. Elci, L.; Kartal, A. A.; Soylak, M.; *J. Hazard. Mater.* **2008**, *153*, 454.
16. Yousefi, S. R.; Shemirani, F.; *Microchim. Acta* **2011**, *173*, 415.
17. Chamjangali, M. A.; Bagherian, G.; Mokhlesian, A.; Bahramian, B.; *J. Hazard. Mater.* **2011**, *192*, 1641.
18. Rezaei, B.; Sadeghi, E.; Meghdadi, S.; *J. Hazard. Mater.* **2009**, *168*, 787.
19. Buke, B.; Divrikli, U.; Soylak, M.; Elci, L.; *J. Hazard. Mater.* **2009**, *163*, 1298.
20. Do Carmo, S. N.; Damásio, F. Q.; Alves, V. N.; Marques, T. L.; Coelho, N. M. M.; *Microchem. J.* **2013**, *110*, 320.
21. Gonzáles, A. P. S.; Firmino, M. A.; Nomura, C. S.; Rocha, F. R. P.; Oliveira, P. V.; Gaubeur, I.; *Anal. Chim. Acta* **2009**, *636*, 198.
22. Sonmez, S.; Divrikli, U.; Elci, L.; *Talanta* **2010**, *82*, 939.
23. Afzali, D.; Mostafavi, A.; Taher, M. A.; Moradian, A.; *Talanta* **2007**, *71*, 971.