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Preconcentration and determination of ultra trace amounts of arsenic(III) and arsenic(V) in tap water and total arsenic in biological samples by cloud point extraction and electrothermal atomic absorption spectrometry

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Abstract

A new approach for developing a cloud point extraction-electrothermal atomic absorption spectrometry has been described and used for determination of arsenic. The method is based on phase separation phenomenon of non-ionic surfactants in aqueous solutions. After reaction of As(V) with molybdate towards a yellow heteropoly acid complex in sulfuric acid medium and increasing the temperature to 55 °C, analytes are quantitatively extracted to the non-ionic surfactant-rich phase (Triton X-114) after centrifugation.

To decrease the viscosity of the extract and to allow its pipetting by the autosampler, 100 μl methanol was added to the surfactant-rich phase. An amount of 20 μl of this solution plus 10 μl of 0.1% *m/v* $Pd(NO_3)_2$ were injected into the graphite tube and the analyte determined by electrothermal atomic absorption spectrometry.

Total inorganic arsenic(III, V) was extracted similarly after oxidation of As(III) to As(V) with $KMnO_4$. As(III) was calculated by difference. After optimization of the extraction condition and the instrumental parameters, a detection limit ($3\sigma_B$) of 0.01 μg l^{-1} with enrichment factor of 52.5 was achieved for only 10 ml of sample. The analytical curve was linear in the concentration range of 0.02–0.35 μg l^{-1}. Relative standard deviations were lower than 5%. The method was successfully applied to the determination of As(III) and As(V) in tap water and total arsenic in biological samples (hair and nail).

Keywords: Cloud point extraction; Electrothermal atomic absorption spectrometry; Biological samples; Arsenic

1. Introduction

Arsenic is the twentieth most abundant element in the earth's crust. Arsenic contamination in natural water is a world-wide problem and has become a challenge for the world scientists. The presence of arsenic in natural water is related to the process of leaching from the arsenic containing source rocks and sediments [1]. Arsenic is widely known as a toxic element and is naturally present in all environmental compartments in various forms, depending on the nature of the sample.

The toxicological behavior and biochemical activity of arsenic depends on its chemical form [2,3]. Arsenic compounds with a +3 oxidation state are toxic more than analogous compounds with a +5 oxidation state, for example, arsenite versus arsenate, monomethylarsonous acid (MMA^{III}) versus monomethylarsonic acid (MMA^{V}), dimethylarsinous acid (DMA^{III}) versus dimethylarsinic acid (DMA^{V}) [4]. As(V) can replace phosphate in several biochemical reactions, whereas As(III) may react with critical thiols in proteins and inhibit their activity [5].

Long term exposure to arsenic contaminated water may lead to various diseases such as conjunctivitis, hyperkeratosis, hyperpigmentation, cardiovascular diseases, disturbance in the peripheral vascular and nervous systems, skin

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Table 1
Values reported of total arsenic in hair and nail[a] ($\mu g\,g^{-1}$) and arsenite and arsenate in drinking water (ng)

	Arsenite	Arsenate	Total arsenic	Ref.
Hair	–	–	0.17–14.39	[6]
Nail	–	–	0.74–36.63	[6]
Drinking water	0.1–0.6	1–5	–	[7]

[a] Collected from arsenic affected areas.

cancer, gangrene, leucomelonisis, non-pitting swelling, hepatomegaly and splenomegaly.

Since different species of the same element may have different chemical and toxicological properties, determination of the total concentration of an element may not provide information about the actual physico-chemical forms of the element, which is required for understanding its toxicity, biotransformation, etc. Thus, in order to obtain information on toxicity and biotransformation of elements in aquatic systems, quantification of individual species of an element is needed. The levels of inorganic arsenic species in water and total arsenic in nail and hair samples reported by some literature is given in Table 1.

Recently, many kinds of conventional analytical techniques, such as electrothermal vaporization inductively coupled plasma mass spectrometry [8], electrothermal atomic absorption spectroscopy [9–11], hydride generation–atomic absorption spectroscopy [12] and hydride generation–atomic fluorescence spectrometry [13,14] have been used for the determination of the low concentration levels of arsenic.

As a result of the lack of selectivity and insufficient sensitivity of some spectrometric detection techniques, analytical methods of the speciation of arsenic often involve a combination of chromatographic separation and preconcentration techniques with the sensitive spectrometric detection [15,16].

Several hyphenated analytical methods, such as ion chromatography coupled to hydride generation–inductively coupled plasma atomic emission spectrometry [17,18], ion chromatography [19,20] or high performance liquid chromatography [21] coupled to inductively coupled plasma mass spectrometry, are also available for the determination of arsenic(III) and arsenic(V) in natural waters.

Separations and preconcentrations based on cloud point extraction (CPE) are becoming an important and practical application of the use of surfactants in analytical chemistry [22]. The technique is based on the property of most nonionic surfactants in aqueous solutions to form micelles and become turbid when heated to the cloud point temperature. Above the cloud point temperature the micellar solution separates in a surfactant-rich phase of a small volume and in a diluted aqueous phase, in which the surfactant concentration is close to the critical micellar concentration (cmc). Any analyte solubilized in the hydrophobic core of the micelles, will separate and become concentrated in the small volume of the surfactant-rich phase.

The small volume of the surfactant-rich phase permits the design of extraction schemes that are simple, cheap, highly efficient, speedy and of lower toxicity to the environment than those extractions that use organic solvents. Another important aspect of CPE technique is the ability to perform metal speciation [23,24].

When cloud point extraction was used for the extraction of metal chelates, flame atomic absorption spectrometry (FAAS) was by far, the most frequently used technique for analyte detection [25–31]. Although FAAS has certain advantages, especially concerning the time required for the final determination, techniques of higher sensitivity would improve considerably detection limits for several analyte. In this sense, electrothermal atomic absorption spectrometry (ETAAS) is an efficient alternative, particularly because the organic matrix, consisting of the surfactant and residual organic substances from the digested material, can be eliminated at least in part during the gradual increase in temperature prior to the atomization of the analyte.

To reduce mentioned matrix interferences and to increase accuracy, the use of a chemical modifier has become indispensable for the stabilization of volatile elements during the pretreatment step. The main purpose of using a modifier or a modifier mixture in ETAAS is to stabilize relatively volatile elements so that higher permissible pyrolysis temperatures can be used to efficiently volatilize the matrix components in a sample prior to atomization of the analyte [32–36]. By using higher permissible pyrolysis temperatures, less interference effects on the analyte are encountered in the atomization step [32]. In this work, cloud point extraction, using molybdate as a complexing agent and the non-ionic surfactant Triton X-114, was applied for determination of As(III) and As(V) in tap water and total arsenic in biological samples (hair and nail) by ETAAS in the presence $Pd(NO_3)_2$ as modifier after cloud point extraction.

2. Experimental

2.1. Apparatus

The experiments were performed using a Shimadzu atomic absorption spectrometer (AA 6800G), equipped with a graphite furnace atomizer GFA-6500 and an autosampler ASC-6100. Deuterium-arc background correction was employed to correct non-specific absorbance. All measurements were performed using integrated absorbance (peak area).

An arsenic hollow cathode lamp (Hamamatsu Photonic Co., Ltd. L233 Series) and pyrolytic graphite coated graphite tubes (Shimadzu part no. 206-69984-02) were used. The sample injection volume was 20 μL in all experiments. The instrumental parameters and temperature program for the graphite atomizer are listed in Table 2.

Argon 99.995% was purchased from Roham Gas Co. (Tehran, Iran) and was used as protected and purge gas. A thermostated bath (fision-Germany, model HAKKE-N_3) maintained at the desired temperature, was used for cloud

Table 2
Instrumental parameters for arsenic determination[a]

Spectrometer parameter				
Wavelength (nm)				193.7
Slit width (nm)				2
Lamp current (mA)				12
Integration time (s)				4
Stage	Temperature (°C)	Time (s)		Argon gas flow (ml min^{-1})
		Ramp	Hold	
Graphite atomizer[b]				
Drying	60	5	20	250
Drying	90	5	10	250
Drying	120	10	10	250
Pyrolysis I	1400	10	15	500
Atomization	2400	–	4	0
Cleaning	2600	–	2	500

[a] Absorbance measurement was by peak area.
[b] Pd $(NO_3)_2$ as a modifier was used.

point preconcentration experiments and phase separation was performed, using a centrifuge (Germany, model BHG).

2.2. Reagents

All reagents were of analytical grade and all solutions were prepared in deionized doubly distilled water. The non-ionic surfactant Triton X-114 was obtained from Sigma (St. Louis, MO, USA) and was used without further purification. The arsenite stock standard solution (1000 mg l^{-1}) was prepared by dissolving 0.1320 g As_2O_3 (Merck) in 2.0 ml of 1.0 mol l^{-1} NaOH. About 5 ml of 0.5 mol l^{-1} HCl was added to this solution and was diluted to 100 ml. Arsenate stock standard solution (1000 mg l^{-1}) was prepared by diluting the Merck Titrasol ampoule. Working standard solutions were obtained by appropriate dilution of the stock standard solution. Ammonium heptamolybdate tetrahydrate was obtained from Mallinckrodt (St. Louis, MO) and working solution of 0.02 mol l^{-1} was prepared in 1.5 mol l^{-1} H_2SO_4. Sulfuric acid was prepared from Merck.

A 0.1% *m*/*v* chemical modifier solution was prepared by diluting palladium stock solution (1% *m*/*v*, Merck). The pipettes and vessels used for trace analysis were kept in a sulfochromic acid mixture (saturated $K_2Cr_2O_7$ in concentrated H_2SO_4) for at least 1 h and were subsequently rinsed four times with deionized doubly distilled water before being used.

2.3. Cloud point preconcentration procedure

For the cloud point preconcentration, aliquots of 10 ml sample or standard solution containing As(V), Triton X-114 (0.06% *m*/*v*), molybdate (5×10^{-6} mol l^{-1}) and sulfuric acid (pH = 2), were kept in a thermostated bath at 55 °C for 5 min. Separation of the aqueous and surfactant-rich phases was accomplished by centrifugation for 10 min at 3500 rpm. After cooling in an ice–NaCl mixture (5 min), the surfactant-rich phase became viscous. Then, the aqueous phases could be separated by inverting the tubes. Later, in order to decrease the viscosity and facilitate sample handling, 100 μl of methanol was added to the surfactant-rich phase and 20 μl of the final solution plus 10 μl of Pd $(NO_3)_2$ (0.1% *m*/*v*) as a chemical modifier was injected to the graphite furnace by autosampler.

Total inorganic arsenic(III, V) was measured after oxidation with $KMnO_4$ [37].

2.4. Preparation of real samples

2.4.1. Water samples

Water samples were filtered using a 0.45 μm pore size membrane filter to remove suspended particulate matter, adjusted to approximately pH 2 by adding concentrated H_2SO_4 and stored in a refrigerator in the dark. Aliquots of water (5 ml) samples were subjected to the cloud point extraction methodology as described above.

2.4.2. Human hair samples

Hair samples were collected from the vertex of the scalp by cutting from the scalp region, and the hair length varied between 3 and 5 cm. Prior to analysis, all hair samples were cut into 2 cm with a stainless steel scissors. The washing procedure carried out, was that proposed by International Atomic Energy Agency (IAEA) [38], and thus, hair samples were first washed with triply distilled water and then washed three times with acetone and finally, they were again washed with triply distilled water (three times). The samples were then oven-dried at 100 °C. Approximately 0.2 g of dried sample was placed in a 50 ml beaker and 12 ml concentrated HNO_3 and 2 ml concentrated $HClO_4$ were added. The contents in the beaker were heated on a hot plate (initially at 100 °C for 45 min and then at 150 °C for 45 min). After dissolving, the solution was cooled to 70 °C and 5 ml of 30% H_2O_2 was added.

The mixture was heated to dryness at 200 °C to yield a white residue. Approximately 10 ml of 1 mol l^{-1} H_2SO_4 was added to the beaker and the contents were heated at 100 °C for 1 h and diluted in a 50 ml volumetric flask. Aliquots (3 ml) of the obtained clear solution were analyzed according to the prescribed procedure.

2.4.3. Nail samples

Finger nail was clipped from all fingers' hand using stainless-steel scissors. Preparation of nail sample was same as that hair sample. In case of finger nail, 0.2 g of sample was used.

3. Results and discussion

3.1. Optimization of the furnace conditions

In these experiments we used Pd (10 μg) as a modifier. When Pd was not added, arsenic loses for pyrolysis tem-

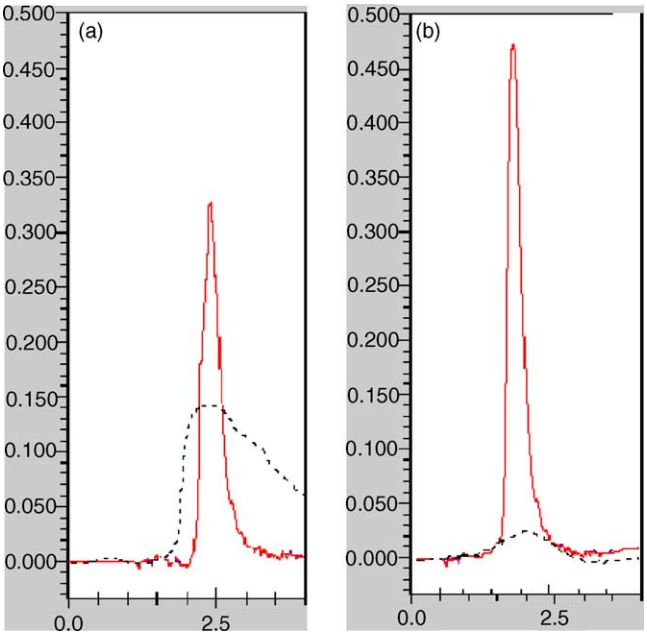

Fig. 1. Peak profiles for arsenate (—) and background (- - -) after cloud point extraction (a) without modifier and (b) using 10 μg of Pd as a modifier. Conditions: 0.3 ng ml^{-1} arsenate, 1 × 10^{-3} mol l^{-1} molybdate, 0.06% (*m*/*v*) Triton X-114, pH 2.

peratures higher than 600 °C. High background signals were observed due to presence of surfactant in the surfactant-rich phase (Fig. 1a). Addition of 0.1% (*m*/*v*) $Pd(NO_3)_2$ solution, leads to reduce of background (Fig. 1b) and extension of the pyrolysis temperature up to 1400 °C without losses of arsenic. The influence of the palladium on the background level and atomic signal was of utmost relevance.

The atomic signals enhanced by ∼42% when Pd injected volume varied from 5 to 10 μl. For volumes larger than 10 μl, the signals were not improved. The volume of modifier was then selected as 10 μl.

3.2. Effect of pH

The separation of metal ions by cloud point method involves the prior formation of a complex with sufficient

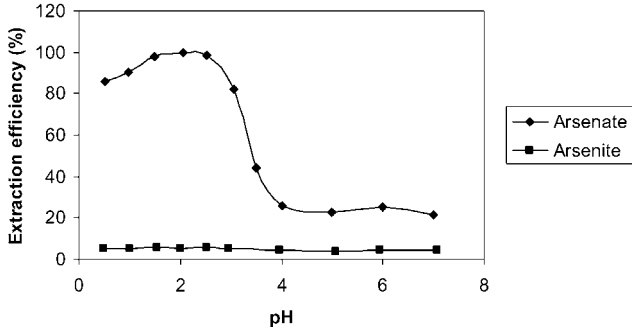

Fig. 2. Effect of pH on the extraction efficiency of arsenite (0.3 ng ml^{-1}) and arsenate (0.3 ng ml^{-1}). Conditions: 1 × 10^{-3} mol l^{-1} molybdate, 0.06% (*m*/*v*) Triton X-114, pH 2.

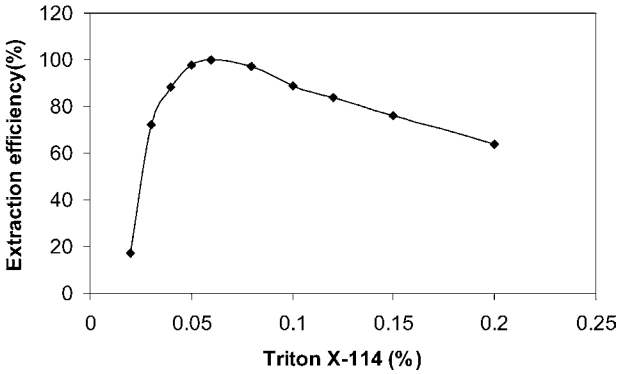

Fig. 3. Extraction efficiency of the arsenate as a function of Triton X-114 concentration. Conditions: 0.3 ng ml^{-1} arsenate, 1 × 10^{-3} mol l^{-1} molybdate, pH 2.

hydrophobicity to be extracted in to the small volume of surfactant-rich phase, thus obtaining the desired preconcentration. Extraction efficiency depends on the pH at which complex formation occurs. The effect of the pH on the cloud point extraction of As(III), As(V) was investigated. CPE was performed in different pH solutions from 0.5 to 7.0.

As(V) was effectively extracted and the maximum and constant extraction efficiency was obtained in the pH range 1.5–2.5, as shown in Fig. 2. As(III) could not be extracted in the pH range studied. Therefore, pH 2 was chosen for subsequent experiments.

3.3. Effect of molybdate

The extraction efficiency as a function of the molybdate concentration is studied. For this study, 10 ml of a solution containing 0.3 μg l^{-1} arsenate in 0.06% *m*/*v* Triton X-114 with various amounts of molybdate were subjected to the cloud point extraction process. Approximately, ∼100% extraction of arsenate ion is achieved above a molybdate concentration of 5 × 10^{-4} mol l^{-1}. A concentration of 1 × 10^{-3} mol l^{-1} molybdate was chosen for subsequent experiments.

3.4. Effect of Triton X-114 concentration

A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio ($V_{org}/V_{aqueous}$), thus improving its concentration factor. Triton X-114 was chosen for the surfactant-rich phase due to its low cloud point temperature and high density of the surfactant-rich phase, which facilitates phase separation by centrifugation.

Fig. 3 highlights the effect of the surfactant concentration in the range of 0.02–0.20% *m*/*v* on the extraction efficiency. Triton X-114 was found to quantitatively extract the hetropolymolybdoarsenate from aqueous sample at surfactant concentrations above 0.06% *m*/*v*, using a single step extraction procedure.

Table 3
Analytical characteristics of the method

Element condition	Concentration range (ng ml^{-1})	EF[a]	r	R.S.D.%[b] (n = 5)	LOD[c] (ng ml^{-1})
As without preconcentration	2–25	–	0.9997	4.3 (10)	1.08
As with preconcentration	0.02–0.35	52.5	0.9991	4.9 (0.1)	0.01

[a] Calculated as the ratio of slope of preconcentrated samples to that obtained without preconcentration.
[b] Values in parentheses are the As concentrations (ng ml^{-1}) for which the R.S.D. was obtained.
[c] Determined as three times the standard deviation of the blank signal.

Fig. 3 also shows a considerable decrease in the integrated absorbance signal with increasing surfactant concentration. An increase in the surfactant amounts also increases the volume of the surfactant-rich phase that is obtained after centrifugation of the analyte. Extract is therefore more diluted when higher amounts of surfactants are used, resulting in a loss of sensitivity. Thus, a concentration of 0.06% *m*/*v* Triton X-114 was chosen for subsequent experiments.

3.5. Effect of equilibration temperature and time

The equilibration temperature above the cloud point temperature and the incubation time were also optimized. It was desirable to employ the shortest incubation time and the lowest possible equilibration temperature, which compromise completion of the reaction and efficient separation of the phases. Excellent extraction efficiency achieved for equilibration temperature from 50 to 70 °C. Higher temperatures lead to the decomposition of hetropolymolybdoarsenate and the reduction of extraction efficiency. A temperature of 55 °C was used in all experiments. The dependence of extraction efficiency upon incubation time was studied in the range of 5–20 min. An incubation time of 5 min was optimal for quantitative extraction.

3.6. Selectivity of the method

The interference effect of a wide variety of anions and cations, usually present in natural- and wastewater was investigated by spiking appropriate amounts of the relative ions to a reference As(V) solution of 0.1 ng ml^{-1}. No adverse effects were observed at 1000 times higher than As(V) from the various cations examined (Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Cd^{2+}, Pb^{2+}).

The anions investigated PO_4^{3-}, SiO_4^{4-}, CrO_4^{4-}, and VO_3^- did not possess any adverse effects on the analytical signal of the target species at concentration levels studied (500 times higher than As(V)).

Above this concentration levels, interferences were reduced or eliminated considerably in the presence of excess molybdate.

3.7. Figure of merit

The figures of merit can be found in Table 3. A Calibration curve was constructed by preconcentrating 10 ml of sample standard solutions with Triton X-114. Under the optimum experimental condition, the calibration curve for As(V) was linear from 0.02 to 0.35 μg l^{-1}. The enhancement factor of about 52 was obtained as the ratio of slope of preconcentrated samples (10 ml) to that obtained without preconcentration. The limit of detection (LOD) was calculated as the ratio of three times of the standard deviation of the blank signals and the slope of the calibration curve after preconcentration. Very low detection limit was achieved for As(V), particularly when compared with similar extraction methods using FAAS as the detection technique; the high sensitivity presented by ETAAS is a decisive factor when analytes have to determine at very low concentration.

Correlation coefficient higher than 0.999 was obtained and only small deviations between sequential determinations were found. The results obtained from the spiking

Table 4
Determination of arsenic in real samples (results of recoveries of spiked samples)

Sample	Spiked (ng ml^{-1})		Found (ng ml^{-1})[a]		Extraction efficiency (%)	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
Tap water[b]	–	–	0.052 ± 0.01	0.212 ± 0.04	–	–
	0.1	0.1	0.149 ± 0.02	0.310 ± 0.05	97	98
	Spiked (μg g^{-1})		Found (μg g^{-1})		Total arsenic	
Nail	–		0.210 ± 0.02		–	
	0.125		0.337 ± 0.01		101.6	
Hair[c]	–		0.121 ± 0.02		–	
	0.125		0.242 ± 0.04		96.8	

[a] Mean of three experiments ± standard deviation.
[b] From drinking water system of Arak, Iran.
[c] Medium dark hair (man, 23 years old).

experiments are shown in Table 4.The extraction efficiencies ranged from 101 to 105% for the spiking experiments.

3.8. Analysis of real samples

In order to validate the method for accuracy and precision, a certified reference material GBW 0706 (Chinese human hair) was analyzed. Certified and obtained values were 0.280 ± 0.04 and 0.271 ± 0.05 $\mu g\, g^{-1}$ (n = 5) respectively and excellent extraction efficiency was obtained (96.8%).

Various water, hair and nail samples and spiked samples were also analyzed (Table 4) in all cases the spike extraction efficiencies were excellent, showing no matrix interferences.

4. Conclusions

We have extended the use of cloud point extraction to the preconcentration of As(V) as a prior step for determination at μg per l level in water, and μg per g level in hair and nail samples by ETAAS. The separation occurred efficiently, resulting in good enrichment factors and low LOD. The use of chemical modifier in the organic extract, simplifies the whole procedure, makes the use of higher pyrolysis temperatures possible, improves the signal shape and improves better sensitivities.

The methodology offers a simple, rapid, sensitive, inexpensive and non-polluting alternative to other separation/preconcentration techniques. Further, in comparisons with solvent extraction methods, it is much safer, since only a small amount of surfactants, which has a low toxicity, is used.

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References

[1] F.N. Robertson, Environ. Geochem. Health 11 (1989) 171.
[2] J.R. Cannon, J.B. Saunders, R.F. Toia, Sci. Total Environ. 31 (1983) 181.
[3] K.A. Franceconi, J.S. Edmonds, Croatica Chem. Acta 71 (1998) 343.
[4] H.V. Aposhian, R.A. Zakharyan, M.J. Kopplin, M.L. Wollenberg, Toxicol. Appl. Pharmacol. 193 (2003) 1.
[5] J.A. Katsoyiannis, A.I. Zouboulis, Water Res. 38 (2004) 17.
[6] G. Samanta, R. Sharma, T. Roychowdhury, D. Chakraborti, Sci. Total Environ. 326 (2004) 33.
[7] L.S. Milstein, A. Essader, E.D. Pellizzari, R.A. Fernando, O. Akinbo, Environ. Int. 28 (2002) 277.
[8] L.F. Dias, T.D. Saint'Pierre, S.M. Maia, M.A. Mesquita da Silva, V.L.A. Frescura, B. Welz, A.J. Curtius, Spectrochim. Acta 57 (2002) 2003.
[9] N. Campillo, P. Viñas, I. López-García, M. Hernández-Córdoba, Analyst 125 (2000) 313.
[10] D. Pozebon, V.L. Dressler, J.A. Gomes Note, A.J. curtius, Talanta 45 (1998) 1167.
[11] K. Anezaki, I. Nukatuska, K. Ohzeki, Anal. Sci. 15 (1999) 829.
[12] Y. Yano, T. Miyama, A. Ito, T. Yasuda, Anal. Sci. 16 (2000) 939.
[13] P. Cava-Montesinos, M.L. Cervera, A. Pastor, M. de la Guardia, Talanta 60 (2003) 787.
[14] N.V. Semenova, L.O. Lead, R. Forteza, V. Cerda, Anal. Chim. Acta 455 (2002) 277.
[15] M. Burguera, J.L. Burguera, Talanta 44 (1997) 1581.
[16] J. Szpunar, Analyst (Cambridge, UK) 15 (2000) 963.
[17] R.T. Gettar, R.N. Garavaglia, E.A. Gautier, D.A. Batistoni, J. Chromatogr. A 884 (2000) 211.
[18] T. Taniguchi, H. Tao, A. Miyazaki, J. Anal. Atom. Spectr. 14 (1999) 651.
[19] E. Vassileva, A. Becker, J.A.C. Broekaert, Anal. Chim. Acta 441 (2001) 135.
[20] J. Mattusch, R. Wennrich, Anal. Chem. 70 (1998) 3649.
[21] K. Wrobel, K. Wrobel, B. Parker, S.S. Kannamkumarath, J.A. Caruso, Talanta 58 (2002) 899.
[22] A. Sanz-Medel, M.R. Fernandez de la Conzalez, M.L. Fernandez-Sanchez, Spectrochim. Acta Part B 54 (1999) 251.
[23] F. Shemirani, S.D. Abkenar, A.A. Mirroshandel, M.S. Niasari, R.R. Kozania, Anal. Sci. 19 (2003) 1453.
[24] D.L. Giokas, E.K. Paleologos, M.I. Karayannis, Anal. Bioanal. Chem. 373 (2002) 237.
[25] C.C. Nascentes, M.A.Z. Arruda, Talanta 61 (2003) 759.
[26] J.L. Manzoori, A. Bavili-Tabrizi, Microchim. Acta 142 (2003) 130.
[27] J.L. Manzoori, G. Karim-Nezhad, Anal. Chim. Acta 484 (2003) 155.
[28] J.L. Manzoori, G. Karim-Nezhad, Anal. Sci. 19 (2003) 579.
[29] J.L. Manzoori, A. Bavili-Tabrizi, Microchim. Acta 141 (2003) 201.
[30] S.A. Kulichenko, V.O. Doroschuk, S.O. Lelyushok, Talanta 59 (2003) 767.
[31] J.L. Manzoori, A. Bavili-Tabrizi, Microchem. J. 72 (2002) 1.
[32] B. He, Z-M. Ni, J. Anal. Atom. Spectr. 11 (1996) 165.
[33] Y. Wei-Ming, N. Zhe-Ming, Spectrochim. Acta Part B 52 (1997) 241.
[34] O. Acar, A.R. Türker, Z. Kilic, Fresenius J. Anal. Chem. 357 (1997) 656.
[35] X–Q. Shan, B. Wen, J. Anal. Atom. Spectr. 10 (1995) 791.
[36] S. Imai, N. Hasegawe, Y. Nishiyama, Y. Hayashi, K. Satio, J. Anal. Atom. Spectr. 11 (1996) 601.
[37] V. Lenoble, V. Deluchat, B. Serpaud, J.-C. Bollinger, Talanta 61 (2003) 267.
[38] S.Y. Rjabuchin, Report IAEA/RL/50, Vienna, 1978.