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Talanta 67 (2005) 942–946

Talanta

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Cloud point extraction for the determination of As(III) in water samples by electrothermal atomic absorption spectrometry

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Received 17 December 2004; received in revised form 10 April 2005; accepted 11 April 2005

Abstract

Cloud point extraction was applied as a preconcentration step for electrothermal atomic absorption spectrometry (ETAAS) determination of As(III) in aqueous solutions. After complexation with ammonium pyrrolidinedithiocarbamate, the analyte was quantitatively extracted to the surfactant-rich phase in the non-ionic surfactant octylphenoxypolyethoxyethanol (Triton X-114) after centrifugation. 0.1 mol L^{-1} HNO_3 in methanol was added to the surfactant-rich phase before ETAAS determination. The precision (R.S.D.) for 11 replicate determinations of 5.0 $\mu g\,L^{-1}$ of As(III) was 3.0%. The concentration factor, which is defined as the concentration ratio of the analyte in the final diluted surfactant-rich extract ready for ETAAS determination and in the initial solution, was 36 for As(III). The linear concentration range was from 0.1 to 20 $\mu g\,L^{-1}$. The developed method was applied to the determination of As(III) in lake water and river water.

Keywords: Cloud point extraction; Preconcentration and complexation; Electrothermal atomic absorption spectrometry; Arsenite

1. Introduction

Micelles and other organized amphiphilic assembles are increasingly utilized in analytical chemistry. Their unique microheterogeneous structures capable of selective interaction with different solute molecules can strongly modify solubility, chemical equilibria, kinetics and the spectroscopic properties of analytes and reagents. Separation procedures based on the peculiar properties of aqueous non-ionic and zwitterionic surfactant solution have also been proposed as an alternative to the use of traditional organic solvents. The first use of the cloud point extraction (CPE) technique was pioneered by Goto et al. [1]. The analytical potential of the CPE has been discussed by several authors [2–7]. Aqueous solutions of almost all non-ionic surfactants become turbid when heated to a temperature known as the cloud point. Above this temperature, the isotropic micellar solution separates into two transparent liquid phases: a surfactant-rich phase of very small volume, composed mostly of the surfactant plus a small amount of water, and an aqueous phase, in equilibrium with the former, which contains a surfactant concentration close to its critical micellar concentration. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient, and of lower toxicity to the environment than those extractions that use organic solvents. The CPE phenomenon has been used for the extraction and preconcentration of organic compounds [8,9] and metal cations [10,11] after the formation of sparingly water-soluble complexes. CPE has been shown to be an effective sample preconcentration technique for improving sensitivity and selectivity prior to atomic spectrometry [10,11], high-performance liquid chromatography (HPLC) [12–14], flow injection analysis (FIA) [15] and capillary electrophoresis (CE) [16,17].

Arsenic exists in nature in the oxidation states +V (arsenate), +III (arsenite), 0 (arsenic) and −III (arsine). In the aqueous environment, inorganic arsenic appears commonly

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0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.04.016

in the oxidation states +V and +III as arsenous acid (As(III)), arsenic acid (As(V)), and their salts. The toxicity of arsenic depends on its binding form. Organic arsenic compounds are less toxic than inorganic arsenic compounds. Arsenic is carcinogenic and may cause lung cancer, bladder cancer, liver cancer, renal cancer, and skin cancer. There is a continuing interesting challenge in the trace determination of arsenic because of its high toxicity and ability to bioaccumulate in many organisms and its abundance in all environmental compartments [18–22]. The analytical methods that have been used for the determination of arsenic in different materials (matrices) are colorimetric methods, atomic (mass) spectrometry, electrochemical methods, chromatographic methods, neutron activation analysis and X-ray fluorescence spectrometry [19–27]. Although atomic absorption spectrometry (AAS) is a powerful analytical tool for the determination of trace elements in a great number of samples, preconcentration and separation are still necessary to improve the sensitivity and selectivity. When CPE technique was used for the extraction of metal chelates, flame AAS (FAAS) was by far the most frequently used technique [11,28–30]. However, few reported the application of CPE technique as a preconcentration step for ETAAS [31,32]. The use of CPE as a preconcentration step for the direct determination of trace As(III) by ETAAS has not been reported before.

The purpose of the present work was to apply CPE as a preconcentration step for ETAAS determination of As(III). In the developed system, ammonium pyrrolidinedithiocarbamate (APDC) was used as the chelating agent and Triton X-114 as the extractant. The proposed work offers many advantages such as low cost, safety and a high capacity to concentrate metal chelate. The present work avoided calculating As(III) by difference [32] and realized that the selective determination of As(III) for the interference of As(V) was negligible (Fig. 1). Potential factors affecting the CPE preconcentration and the subsequent ETAAS determination of As(III) were investigated in detail.

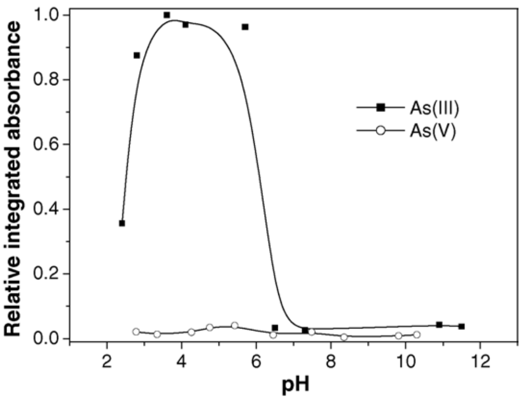

Fig. 1. Effect of pH on the cloud point extraction of 5.0 μg L^{-1} As(III). The values for relative integrated absorbance were calculated relative to the highest response (peak area). Other CPE conditions: 0.005% (w/v) APDC, 0.125% (v/v) Triton X-114, equilibration temperature 35 °C, equilibration time 9 min. ETAAS conditions as in Table 1.

2. Experimental

2.1. Instrumentation

A Solaar AA Series Spectrometer (Thermo Elemental, USA), equipped with a GFS 97 graphite furnace, a GFS 97 furnace autosampler and a circulating cooling unit (Labtech Ltd., 220 V/50 Hz, H90A) were used in all measurements. Deuterium-arc background correction was employed to correct for non-specific absorbance. All measurements were performed using integrated absorbance (peak area). An arsenic hollow cathode lamp (Beijing Shuguangming Electronic Light Sources Instruments Co. Ltd., Beijing, China) was used as the radiation source at a wavelength of 193.7 nm with a 11 mA lamp current and a 0.5 nm slit-width (low). The injection volume was 20 μL. Argon >99.995% (Tangan Gas Co. Ltd., Beijing, China) was used as protective and purge gas. Pyrolytically coated graphite tubes (Varsal Instruments Co. Ltd., Beijing, China) were used throughout. The detailed graphite furnace temperature program used for the determination of As(III) is shown in Table 1. The Solaar software was used to acquire and process spectral data.

A thermostated water bath maintained at the desired temperatures (Tianjin MinLi Science Instrument Co., Tianjin, China) was used for cloud point temperature experiments and the phase separation was assisted with a centrifuge (Shanghai Operation Apparatus Co., Shanghai, China).

2.2. Reagents

All chemicals were at least of the analytical grade. Doubly deionized water (DDW, 18 MΩ cm) obtained from a WaterPro water system (Labconco Corporation, Kansas, MO, USA) was used throughout. Triton X-114 (Sigma) was used as the non-ionic surfactant. Ammonium pyrrolidinedithiocarbamate (APDC) (Sigma) was used as the chelating agent to form the hydrophobic metal complexes. A 0.1% (w/v) of APDC solution was prepared by dissolving suitable amount of APDC in DDW. The pH of the sample solution was adjusted to pH 4.2 with HAc.

Stock standard solution of As(III) at a concentration of 1000 mg L^{-1} was prepared by dissolving appropriate amount of As_2O_3 (Beijing Chemicals Co., Beijing, China) in 1 M KOH and adjusting the pH to 7.0 with 50% HCl. Working

Table 1
Graphite furnace temperature program for the determination of As(III) by CPE

Stage	Temperature (°C)	Ramp (°C/s)	Hold (s)	Ar flow rate (mL min^{-1})
Drying	80	10	60.0	200
Pyrolysis	550	150	20.0	200
Atomization	1850	0[a]	3.0	0
Cleaning	2600	0[a]	3.0	200

[a] Ramp time is very short.

standard solutions were prepared by stepwise diluting the stock solutions just before use.

2.3. Samples

Three lake water and one river water samples were collected locally. After sampling, the samples were filtered through 0.45 μm filter and analyzed immediately.

2.4. Procedures

For CPE preconcentration, aliquots of 10.0 mL of the solution (pH 4.2) containing the analytes, 0.005% (w/v) APDC and 0.125% (v/v) Triton X-114 were heated in a thermostatted water bath at 35 °C for 9 min. The mixture was centrifuged at 4000 rpm for 5 min for phase separation, and then cooled in an ice-bath for 10 min to increase the viscosity of the surfactant-rich phase. The supernatant aqueous phase was carefully removed with a pipette. Hundred microliters of a solution containing 0.1 mol L^{-1} HNO_3 in methanol was added to the surfactant-rich phase (ca. 100 μL) to reduce its viscosity before ETAAS determination. A low-density polyethylene (LDPE) vial with the volume of about 500 μL was designed to place the sample solutions for the autosampler.

3. Results and discussion

3.1. Factors affecting the CPE preconcentration

The CPE can be used for the preconcentration of metal ions after the formation of sparingly water-soluble complexes. The CPE efficiency depends on the hydrophobicity of the ligand and the complex formed, the apparent equilibrium constants in the micellar medium, the kinetics of the complex formation, and the transference between the phases [33]. In this work, APDC was used as the chelating agent due to the highly hydrophobic nature of its metal complexes. The concentration of APDC tested ranged from 0.001 to 0.025% (w/v). The CPE efficiency for As(III) increased rapidly as the concentration of APDC increased from 0.001 to 0.003% (w/v), then kept almost constant with further increase in the APDC concentration upto 0.025% (w/v). Therefore, a APDC concentration of 0.005% (w/v) was employed for further experiments.

Because pH plays a unique role in metal-chelate formation and subsequent extraction [33], the pH of the sample solution was the next critical factor evaluated for its effect on the CPE preconcentration of As(III). The examined pH of As(III) sample solution ranged from 2.4 to 11.5. As shown in Fig. 1, the maximum absorbance for As(III) was achieved in the range of 3.6–5.7. In order to avoid As(V) interference and selectively determine As(III), the pH of As(V) was also examined as in Fig. 1 The pH of As(V) was in the range of 2.8–10.3, the preconcentration efficiency of As(V)–PDC complex was very low and changed a little. The interference of As(V) was negligible. Considering the above two reasons, pH 4.2 was used in the rest of the work.

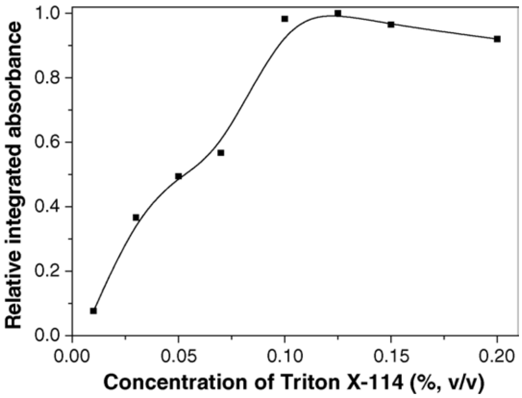

Fig. 2. Effect of the concentration of Triton X-114 on the cloud point extraction of 5.0 μg L^{-1} As(III). Other CPE conditions: 0.005% (w/v) APDC, pH 4.2, equilibration temperature 35 °C, equilibration time 9 min. ETAAS conditions as in Table 1.

The effect of Triton X-114 concentration was investigated between 0.01 and 0.25% (v/v). Fig. 2 shows variation of peak area of the analytes as a function of the surfactant concentration. The absorbance of the analytes increased as the concentration of Triton X-114 increased from 0.01 to 0.07% (v/v), and leveled off between 0.07 and 0.20% (v/v). Black smoke appeared with the increase in the concentration of Trition X-114 >0.2% (v/v). So, a 0.125% (v/v) of Triton X-114 was employed.

To achieve easy phase separation and preconcentration as efficient as possible, optimal incubation time and temperature are necessary to complete reactions. The effect of the equilibration temperature was investigated from 25 to 80 °C. It was found that the CPE efficiency reach maximum in the range of 30–40 °C. Over 40 °C, the CPE efficiency decreased probably due to the stability problems for chelates and chelating agents [33]. So, an equilibration temperature of 35 °C was used. Studies on the effect of the incubation time showed that the maximum extraction efficiency was observed from 8 to 10 min for As(III), and further increase in the incubation time resulted in a significant decrease of the efficiencies probably due to the thermal instability of the formed APDC complexes. For the rest experiments, an incubation time of 9 min was used. Further study is required to understand why the CPE efficiency for As(III) decreased as incubation temperature over 40 °C and incubation time increased over 10 min.

3.2. Pyrolysis and atomization curves

The pyrolysis temperature and atomization temperature were investigated in the range of 300–1000 °C and 1500–2100 °C, respectively (Fig. 3). When the pyrolysis temperature was close to 600 °C, the maximum absorbance was achieved. When the temperature was further increased,

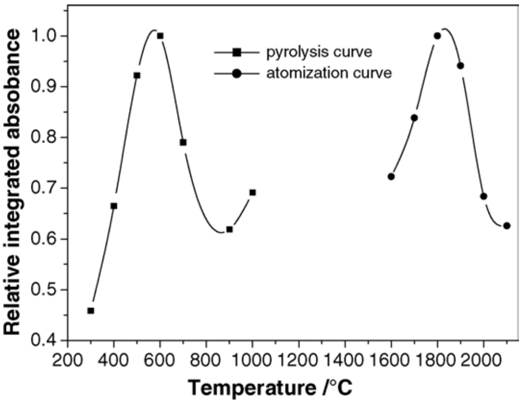

Fig. 3. Pyrolysis curve and atomization curve for the cloud point extraction of 5.0 μg L^{-1} As(III). CPE conditions: 0.005% (w/v) APDC, 0.125% (v/v) Triton X-114, pH 4.2, equilibration temperature 35 °C, equilibration time 9 min. ETAAS conditions as in Table 1.

the absorbance fell down. Increasing the atomization temperature to 1850 °C, the absorbance reached to the maximum. So the pyrolysis temperature of 550 °C and atomization temperature of 1850 °C were selected for the further work.

3.3. Interference studies

The potential interference in the present system was investigated. The interference is due to the competition of other heavy metal ions for the chelating agent and their subsequent co-extraction with the As(III). To evaluate the selectivity of the proposed method, the effect of typical potential interfering ions was investigated. The tolerable limit was taken as a relative error ≤±5%. The tolerable concentration ratio of foreign ions to 5.0 μg L^{-1} As(III) was found to be 40 for Cu(II), Se(IV) and Hg(II), 3 for Fe(III), and 1 for Pb(II) and Ni(II). To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the magnitude of CPE [33]. An increase in the ionic strength in the micelle-mediated extraction systems does not seriously alter the efficiency of extraction of the chemical forms [33]. The quantitative recovery of the As(III) spiked in the lake water and river water in our study also demonstrated no interference from lake water and river water matrices.

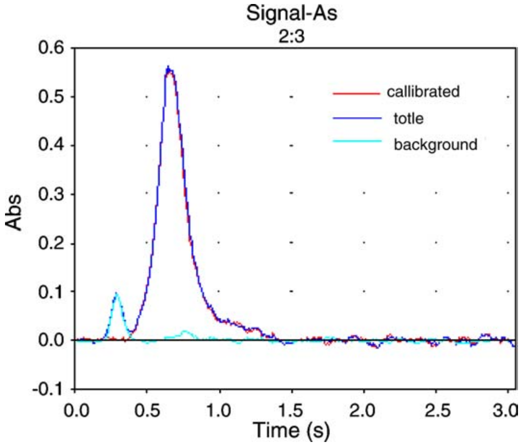

Fig. 4. Time–absorbance profile of a standard solution of 5.0 μg L^{-1} As(III) under the optimal conditions. CPE conditions: 0.005% (w/v) APDC, 0.125% (v/v) Triton X-114, pH 4.2, equilibration temperature 35 °C, equilibration time 9 min. ETAAS conditions as in Table 1.

3.4. Analytical figures of merit

Analytical characteristic data of the proposed CPE-ETAAS for As(III) were as follows. The precision (R.S.D.) for 11 replicate determinations of 5.0 μg L^{-1} of As(III) was 3.0%. The concentration factor, which is defined as the concentration ratio of analyte in the final diluted surfactant-rich extract ready for ETAAS determination and in the initial solution was 36 for As(III). The linear concentration ranges were from 0.1 to 20 μg L^{-1} for As(III). The calibration function was $A = 0.008 + 0.02C$ (six standards, $n = 3$) with a correlation coefficient 0.998, where C was the concentration of As(III) in μg L^{-1}. The detection limits, calculated according to $3s_0/s$ (3σ), where s_0 was obtained from the standard deviation for 11 replicate measurements of a blank solution, and s is the slope of the calibration graph was 0.04 μg L^{-1}. Fig. 4 is time (s)–absorbance (peak area) profile of 5.0 μg L^{-1} As(III) under the optimal CPE and ETAAS conditions.

3.5. Application to real samples

The proposed method was also employed for the determination of As(III) in four local natural water samples involving river water and lake water. The analytical results obtained by

Table 2
Analytical results for the determination of As(III) in water samples

Samples	Concentration (mean ± σ, $n = 3$) (μg L^{-1})		
	As(III) added (μg L^{-1})	Determined by the present method	Determined by a published method [23]
River water	0	0.35 ± 0.02	0.37 ± 0.01
	3.0	3.59 ± 0.08	3.40 ± 0.06
Lake water 1	0	0.13 ± 0.005	0.14 ± 0.005
	3.0	3.06 ± 0.09	3.13 ± 0.04
Lake water 2	0	0.31 ± 0.01	0.35 ± 0.01
	5.0	5.36 ± 0.25	5.33 ± 0.18
Lake water 3	0	0.50 ± 0.02	0.48 ± 0.01
	5.0	5.49 ± 0.31	5.42 ± 0.30

the present method using a simple aqueous standard calibration technique are given in Table 2. The recoveries for As(III) spiked in the natural water samples studied were calculated to be in the range of 97–108%, indicating no interference encountered from these sample matrices. The concentrations of As(III) in the natural water and spiked natural water by the present method were in good agreement with those determined by a flow injection on-line sorption preconcentration coupled with hydride generation atomic fluorescence spectrometry [23].

4. Conclusions

This work demonstrates the routine ETAAS determination of (ultra)trace As(III) in water samples solutions by CPE preconcentration. The detection limit of the present CPE-ETAAS method for the determination of As(III) was $0.04\,\mu\mathrm{g\,L}^{-1}$. It is lower than many published reports by ETAAS [34–40] for As(III). As can be seen, CPE technique employed can effectively improve the analytes sensitivity.

Acknowledgements

This work was supported by the National Natural Science Foundation of China for Distinguished Young Scholars (Grant No. 20025516), and the Research Foundation for the Excellent Young Teachers, State Education Ministry.

References

[1] Z.K. Shihabi, J. Chromatgr. A 902 (2000) 107.
[2] A. Eiguren Fernández, Z. Sosa Ferrera, J.J. Santana Rodríguez, Quim. Anal. 16 (1997) 283.
[3] A. Eiguren Fernández, Z. Sosa Ferrera, J.J. Santana Rodríguez, Anal. Chim. Acta 358 (1998) 145.
[4] W.L. Hinze, Ann. Chim. (Rome) 77 (1987) 167.
[5] N.D. Gullickson, J.F. Scamehom, J.H. Harwell, J.F. Schamehorn, J.H. Harwell, New York, 1989, p. 145.
[6] H. Hoshino, T. Saitoh, H. Taketoni, T. Yotsuyanagi, H. Watanabe, K. Tachikawa, Anal. Chim. Acta 147 (1983) 339.
[7] T. Saitoh, W.L. Hinze, Talanta 42 (1995) 119.
[8] S.R. Sirimanne, J.R. Barr, D.G. Patterson, Anal. Chem. 68 (1996) 1556.
[9] T. Saitoh, W.L. Hinze, Anal. Chem. 63 (1991) 2520.
[10] J.L. Manzoori, A. Bavili-Tabrizi, Anal. Chim. Acta 470 (2002) 215.
[11] J.R. Chen, K.C. Teo, Anal. Chim. Acta 450 (2001) 215.
[12] C. García Pinto, J.L. Pérez Pavón, B. Moreno Cordero, Anal. Chem. 67 (1995) 2606.
[13] R. Carabias Martínez, E. Rodríguez Gonzalo, M.G. Garcia Jiménez, C. García Pinto, J.L. Pérez Pavón, J. Hernández Méndez, J. Chromatogr. A 754 (1996) 85.
[14] A.-N. Tang, D.-Q. Jiang, Y. Jiang, S.-W. Wang, X.-P. Yan, J. Chromatogr. A 1036 (2004) 183–188.
[15] Q. Fang, M. Du, C.W. Huie, Anal. Chem. 73 (2001) 3502.
[16] R. Carabias-Martínez, E. Rodríguez-Gonzalo, J. Domínguez-Alvarez, J. Hernández-Méndez, Anal. Chem. 71 (1999) 2468.
[17] A.-N. Tang, D.-Q. Jiang, X.-P. Yan, Anal. Chim. Acta 507 (2004) 199.
[18] W.H. Lederer, R.J. Fensterheim, VNR, Arsenic. Industrial, Biomedical, Environmental Perspectives, New York, 1983.
[19] K.J. Irgolic, in: M. Stoeppler (Ed.), Hazardous Metals in the Environment, Elsevier, Amsterdam, 1992, p. 287.
[20] R. Iffland, in: H.G. Seiler, A. Sigel, H. Sigel (Eds.), Handbook on Metals in Clinical and Analytical Chemistry, Marcel Dekker, New York, 1994, p. 237.
[21] L. Ebdon, L. Pitts, R. Cornelis, H. Crews, O.F.X. Donard, P. Quevauviller (Eds.), Trace Element Speciation for Environment, Food and Health, RSC, Cambridge, 2001.
[22] B.K. Mandal, K.T. Suzuki, Talanta 58 (2002) 201.
[23] X.-P. Yan, X.-B. Yin, X.-W. He, J. Yan, Anal. Chem. 74 (2002) 2162.
[24] X.-B. Yin, X.-P. Yan, Y. Jiang, X.-W. He, Anal. Chem. 74 (2002) 3720.
[25] M.L. Cervera, R. Montoro, Fresenius J. Anal. Chem. 348 (1994) 331.
[26] W. Goessler, D. Kuehnelt, in: W.T. Frankenberger Jr. (Ed.), Environmental Chemistry of Arsenic, Marcel Dekker, New York, 2001, p. 27.
[27] S. McSheehy, J. Szpunar, R. Morabito, P. Quevauviller, Trends Anal. Chem. 22 (2003) 191.
[28] J. Chen, K.C. Teo, Anal. Chim. Acta 434 (2001) 325.
[29] E.K. Paleologos, D.L. Giokas, S.M. Tzouwara-Karayanni, M.I. Karayannis, Anal. Chim. Acta 458 (2002) 241.
[30] M.O. Luconi, M.F. Silva, R.A. Olsina, L.P. Fernańdez, Talanta 51 (2000) 123.
[31] D.L.G. Borges, M.A.M. Silva da Veiga, V.L.A. Frescura, B. Welz, A.J. Curtius, J. Anal. At. Spectrom. 18 (2003) 501.
[32] F. Shemirani, M. Baghdadi, M. Ramezani, Talanta 65 (2005) 882.
[33] C.D. Stalikas, Trends Anal. Chem. 21 (2002) 343.
[34] M. Sperling, X. Yin, B. Welz, Spectrochim. Acta 46B (1991) 1789.
[35] G.E. Pacey, J.A. Ford, Talanta 28 (1981) 935.
[36] A.A. Grabinski, Anal. Chem. 53 (1981) 966.
[37] A. Väisänen, R. Suontamo, J. Anal. At. Spectrom. 17 (2002) 739.
[38] N. Campillo, P. Viñas, I. López-García, M. Hernández-Córdoba, Analyst 125 (2000) 313.
[39] C.L. Éder, V.B. Ronílson, L.B. Jorge, H.D.P.S. Ana, J. Anal. At. Spectrom. 17 (2002) 1523.
[40] V. Ari, S. Reijo, R. Jukka, J. Anal. At. Spectrom. 16 (2001) 533.