http://dx.doi.org/10.5935/0103-5053.20150136

J. Braz. Chem. Soc., Vol. 26, No. 8, 1642-1647, 2015.
Printed in Brazil - ©2015 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Separation and Preconcentration of Trace Amounts of Lead from Water Samples Using Solvent-Assisted Dispersive Solid Phase Extraction

Reyhaneh Rahnama* and Raofeh Ghadiri

Department of Chemistry, Payame Noor University (PNU), P.O. BOX 19395-3697 Tehran, Iran

This paper describes a new approach for the preconcentration of lead (Pb^{2+}) by solvent-assisted dispersive solid phase extraction (SADSPE) prior to analyzing by flame atomic absorption spectrometry (FAAS). In this method, the dispersion of the sorbent was achieved by injecting a solution of the sorbent into the aqueous sample. Thereby, a cloudy solution formed. The cloudy state resulted from the dispersion of the fine particles of the sorbent in the bulk aqueous sample. Pb ions reacted with 1-(2-pyridylazo)-2-naphthole (PAN) as chelating agent to form a hydrophobic complex. After extraction, phase separation was performed by centrifugation and as a result, the enriched analyte in this demented phase could be determined by FAAS. Some parameters that influenced solvent-assisted dispersive solid phase extraction and subsequent determination were evaluated in detail. Under optimized conditions (pH 9, PAN concentration: 1.0×10^{-3} mol L^{-1}, sorbent: 0.1% m/v 1,4-dichlorobenzene, disperser solvent: 0.5 mL ethanol), a preconcentration factor of 50 could be obtained, and the limit of detection (LOD) for lead was 1.3 µg L^{-1}. Relative standard deviation for ten replicate determinations of the standard solution containing 20 µg L^{-1} lead was 5.0%. The proposed method was successfully applied for the determination of lead in water samples with satisfactory results.

Keywords: solvent-assisted dispersive solid phase extraction, 1-(2-pyridylazo)-2-naphthole, lead, water sample

Introduction

Recently, the chemical pollution with heavy metals has been one of the serious problems for the sustainable environment. Human activities have been considered to be responsible for environmental pollution by large amounts of toxic elements like lead. Lead and other toxic metals are released into the environment by several processes including waste and coal burning, industrial processes, volcanic emissions, metal mining, and smelting.[1,2] Exposure to these toxic elements imposes risks not only to human health, but also to plants, animals and microorganisms.[3] According to the World Health Organization (WHO) the upper permissible level of lead in drinking water is 10.0 µg L^{-1}.[4] Hence, the determination of lead in sub-micron levels is still a challenging task.

In spite of the increase in sophisticated analytical instrumentation aiming to improve the detection limits, many methods for metal determination at µg L^{-1} levels are still commonly performed using preconcentration procedures associated with techniques such as flame atomic absorption spectrometry (FAAS), inductively coupled plasma optical emission spectrometry (ICP OES),[5,6] electrothermal atomic absorption spectrometry (ETAAS),[7,8] and inductively coupled plasma mass spectrometry (ICP-MS).[9] Various preconcentration techniques were used for the separation and preconcentration of trace amounts of metal ions such as liquid-liquid extraction,[10] dispersive liquid-liquid microextraction (DLLME),[11] coprecipitation,[12] electrochemical methods,[13] ion exchange,[14] solid phase extraction,[15,16] solid phase extraction coupled with dispersive liquid-liquid microextraction (SPE-DLLME).[17] This latter technique has been the most used for this purpose, because it generally provides higher enrichment factors than liquid-liquid extraction without requiring hazardous organic solvents. Solid phase extraction techniques are surface-dependent processes since their efficiency directly depends on the particle size and the surface area of the sorbent.[18] Dispersive solid phase extraction (DSPE) has risen as an alternative to conventional solid phase extraction. DSPE was introduced by Anastassiades *et al.*[19] in 2003. It is based on the dispersion of the sorbent at a very low milligram level in the aqueous sample by an external energy (usually a vortex stirring). In this step, the hydrophobic

---

*e-mail: r_rahnama@ymail.com

analytes interact with the fine particles of the sorbent, and consequently, are extracted from the initial solution. After extraction, phase separation is performed by centrifugation and the enriched analyte can be directly monitored on the sorbent surface by using a spectroscopic technique[20,21] or can be eluted/desorbed for the subsequent analysis of the eluted fraction.[22-25] DSPE has attracted a considerable amount of attention due to its simplicity, short analysis time, and low consumption of sorbent compared to the conventional SPE.

Solvent-assisted dispersive solid phase extraction (SADSPE) is based on the DSPE methodology, but the dispersion of sorbent in the aqueous sample is performed by rapidly injecting the appropriate mixture of sorbent and disperser solvent in the bulk aqueous sample.[26] Simplicity of the operation, rapidity, low sample volume, low cost, high recovery, and high enrichment factor are some advantages of SADSPE.

In this study, FAAS was investigated in order to be coupled with the proposed SADSPE for the determination of lead. FAAS is used for determination because of its fast analysis time, relative simplicity, and lower cost. The proposed method was very simple and rapid. Various factors affecting extraction efficiency were evaluated and optimized. Under optimum conditions, the developed method was used for the preconcentration, separation, and determination of lead in water samples with satisfactory results.

Experimental

Reagents and solutions

All chemicals were of analytical reagent grade. Stock standard solution (1000 mg L^{-1} in 0.5 mol L^{-1} HNO_3) of lead was prepared using $Pb(NO_3)_2$ that was obtained from Merck (Darmstadt, Germany). The working standard solutions were prepared by appropriate stepwise dilution of the stock standard solution with deionized water.

Other reagents used namely nitric acid, sodium hydroxide, ethanol, methanol, acetonitrile, acetone, sodium chloride, 1-(2-pyridylazo)-2-naphthole (PAN), 1,4-dichlorobenzene, naphthalene, and benzophenone were obtained from Merck (Darmstadt, Germany). All glassware was rinsed with deionized water, decontaminated for at least 24 h in 10% (v/v) nitric acid solution, and rinsed again five times with deionized water.

Instruments

A SensAA (GBC, Australia) atomic absorption spectrometer equipped with deuterium background correction and lead hollow cathode lamp was used for the determination of lead at a wavelength of 217.0 nm. The instrumental parameters were adjusted according to the manufacturer's recommendations. Phase separation was assisted using a centrifuge (Hettich, EBA 20). The pH-meter model 827 from Metrohm (Herisau, Switzerland) with combined glass electrode was used for pH measurements.

Extraction procedure

For SADSPE preconcentration, 50 mL analytical solution containing lead ion, 0.04 mol L^{-1} ammonia buffer (pH 9), 1×10^{-3} mol L^{-1} PAN and 10% m/v NaCl, was placed in a screw cap glass tube and then, 0.5 mL of ethanol solution (as disperser solvent) containing 1,4-dichlorobenzene (10.0% m/v) (as sorbent) was rapidly injected into a sample solution by using 1.0 mL syringe, and then, the mixture was gently shaken. A cloudy solution was formed in the test tube (the cloudy state was stable for a long time). This cloudy state resulted from the dispersion of fine particles of 1,4-dichlorobenzene in the bulk aqueous sample. Then, the mixture was centrifuged at 4000 rpm for 15 min. Accordingly, the dispersed fine particles of 1,4-dichlorobenzene were sedimented in the bottom of the conical test tube. The aqueous phase was then separated completely by a syringe. Later, this demented phase was dissolved and made up to 1.0 mL by adding ethanol. The resultant solution was introduced into the flame by conventional aspiration.

Results and Discussion

To obtain quantitative recoveries of lead using SADSPE method, the separation/preconcentration procedure was optimized for various parameters such as sorbent type and amount, type and volume of dispersive solvent, pH, chelating agent concentration, centrifuge conditions, and ionic strength. Triplicate extractions were performed for all experiments and the average of these results is reported in figures or tables. Finally, these optimal conditions were applied to extract and detect lead in various water samples.

The effect of pH

The pH of the sample solution is an important factor affecting the formation of complexes and the subsequent extraction. The effect of pH on the SADSPE of 20 μg L^{-1} of lead was studied in the range of 2-12. Figure 1 shows the effect of pH on the extraction of lead. It is clear from the figure that the recovery is nearly constant in the pH range of

9-12. At pH values below 9, however, the percent recovery decreased. Therefore, pH 9 was chosen for further work. In further work, 0.04 mol L^{-1} of ammonia buffer (pH 9) was used for adjusting the pH of the solution.

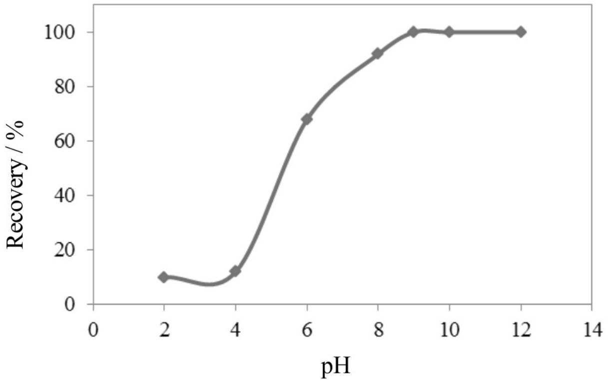

Figure 1. The effect of pH on extraction recovery of lead (sample volume: 50 mL; lead concentration: 20.0 µg L^{-1}; PAN concentration: 1.0×10^{-3} mol L^{-1}; sorbent: 0.1% m/v 1,4-dichlorobenzene; disperser solvent: 0.5 mL ethanol; sodium chloride: 10% m/v).

The effect of chelating agent concentration

PAN acts as a tridentate ligand and can form very stable complexes with metal ions (as ML or ML_2) through hydroxyl oxygen atom, nitrogen atom of pyridine, and one of the azo group nitrogen atoms.[27] PAN complexes of lead can be easily interacted with 1,4-dichlorobenzene, which increases extraction efficiency of lead. At 20 µg L^{-1} of lead, the effect of PAN concentration on extraction efficiency was studied by changing the concentration of PAN in the range of 1×10^{-5}-1.4×10^{-3} mol L^{-1} (Figure 2). Results showed that increasing the concentration of PAN up to 5×10^{-4} mol L^{-1} will cause an increase in the extraction recovery; after that, it remained constant, which is considered as complete extraction. Hence, 1.0×10^{-3} mol L^{-1} PAN was chosen to account for other extractable species.

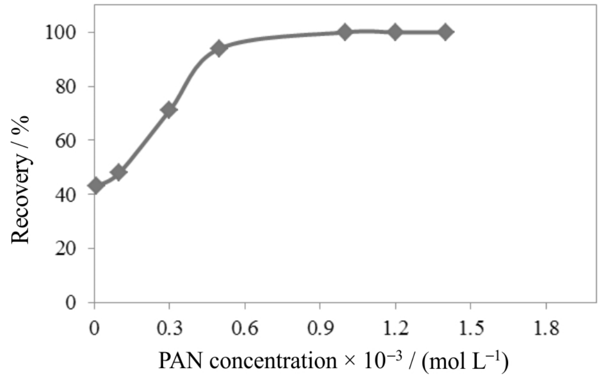

Figure 2. The effect of PAN concentration on extraction recovery of lead (sample volume: 50 mL, lead concentration: 20.0 µg L^{-1}, pH: 9, sorbent: 0.1% m/v 1,4-dichlorobenzene, disperser solvent: 0.5 mL ethanol, sodium chloride: 10% m/v).

The effect of type and volume of disperser solvent

In SADSPE, solvents that are miscible in aqueous solution and have the ability to dissolve the sorbent can be used as disperser solvents. These solvents can disperse the sorbent into very fine droplets in the aqueous phase. Therefore, acetone, acetonitrile, ethanol, and methanol were selected as disperser solvents and the effect of these solvents on the performance of SADSPE was investigated. For this purpose, various experiments were performed using 0.50 mL of each disperser solvent containing 10.0% m/v 1,4-dichlorobenzene (sorbent) and the recoveries were investigated. Results showed that recoveries with ethanol (100.0 ± 2.2%) and methanol (100.0 ± 2.1%) are equal and recoveries with acetone (84.0 ± 3.2%) and acetonitrile (79.0 ± 2.5%) are less. Thus, we chose ethanol among these solvents because of higher recoveries and less toxicity.

After choosing ethanol as a disperser solvent, it is necessary to optimize its volume, because at low volumes, ethanol cannot disperse the extraction solvent properly, and hence, the cloudy solution is not formed completely; at high volumes, the solubility of the complex in water increases, decreasing the extraction efficiency. For obtaining the optimized volume of ethanol, various experiments were performed by using different volumes of ethanol (0.1-1.5 mL) containing different amounts of 1,4-dichlorobenzene. Figure 3 shows the curves of the recovery of lead versus the volume of ethanol. According to the results, 0.5 mL of ethanol was selected as the optimum volume.

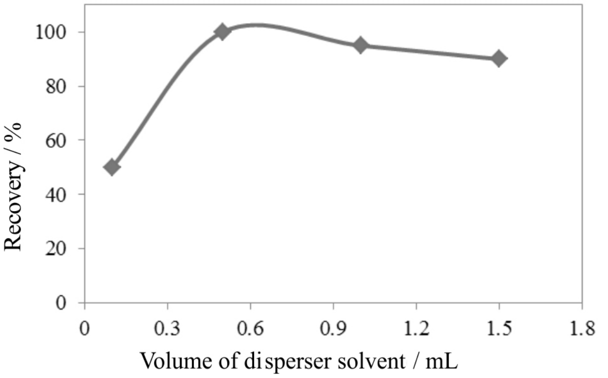

Figure 3. The effect of amount of disperser solvent on extraction recovery of lead (sample volume: 50 mL, lead concentration: 20.0 µg L^{-1}, pH: 9, PAN concentration: 1.0×10^{-3} mol L^{-1}, sorbent: 1,4-dichlorobenzene, disperser solvent: ethanol, sodium chloride: 10% m/v).

The effect of sorbent type and amount

In the selection of sorbent, some properties must be considered: it should have (*i*) high solubility in the disperser solvent, (*ii*) extraction capability of the concerning compounds, and (*iii*) low solubility in water. Hence, various sorbents (naphthalene, benzophenone, and 1,4-dichlorobenzene) were studied to achieve maximum extraction recovery. The results are shown in Figure 4. It can be seen that maximum extraction efficiency was obtained by 1,4-dichlorobenzene. Thus, this sorbent was selected for further experiments.

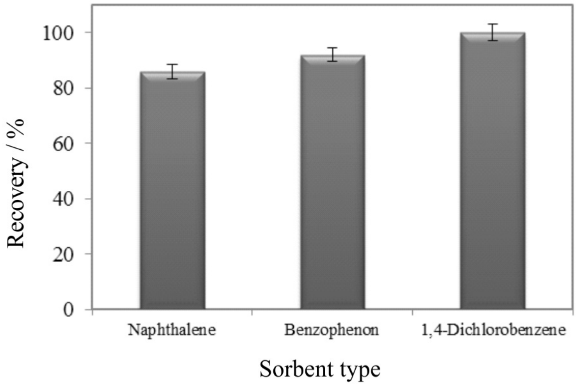

Figure 4. The effect of sorbent type on extraction recovery of lead (sample volume: 50 mL, lead concentration: 20.0 µg L^{-1}, pH: 9, PAN concentration: 1.0×10^{-3} mol L^{-1}, sorbent: 0.1% m/v, disperser solvent: 0.5 mL ethanol, sodium chloride: 10% m/v).

In order to study the effect of the sorbent amount on the extraction of lead, various amounts of 1,4-dichlorobenzene (0.03-0.12% m/v) were added to the sample solution and the recoveries were studied (Figure 5). The obtained results showed that by increasing the adsorbent amounts from 0.03 up to 0.10% m/v, extraction efficiency increased due to the increase in accessible sites, and then remained constant. So, a 0.10% m/v of the 1,4-dichlorobenzene was selected for all subsequent experiments. In comparison with the traditional SPE, SADSPE offers a significantly higher surface area-to-volume ratio. Therefore, satisfactory results can be achieved with fewer amounts of sorbent.

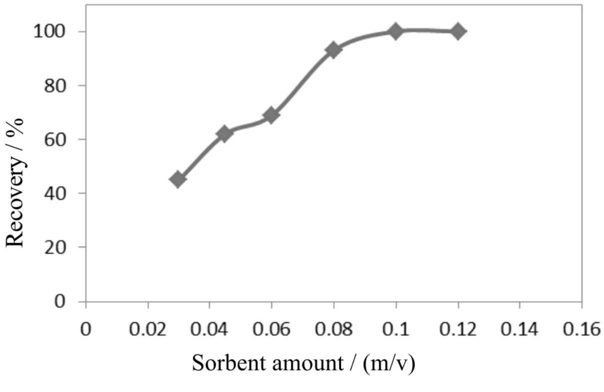

Figure 5. The effect of sorbent amount on extraction recovery of lead (sample volume: 50 mL, lead concentration: 20.0 µg L^{-1}, pH: 9, PAN concentration: 1.0×10^{-3} mol L^{-1}, sorbent: 1,4-dichlorobenzene, disperser solvent: 0.5 mL ethanol, sodium chloride: 10% m/v).

The effect of extraction time

In SADSPE, the extraction time is defined as the time interval between the injection of the mixture of disperser solvent and sorbent in the sample and the beginning of centrifugation. The extraction time was varied from 1 to 10 min during the enrichment of lead using SADSPE method. The results showed that as low as 1 min of extraction time was enough for quantitative extraction of lead. According to the obtained results, this extraction method is time-independent, due to an infinitely large surface area between sorbent and aqueous phase. Therefore, this method is very fast, which is one of the main characteristics of dispersion procedures.

The effects of centrifuge conditions

Centrifugation was applied for separating the sorbent from the aqueous solution in the proposed method. In order to attain the best phase separation, the centrifugation rate and time was optimized. The results showed that for the optimum conditions, 4000 rpm and 15 min were the optimum points.

The effect of ionic strength

The influence of ionic strength on the extraction efficiency of lead ions was examined by using aqueous solutions containing various concentrations of sodium chloride (0.0-35.0% m/v). The results showed that the extraction recovery is nearly constant in the range of 10.0-20.0% m/v. However, further increase in the concentration of sodium chloride resulted in a decrease in the extraction recovery of lead. Therefore, the concentration of 10% m/v of sodium chloride was selected as optimum.

Matrix effects

The influence of some cations and anions on the recovery of lead ions using the proposed method was investigated. A variation on the recovery higher than ± 5% was considered as interference for the preconcentration and determination of lead. The results are given in Table 1. These results indicate that this method is suitable for the determination of lead in environmental samples.

Figures of merit

Tables 2 summarizes the analytical performance characteristics of the SADSPE of lead. The results exhibited that there was an excellent linear correlation between

Table 1. Effect of interfering ions on the extraction of lead

Interfering ions	Ion/Pb^{II} ratio (m/m)	Recovery / %
K^+, Na^+, Li^+, Ca^{2+}, Mg^{2+}, Br^-, F^-, I^-, Cl^-, NO_3^-, H_2PO^{4-}, Co^{2+}, Ni^{2+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Fe^{3+}, Cd^{2+}, Cr^{3+}, HCO^{3-}, Hg^{2+}, Cu^{2+}, Cr^{VI}	10000	100.0
Ag^+, Ba^{2+}	5000	99.4

Table 2. Analytical characteristics of the method

Parameter	Analytical feature
Linear range / (μg L^{-1})	4.0-100.0
Limit of detection / (μg L^{-1}) (n = 10)	1.3
RSD[a] / %	5.0
Preconcentration factor	50

[a] Lead concentration was 20 μg L^{-1} for which RSD was obtained.

Table 3. Comparison of the presented method with other preconcentration methods for determination of lead

Method	LOD / (μg L^{-1})	RSD / %	Linear dynamic range (LDR) / (μg L^{-1})	Preconcentration factor (PF)	Sample volume / mL	Reference
SPE-FAAS	16.7	–	–	120	1200	28
SPE-FAAS	5.5	–	–	200	2000	29
SPE-FAAS	6.1	4.7	–	30	300	30
Coprecipitation-FAAS	2.0	2.45	2.5-200	200	1000	31
SADSPE-FAAS	1.3	5.0	4-100	50	50	This work

the absorbance and the concentration of lead from 4 to 100 μg L^{-1} and a good correlation coefficient of 0.9999. The precision of this method was 5.0% (relative standard deviation, RSD, n = 10) at the spiked concentration of 20 μg L^{-1}. The limit of detection (LOD), defined as $C_L = 3S_B/m$ (where C_L, S_B, and m are the limit of detection, standard deviation of the blank, and slope of the calibration graph, respectively), was 1.3 μg L^{-1}. The preconcentration factor was 50 for 50 mL sample solution.

Comparison of the present method with other preconcentration methods

The efficiency of the presented SADSPE method for lead was compared with other sample preparation techniques from the viewpoint of linearity, LOD, RSD, and preconcentration factor, which are shown in Table 3. It can be observed that the analytical performance of the present method is comparable with other reported extraction methods. The proposed method has the advantages of (*i*) being fast, (*ii*) inexpensive, (*iii*) having a simple operation, and (*iv*) being time-saving/efficient. These characteristics are of great interest for the routine laboratories interested in the trace analysis of lead.

Analysis of real samples

The method was applied for the determination of lead in water samples, including tap, river, mineral, and sea water under the optimized experimental conditions. Before the analysis of water samples, the collected water samples were filtered through a 0.45 μm Millipore membrane. The water samples were extracted using the proposed method and analyzed by FAAS. The results listed in Table 4 indicate that the lead concentration in tap and river water was 5.6 and 8.0 μg L^{-1} respectively, and mineral and sea water were free of lead contamination. The water samples were spiked at different concentration levels (20 and 50 μg L^{-1}) for evaluating the recovery. The recoveries for the spiked water samples were in the range of 95.0-101.6%. The RSDs were better than 5.3% for 3 replicate analyses. Therefore, based on these analytical results, it was found that the preconcentration technique was suitable for the determination of ultra-traces of lead in water samples.

Table 4. Determination of lead in water samples

Sample	Lead amount / (μg L^{-1})		Relative recovery / %
	Added	Found	
Tap water	0.0	5.6	–
(Drinking water system	20.0	24.6 (5.1)[a]	95.0
of Sari, Iran)	50.0	53.7 (5.0)[a]	96.2
River water	0.0	8.0	–
(Tajan river, Sari, Iran)	20.0	27.4 (5.0)[a]	97.0
	50.0	57.3 (5.2)[a]	98.6
Mineral water	0.0	n.d.	–
(Damavand mineral	20.0	19.9 (4.9)[a]	99.5
water, Iran)	50.0	48.9 (4.7)[a]	97.8
Sea water	0.0	n.d.	–
(Caspian sea water,	20.0	20.1 (5.3)[a]	100.5
Bahnamir, Iran)	50.0	50.8 (4.5)[a]	101.6

[a] RSD of three replicate experiments; n.d.: not determined.

Conclusion

A simple, fast, and economic SADSPE procedure for FAAS determination of lead has been established in the present research. The proposed method displays several good characteristics, such as fast extraction, low price, low LOD, low consumption of sorbent, high enrichment factor, and proper selectivity for lead. The developed method is applicable for the determination of ultra-trace amounts of Pb in water samples with varying water hardness and with low LOD, high accuracy (recovery > 95%), and high precision (RSD < 5.3%). The proposed method shows very good sensitivity and precision and has some good advantages over some of the previously reported preconcentration methods (Table 3).

Acknowledgments

The author thanks the research council at Payame Noor University for financial support.

References

1. Lee, J. T.; Kim, H.; Song, H.; Hong, Y. C.; Cho, Y. S.; Shin, S. Y.; Hyun, Y. J.; Kim, Y. S.; *Epidemiology* **2002**, *13*, 481.
2. Godish, T.; *Air Quality,* 4th ed.; Lewis Books: Boca Raton, 2003.
3. Miró, M.; Estela, J. M.; Cerdà, V.; *Talanta* **2004**, *63*, 201.
4. World Health Organization (WHO), *Guidelines for Drinking-Water Quality*, 4th ed.; WHO Library Cataloguing-in-Publication Data: Geneva, 2008.
5. Silva, M. M.; Arruda, M. A. Z.; Krug, F. J.; Oliveira, P. V.; Queiroz, Z. F.; Gallego, M.; Valcarcel, M.; *Anal. Chim. Acta* **1998**, *368*, 255.
6. Ferreira, S. L. C.; Queiroz, A. S.; Fernandes, M. S.; Santos, H. C.; *Spectrochim. Acta, Part B* **2002**, *57*, 1939.
7. Mattos, J. C. P.; Nunes, A. M.; Martins, A. F.; Dressler, V. L.; Flores, É. M. M.; *Spectrochim. Acta, Part B* **2005**, *60*, 687.
8. Dadfarnia, Sh.; Salmanzadeh, A. M.; Haji Shabani, A. M.; *Anal. Chim. Acta* **2008**, *623*, 163.
9. Packer, A. P.; Gine, F.; Miranda, M.; Reis, B. F.; *J. Anal. At. Spectrom.* **1997**, *12*, 563.
10. Ikeda, K.; Abe, Sh.; *Anal. Chim. Acta* **1998**, *363*, 165.
11. Naseri, M. T.; Hemmatkhah, P.; Hosseini, M. R. M.; Assadi, Y.; *Anal. Chim. Acta* **2008**, *623*, 163.
12. Kagaya, Sh.; Araki, Y.; Hirai, N.; Hasegawa, K.; *Talanta* **2005**, *67*, 90.
13. Tatyana, N. V.; Vladimir, E. K.; *Procedia Chem.* **2014**, *10*, 43.
14. Kenduzler, E.; Turker, A. R.; Yalcınkaya, O.; *Talanta* **2006**, *69,* 835.
15. Yang, B.; Gong, Q.; Zhao, L.; Sun, H.; Ren, N.; Qin, J.; Xu, J.; Yang, H.; *Desalination* **2011**, *278*, 65.
16. Burham, N.; *Desalination* **2009**, *249*, 1199.
17. Shamsipur, M.; Fattahi, N.; Sadeghi, M.; Pirsaheb, M.; *J. Iran. Chem. Soc.* **2014**, *11*, 249.
18. Fritz, J. S.; Macka, M.; *J. Chromatogr. A* **2000***, 902*, 137.
19. Anastassiades, M.; Lehotay, S. J.; Stajnbaher, D.; Schenck, F. J.; *J. AOAC Int.* **2003***, 86,* 412.
20. Alcudia-Leon, M. C.; Lucena, R.; Cardenas, S.; Valcarcel, M.; *Anal. Chem.* **2009**, *81*, 1184.
21. Garg, P.; Pardasani, D.; Mazumder, A.; Purohit, A.; Dubey, D. K.; *Anal. Bioanal. Chem.* **2011**, *399,* 955.
22. Tsai, W. H.; Huang, T. C.; Huang, J. J.; Hsue, Y. H.; Chuang, H. Y.; *J. Chromatogr. A* **2009***, 1216*, 2263.
23. Wu, Q.; Wang, C.; Liu, Z.; Wu, C.; Zeng, X.; Wen, J.; Wang, Z.; *J. Chromatogr. A* **2009**, *1216,* 5504.
24. Drozdzynski, D.; Kowalska, J.; *Anal. Bioanal. Chem.* **2009**, *394,* 2241.
25. Roman, I. P.; Chisvert, A.; Canals, A.; *J. Chromatogr. A* **2011**, *1218,* 2467.
26. Jamali, M. R.; Firouzjah, A.; Rahnama, R.; *Talanta* **2013***, 116,* 454.
27. Marczenko, Z.; *Separation and Spectrophotometric Determination of Elements*, Ellis Harwood Limited: Chichester, 1986.
28. Hashemi, O. R.; Kargar, M. R.; Raoufi, F.; Moghimi, A.; Aghabozorg, H.; Ganjali, M. R.; *Microchem. J.* **2001**, *69Ž*, 1.
29. Hajiaghababaei, L.; Badiei, A.; Ganjali, M. R.; Heydari, S.; Khaniani, Y.; Mohammadi Ziarani, Gh.; *Desalination* **2011,** *266,* 182.
30. Matoso, E.; Kubota, L. T.; Cadore, S.; *Talanta* **2003***, 60,* 1105.
31. Prasad, K.; Gopikrishna, P.; Kala, R.; Rao, T. P.; Naidu, G. R. K.; *Talanta* **2006,** *69*, 938.

Submitted: March 5, 2015