2013

Dispersive liquid–liquid microextraction and microsample injection system coupled with inductively coupled plasma-mass spectrometry for inorganic arsenic speciation in natural waters

Latif Elci
University of Massachusetts Amherst

Aydan Elci
University of Massachusetts Amherst

Tiffany Berg
University of Massachusetts Amherst

Julian Tyson
University of Massachusetts Amherst

Dispersive liquid–liquid microextraction and microsample injection system coupled with inductively coupled plasma-mass spectrometry for inorganic arsenic speciation in natural waters

Latif Elçi*†, Aydan Elçi‡, Tiffany A. Berg and Julian F. Tyson

Department of Chemistry, University of Massachusetts, 710N. Pleasant St., Amherst, MA 01003-9336, USA

(*Received 23 July 2012; final version received 3 December 2012*)

A method was developed for inorganic arsenic speciation analysis of water samples by a microsample injection system coupled with inductively coupled plasma mass spectrometry (MIS-ICP-MS) following a validated dispersive liquid–liquid microextraction (DLLME). Prior to DLLME speciation analysis, a simple robust microsample injection system was successfully adapted to ICP-MS. A sampling volume of 90 μL provided almost the same signals as the signals obtained by means of a conventional continuous nebulization sampling system for the ICP-MS instrument. After DLLME, the final solution was injected into nebulizer of ICP-MS using the microsample injection system. Under the optimized conditions, the analyte from only 5.0 mL water sample was concentrated by a factor of 48 with detection limits reaching 0.0031 $\mu g\,L^{-1}$ for arsenic. The calibration curve had a linear range of 0.0084–0.0800 $\mu g\,L^{-1}$ ($r^2 = 0.999$). The relative standard deviations (RSD, $n = 6$) were $< 4\%$. The proposed method was applied to the speciation of inorganic arsenic in various water samples with satisfactory results. The determination of arsenite and total As in river, pond, tap and bottled water samples was acheived by the standard addition method. The recoveries for spiked As(III) and As(V) from understudied water samples were in the range of 95–108%.

Keywords: arsenic; speciation; dispersive liquid–liquid microextraction; microsample injection; inductively coupled plasma mass spectrometry; water samples

1. Introduction

Arsenic compounds are widely distributed in the environment originating from natural sources as well as from anthropogenic activities. The toxicity and carcinogenicity of these compounds has stimulated many studies in the fields of analytical chemistry, environmental studies, food sciences, biology and pharmacy [1–6]. The most toxic species of arsenic are the inorganic forms, arsenite and asenate, which are usually present in sediment, soils and water samples. The persistence, fate, bioavailability, and toxicological and physiological effects of arsenic species in the environment strongly depend on the oxidation state of arsenic in the compound. The toxicity of arsenite is 10–20 times higher

*Corresponding author. Email: elci@pau.edu.tr
†Permanent address: Pamukkale University, Art and Science Faculty Chemistry Department, 20017 Denizli, Turkey
‡Permanent address: Ege University, Science Faculty, Chemistry Deparment, 35040 Bornova, Turkey

than that of arsenate and its oxide form has been shown to cause several types of cancer [7]. Humans take up arsenic predominantly through drinking water, which is considered the most significant source of arsenic contamination worldwide [8]. Drinking water regulations for maximum allowable levels of arsenic vary by country across the range of 7–50 $\mu g\,L^{-1}$, with the World Health Organization setting the permissible level for total arsenic in drinking water below 10 $\mu g\,L^{-1}$ [9]. A convenient methodology that provides the required information about the oxidation state of inorganic arsenic species in natural water samples is necessary in order to estimate the environmental impact and health risks of arsenic compounds [10,11].

In general, several element-specific and sensitive analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are available for the determination of total arsenic. To obtain speciation data, separation and preconcentration of species are required prior to measurement by a sensitive detection technique. Although combining chromatographic methods with element-specific detectors is a powerful speciation tool, non-chromatographic methodologies are still an attractive alternative. These non-chromatographic speciation analysis methods are in general more accessible, simple, inexpensive and faster for the determination of toxic forms of trace elements [12]. Recently, several methods including solvent extraction [13], solid phase extraction [14,15] and coprecipitation [16,17] have been developed to differentiate between trivalent and pentavalent oxidation states of arsenic using particular complexing agents under controlled pH conditions. Although disadvantages such as large sample volume necessity, significant chemical additives, solvent losses, large secondary wastes and high time consumption limit the use of these methods. In order to overcome these problems, some microextraction techniques including cloud point extraction (CPE), homogeneous liquid–liquid extraction (HLLE), single drop microextraction (SDME) and dispersive liquid–liquid microextraction (DLLME) have been proposed [18]. Among these techniques, DLLME offers simplicity of the operation, rapidity, low consumption of organic solvents, low sample volume and high enrichment factors [18,19]. Up to the present, the combination of DLLME with several analytical techniques including flame AAS (FAAS), elecrothermal atomization AAS (ETA-AAS), and ICP-AES have been successfully applied for the preconcentration of trace metals in water samples [18,20,21]. However, to our knowledge there is no study reporting the use of DLLME as a preconcentration and speciation step for the determination of inorganic arsenic species by ICP-MS. The necessity of large sampling volumes and the use of chlorinated organic solvents limit the application of DLLME as a speciation tool for the determination arsenic by ICP-MS [22,23]. The sample volume limitation can be compensated for by using a microsample injection system(MIS). There is no previous report of the use of MIS in the determination of any analyte by ICP-MS.

The main objectives of this paper are to develop a simple microsample injection system(MIS) adopted to ICP-MS and to study the applicability of proposed DLLME followed by MIS-ICP-MS for the quantitative speciation of inorganic arsenic in pond, river and bottled drinking water samples.

2. Experimental

2.1 *Apparatus*

A Perkin Elmer Elan 6000 plasma source mass spectrometer equipped with a quadrupole mass analyzer and an electron multiplier for detection'' was used throughout this study.

The operational conditions are summarized in Table 1 unless otherwise stated. The signal at m/z 75 was measured with the PE Elan time-resolved analysis software. In this study, a microsample injection system was used to introduce sample to the nebulizer of the ICP-MS.

A centrifuge (model TDL-40B, China) was used to accelerate the phase separation during DLLME.

To decrease the risk of contamination, no glassware was used. Plastic (polypropylene) vessels were used for preparing, storing and centrifuging the solutions. Pipette tips were also polypropylene. All plastic was rinsed with ultrapure water. HPLC vials were used to evaporate the sediment phases.

2.2 *Solutions and reagents*

High purity (18.1 MΩ cm) water was produced by a Barnstead E-pure system (Dubuque, IA) and was used throughout the experiment. Stock standard solutions of arsenic (III) and arsenic (V) (1000 mg L^{-1}, as As) were prepared by dissolving in water appropriate amounts of Na_3AsO_3(Fluka, Buchs SG, Switzerland) and $Na_3AsO_4 \cdot 12H_2O$ (99.0%, J.T. Baker, NJ, USA), respectively. Working standard solutions of analytes were prepared by successive dilution of the stock solutions in water. The chelating agent, 0.1 mg mL^{-1} ammonium pyrrolidine dithiocarbamate (APDC) solution, was prepared daily by dissolving the appropriate amount of APDC in methanol (analytical grade, Merck). All other reagents including carbon tetrachloride and chloroform as extraction solvents, and methanol as a disperser solvent were at least of analytical grade from Merck, Darmstadt.

2.3 *Sample collection and preparation*

Tap water was taken from the Tyson's laboratory at the University of Massachusetts, Amherst, MA. River water was collected from the Connecticut River at a station close to the Sunderland bridge in Sunderland, MA. Pond water was taken from Puffers pond in Amherst, MA. The tap water and river water samples were filtered through a polyether sulphone (PES) micro syringe having 0.45 μm pore size and 25 mm diameter

Table 1. ICP-MS parameters.

Parameter	Setting/Type
Nebulizer	Cross flow nebulizer
Spray chamber	Scott spray chamber
RF Power	1500 W
Plasma Ar flow	15.00 L/min
Nebulizer Ar flow	0.95 L/min
Auxiliary Ar flow	1.2 L/min
Monitored ion m/z	As 74.9216
Sweeps/reading	10
Readings/replicate	1
Replicates	10
Sample flush	35 s
Read delay	15 s

(Thermo scientific, nalgane), to remove suspended particulate. After the filtration, all the samples were immediately treated by DLLME. If the samples were not immediately treated, they were kept in a refrigerator at 4°C. Drinking water analysis was carried out without filtration after opening a bottle of store-bought water.

2.4 *Preparation of handmade microsample injection system (MIS)*

In conventional ICP-MS analysis, the sample solution is continuously introduced to the plasma. Therefore a sampling volume of at least 1.0–2.0 mL is required for each analysis. This creates a limitation for the combination of ICP-MS and a microextraction technique given the small concentrated final volume. To compensate for this, we constructed a simple microsample injection system (MIS), based on the use of a micropipette tip (capacity 20–200 μL) connected to the nebulizer of the ICP-MS instrument via the peristaltic pump tubing [24]. To achieve the best sensitivity, 90 μL of sample was injected. The signals as peak height were measured within 5 to 10 s of the injection.

2.5 *Dispersive liquid–liquid microextraction procedure*

The DLLME procedure is based on that described by Rivas *et al*. [20]. A 5.0 mL aliquot of sample solution containing 0.1 mL of 5 mol L^{-1} HNO_3 was placed in a 15 mL screwcap polypropylene test tube with a conical bottom. A standard solution of arsenite was spiked into the sample at the concentrations varying from 0.01 to 0.16 μg L^{-1}. Four hundred μL of methanolic APDC solution (disperser solvent) containing 50 μL of carbon tetrachloride (extracting solvent) was injected rapidly into the sample solution by using a 500-μL syringe (gastight, Hamilton, Nevada, USA). A cloudy solution formed in the test tube, which was shaken for a few seconds. The solution was centrifuged at 5000 rpm for 2 min and the dispersed fine droplets of carbon tetrachloride were sedimented at the bottom of the conical test tube (38 ± 2 μL, $n = 19$). The sedimented organic phase was quantitatively transferred to a 2 mL HPLC autosampler vial and allowed to evaporate at room temperature in a fumehood. Finally the residue was dissolved into 100 μL of 0.1 mol L^{-1} nitric acid. The arsenic concentration in the final solution was determined by MIS-ICP-MS. A 90 μL sample volume was injected into the MIS.

Total arsenic was determined after the reduction of arsenate to arsenite by 0.1 mL of a 0.2 mol L^{-1} sodium thiosulfate at neutral pH. The concentration of As(V) was calculated by subtracting the As(III) concentration from the total arsenic concentration.

Calibrations were performed against aqueous standards and subjected to the same the DLLME procedure. The enrichment factor was calculated as the ratio of the slopes of calibration curves. A blank was prepared following the same procedure as described above.

3. Results and discussion

3.1 *DLLME/MIS-ICP-MS combination and method development*

DLLME is a miniaturized sample pre-treatment technique with an extracting phase of 8–250 μL [25]. It requires a microsampling analysis technique to obtain a higher preconcentration factor, better sensitivity and lower detection limit. In conventional ICP-MS analysis, the sample solution is introduced to the plasma continuously so at least

1.0–2.0 mL of solution is required for each analysis. Accordingly, there is a limitation for the combination of DLLME with ICP-MS. Based on our experiences we concluded that this limitation could be compensated for by using a simple microsample injection system (MIS), which has been succesfully coupled with FAAS detection [24]. Only 10 s is needed to obtain the transient signal produced by microsample injection. The sample injection volume was optimized. For achieving the best injection volume, a fixed amount of sample solution in the range of 25–100 μL was pumped by a peristaltic pump and aspirated into the argon plasma. The injection volume effect was evaluated by MIS-ICP-MS under the conditions listed in Table 1. Transient peaks were obtained whose height increased with increasing injection volumes up to about 100 μL (Figure 1). The signals obtained with the sample injections of 90 and 100 μL are similar to the signals obtained with the continuous aspiration of sample under the same instrumental conditions. Therefore, an injection volume of 90 μL was selected. The relative standard deviations for the signals decreased from 7.5 % to 1.6 % with increasing injection volume.

Another limitation for the determination of arsenic by DLLME-ICP-MS is related to the chloride interference. In many instances, DLLME requires the use of chlorinated solvents which often have densities higher than that of water. It is well known that high concentrations of chlorine in the plasma can cause the formation of the argon chloride species $^{40}Ar^{35}Cl^{+}$ that has the same m/z as arsenic ($^{75}As^{+}$) [26]. Since As is monoisotopic, it is impossible to avoid this isobaric overlap with conventional quadrupole mass analyzers [27]. The ICP-MS used in this study was not an instrument equipped a collision/reaction cell like dynamic reaction cell (DCR) to evaluate chloride interferences. Even if the plasma could tolerate such a solvent, the chlorinated sediment phase of DLLME cannot be directly introduced into the plasma. Thus the removal of chlorine containing compounds during the sample preparation procedure is a prerequisite of the reliable analysis.

The chlorinated hydrocarbon sediment phase of DLLME, carbon tetrachloride, was evaporated to dryness. Several procedures were evaluated, such as heating in a water bath (90°C), on a hot plate (40°C) and with steeping at room temperature (18°C). The residues

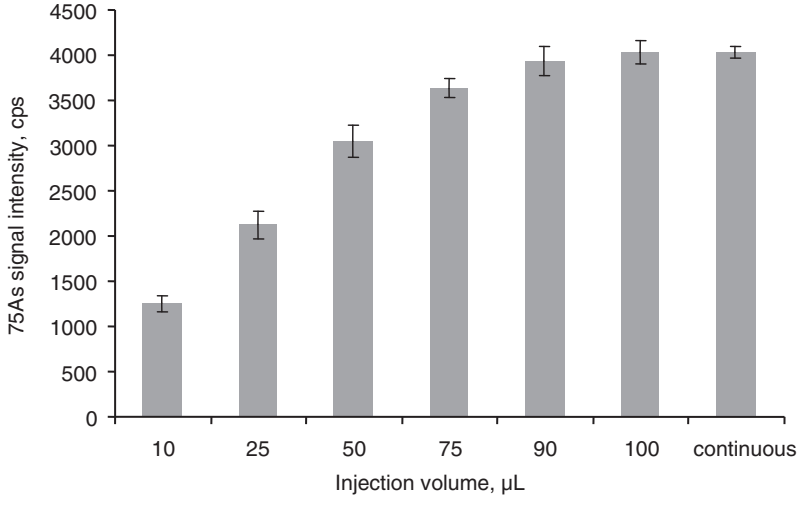

Figure 1. Effect of the injection volume on the signals of 2 μg L^{-1} arsenic (error bars are standard deviation, $n = 10$).

were diluted up to 100 μL with 0.1 mol L^{-1} HNO_3. The quantification of arsenic was performed using MIS-ICP-MS. The recovery values ($n = 4$) were 98 ± 8 % at the room temparature, 73 ± 11 % at 40°C and ≤10% at 90°C. It may be concluded that there is arsenic loss with increasing temperature owing to the volatile nature of dithiocarbamates [28,29]. Thus, the evaporation was performed in fumehood at room temperature.

3.2 *Analytical performance of combination of DLLME with microinjection-ICP-MS*

A DLLME method with MIS-ICP-MS was developed for arsenic speciation analysis of water. The DLLME procedure is based on that of Rivas *et al*. with some modifications [20]. The optimum parameters of the DLLME such as volume of the extractant and dispersant, and concentrations of the acid and the chelating agent were explained in experimental section. In this study, the effect of pH on the extraction of arsenic from water samples was controlled by using 0.1, 0.01 and 0.001 mol L^{-1} HNO_3. It was found that the recoveries are precise and quantitative (≥95%, *n*:5). The low concentration of arsenic in water samples makes it necessary to achieve high enrichment ratios to enable quantification of the analyte. Hence the effect of sample volume on the recovery of arsenic was investigated in range of 2.5 to 10 mL and the recovery values(*n*:5) for 2.5, 5.0, 7.5 and 10 mL sample were found to be 95 ± 2%, 101 ± 5%, 63 ± 4% and 19 ± 2, respectively. It was seen that quantitative recovery was obtained in solutions of 2.5–5.0 mL, therefore 5.0 mL as suitable sample volumes were taken for analysis. In addition, 5 mL sample volume allows for the detection of lower concentrations of arsenic (0.01–0.08 μg L^{-1}) than that of the previous study [20].

To check the reliability of DLLME/MIS-ICP-MS, several solutions containing different mixtures of both oxidation states of arsenic were analyzed (Table 2). The results indicate that speciation at very low concentrations is possible. A statistical study of these data showed the absence of significant differences (95% confidence level) between the amounts of analyte spiked and those found. The relative standard deviations ($n = 5$) for total arsenic and arsenite determinations were lower than 7.7% and 5.7%, respectively.

For limit of detection (LOD) and limit of quantification (LOQ), a blank solution was measured ($n = 10$) under the working conditions. A mixture of 5 mL of 0.1 mol L^{-1} HNO_3, 400 μL of methanol containing 50 μL of carbon tetrachloride and 0.00010 g APDC, chosen as the blank solution, was subjected to the DLLME. In accordance with IUPAC recommendations, the LODs were calculated as the concentration giving a response three

Table 2. Results for the determination of As (III) and As (V) in aqueous solutions.

Added, μg L^{-1}		Found, mean ± s, μg L^{-1}, $n = 3$			Recovery, %	
As(III)	As(V)	As(III) + As(V)	As(III)	As(V)*	As(III)	As(V)
0.08	0	0.081 ± 0.005	0.075 ± 0.002	BLOQ	94 ± 3	–
0.05	0.02	0.072 ± 0.004	0.053 ± 0.003	0.019	106 ± 5	95 ± 5
0.04	0.04	0.078 ± 0.006	0.041 ± 0.002	0.037	102 ± 4	92 ± 5
0.02	0.05	0.068 ± 0.003	0.019 ± 0.001	0.049	95 ± 5	98 ± 3
0	0.08	0.078 ± 0.005	–	0.078	–	98 ± 3

Note: *Calculated, BLOQ: below limit of quantitation

times the standard deviation of the blank signal, and the LOQ was calculated as the concentration giving a signal equal to ten times the standard deviation of the blank signal [30,31]. The LOD and LOQ were 0.0031 and 0.0084 $\mu g\,L^{-1}$, respectively. Without DLLME, LOD and LOQ values were calculated to be 0.0110 and 0.0595 $\mu g\,L^{-1}$, respectively. Thus, the LOD and LOQ were improved 3.6 fold and 7.1 fold, respectively.

The DLLME allowed the determination of As in the concentration range of 0.000–0.080 $\mu g\,L^{-1}$ by MIS-ICP-MS. The calibration equation was $S = 64{,}625 \times C + 2391$ ($r^2 = 0.9989$), where S is the peak height signal in counts per second and C is the arsenic concentration in $\mu g\,L^{-1}$. Without preconcentration, the linear range was 0.0595–4.000 $\mu g\,L^{-1}$ As, the calibration equation was $S = 1346 \times C + 1374$ ($r^2 = 0.9993$), where S is the steady state signal in counts per second and C is the arsenic concentration in $\mu g\,L^{-1}$. The experimental enhancement factor, calculated as the ratio of the slope of the calibration curve for the preconcentrated samples to that of the calibration curve without preconcentration [32], was 48. The theoretical preconcentration factor, calculated as the ratio of the sample volume (5.0 mL) to the final effluent volume (100 μL), was 50.

3.3 *Application*

To evaluate the applicability of the proposed method to real samples, the developed procedure was applied to the preconcentration and speciation of inorganic arsenic species in several samples including bottled water, tap water, pond water and river water samples; 5.0 mL of each of the samples was analyzed according to the proposed method. Analytical results for the original sample solutions and for the spiked sample solutions, to which known amounts of arsenite and arsenate were added, are presented in Table 3. The recoveries for different inorganic species of arsenic were 95 ± 5–108 ± 6%, (*n*:4). The satisfactory recovering spiked As(III) or As(V) during the proposed procedure revealed no arsenic redox transformation between them. The recovery deviations for each spiked As(III) and As(V) were all smaller than 5% (out of 106 ± 5% in Table 2 and 108 ± 6% in Table 3).The relative standard deviations were smaller than 9.8% (except of arsenite and the bottled water).

Table 3. Determination of inorganic arsenic species in water samples (Sample vol.:5.0 mL, Final vol.:100 μL, $n = 4$).

Samples	Added, $\mu g\,L^{-1}$		Found, mean ± standard deviation, $\mu g\,L^{-1}$			Recovery, %	
	As(III)	As(V)	Total arsenic	As(III)	As(V)*	As(III)	As(V)
Puffer's Pond Water	0	0	0.017 ± 0.001	BLOQ	0.017 ± 0.001	–	–
	0.04	0.04	0.099 ± 0.003	0.039 ± 0.003	0.060 ± 0.004	98 ± 5	108 ± 6
Connecticut	0	0	0.041 ± 0.004	0.014 ± 0.001	0.027 ± 0.003	–	–
River water	0.04	0.04	0.120 ± 0.010	0.053 ± 0.005	0.067 ± 0.004	98 ± 2	100 ± 4
Tap water	0	0	BLOQ	BLOQ	BLOQ	–	–
	0.04	0.04	0.079 ± 0.005	0.038 ± 0.003	0.041 ± 0.002	95 ± 5	102 ± 4
Bottled water	0	0	0.021 ± 0.002	0.008 ± 0.001	0.013 ± 0.001	–	–
	0.04	0.04	0.105 ± 0.004	0.049 ± 0.004	0.055 ± 0.004	102 ± 5	105 ± 4

Note: *BLOQ: below limit of quantitation.

Table 4. Comparison of the published methods with the proposed method in this work.

Extraction method	Detection method	Sample volume, mL	Enrichment factor	Detection limit, $\mu g\,L^{-1}$	Calibration range, $\mu g\,L^{-1}$	RSD, %	Refs.
DLLME	GFAAS	5	115	0.01	0.06–2	3.1	[20]
DLLME	GFAAS	5	45	0.036	0.1–10	3.1	[21]
SPE- SWCNTs	HG-DC-AFS	22.5	25.4	0.0038	0.01–2.0	4.2	[33]
SPE	ICP-MS	100	33.3	0.0045	–	2.6–1.9	[34]
SPE	ICP-OES	20	12	0.1	0.5–20	3–5	[35]
LLE	GFAAS	200	20	0.2	5–100	–	[36]
SFDME	ETAAS	20	1000	0.0092	0.1–0.7	8.6	[37]
DLLME	ICP-MS	5	48	0.0031	0–0.08	≤9.8	This work

3.4 *Comparison to other methods*

A comparison between the figures of merit for the proposed of DLLME-MIS-ICP-MS method and some of the published methods for preconcentration and speciation of inorganic arsenic are summarized in Table 4. Generally, the results obtained by the present method are similar to or better than those of the methods reported in the literature. The main advantages of our proposed method include high sensitivity with good precision, short sample preparation time, low consumption of organic solvents, and simplicity of operation. However the method is relatively high cost because of ICP-MS.

4. Conclusion

An MIS-ICP-MS procedure combined with an improved DLLME method has been developed and successfully applied for the determination of arsenite and arsenate in various real water samples. The detection capability is low enough to allow determination in several of the samples, though not in Amherst, MA tapwater. High preconcentration factor was obtained easily through this method with only 5.0 mL of sample. By using a combination of microsample injection system (MIS) and DLLME, the limit of detection and limit of quantitation values was improved by 3.6 and 7.1 fold, respectively. The recovery of the method was verified by the analysis of samples spiked with known amounts of As(III) and As(V). These results demonstrated that the matrices of the studied water samples had little effect on DLLME for determination of As(III) and As(V).

Acknowledgement

L. Elçi is grateful for the financial support of The Scientific and Technological Research Council of Turkey (TUBITAK).

References

[1] C.F. Harrington, R. Clough, L.R. Drennan-Harris, S.J. Hill, and J.F. Tyson, J. Anal. At. Spectrom. **26**, 1561 (2011).
[2] R. Clough, L.R. Drennan-Harris, C.F. Harrington, S.J. Hill, and J.F. Tyson, J. Anal. At. Spectrom. **27**, 1185 (2012).

[3] O.T. Butler, W.R.L. Cairns, J.M. Cook, and C.M. Davidson, J. Anal. At. Spectrom. **25**, 103 (2010).
[4] E.H. Evans, J.A. Day, C. Palmer, and C.M.M. Smith, J. Anal. At. Spectrom. **25**, 760 (2010).
[5] H. Al-Assaf Khalid;, J.F. Tyson, and P.C. Uden, J. Anal. At. Spectrom. **24**, 376 (2009).
[6] J.-H. Huang, G. Ilgen, and P. Fecher, J. Anal. At. Spectrom. **25**, 800 (2010).
[7] World Health Organization (WHO), Arsenic and arsenic compounds, Environmental Health Criteria **224**, 521 (2001).
[8] J.T. Hindmarsh, J. Trace Elem. Exp. Med. **13**, 165 (2000).
[9] World Health Organization (WHO), Drinking Water Guidelines and Standard, 1996.
[10] Z. Gong, X. Lu, M. Ma, C. Watt, and X.C. Le, Talanta **58**, 77 (2002).
[11] A.K. Das, M. de la Guardia, and M.L. Cervera, Talanta **55**, 1 (2001).
[12] A. Gonzalvez, M.L. Cervera, S. Armenta, and M. de la Guardia, Anal. Chim. Acta. **636**, 129 (2009).
[13] M. Huang, Y. Wang, and P.C. Ho, J. Pharmaceut. Biomed. Anal. **48**, 1381 (2008).
[14] I. López-García, R.E. Rivas, and M. Hernández-Córdoba, Talanta **86**, 52 (2011).
[15] O.D. Uluozlu, M. Tuzen, D. Mendil, and M. Soylak, Food Chem.Toxicol. **48**, 1393 (2010).
[16] Q. Zhang, H. Minami, S. Inoue, and I. Atsuya, Anal. Chim. Acta **508**, 99 (2004).
[17] L. Elci, U. Divrikli, and M. Soylak, Int. J. Environ. Anal. Chem. **88**, 711 (2008).
[18] F. Pena-Pereira, I. Lavilla, and C. Bendicho, Spectrochim. Acta Part B **64**, 1 (2009).
[19] M. Rezaee, Y. Assadi, M.R.M. Hosseini, E. Aghaee, F. Ahmadi, and S. Berijani, J. Chromatogr. A **1116**, 1 (2006).
[20] R.E. Rivas, I. López-García, and M. Hernández-Córdoba, Spectrochim. Acta Part B **64**, 329 (2009).
[21] P. Liang, L. Peng, and P. Yan, Microchim. Acta **166**, 47 (2009).
[22] Z. Xiao-Huan, W.U. Qiu-Hua, Z. Mei-Yue, X.I. Guo-Hong, and W. Zhi, Chin. J. Anal. Chem. **37**, 161 (2009).
[23] I. Komorowicz and D. Barałkiewicz, Talanta **84**, 247 (2011).
[24] J. Ahmed Baig, A. Hol, A. Akdogan, A. Arslan Kartal, U. Divrikli, T. Gul Kazi, and L. Elci, J. Anal. At. Spectrom. **27**, 1509 (2012).
[25] M. Rezaee, Y. Yamini, and M. Faraji, J. Chromatogr. A **1217**, 2342 (2010).
[26] D.Q. Hung, O. Nekrassova, and R.G. Compton, Talanta **64**, 269 (2004).
[27] M. Leermakers, W. Baeyens, M. De Gieter, B. Smedts, C. Meert, H.C. De Bisschop, and R. Morabito, Ph. Quevauviller, Trends Anal. Chem **25**, 1 (2006).
[28] P.C. Juden, J. Chromatogr. A **313**, 3 (1984).
[29] A.J. Laghari, M.Y. Khuhawar, and L.A. Zardari, J. Sep. Sci. **30**, 2727 (2007).
[30] Analytical Methods Committee, Analyst **112**, 199 (1987).
[31] IUPAC, Analytical Chemistry Division, Spectrochim. Acta Part B **33**, 242 (1978).
[32] S. Sönmez, U. Divrikli, and L. Elci, Talanta **82**, 939 (2010).
[33] H. Wu, X. Wang, B. Liu, Y. Liu, S. Li, J. Lu, J. Tian, W. Zhao, and Z. Yang, Spectrochim. Acta Part B **66**, 74 (2011).
[34] S.Z. Chen, X.L. Zhan, D.B. Lu, C. Liu, and L. Zhu, Anal. Chim. Acta **634**, 192 (2009).
[35] K. Jitmanee, M. Oshima, and S. Motomizu, Talanta **66**, 529 (2005).
[36] S. Sounderajan, A.C. Udas, and B. Venkataramani, J. Hazard. Mater. **149**, 238 (2007).
[37] M. Ghambarian, M.R. Khalili-Zanjani, Y. Yamini, A. Esrafili, and N. Yazdanfar, Talanta **81**, 197 (2010).