THE USE OF A MEMBRANE GAS–LIQUID SEPARATOR FOR FLOW INJECTION HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROMETRY ON-LINE SPECIATION AND DETERMINATION OF As(III) AND As(V)

Milan KRENZELOK[1] and Petr RYCHLOVSKY[2]

Department of Analytical Chemistry, Charles University, 128 40 Prague 2, Czech Republic;
e-mail: [1] krenzel@prfdec.natur.cuni.cz, [2] rychlov@prfdec.natur.cuni.cz

This method employs a membrane gas–liquid separator and the hydride generation technique in the FIA AAS method for speciation of As(V) and As(III). The gas–liquid membrane separator achieves high measurement sensitivity and shows a very fast response (short delay time) because of its minimum dead volume. Conditions were optimized for the determination of arsenic by the flow injection hydride generation atomic absorption spectrometry method using this membrane separator. An apparatus was proposed for on-line speciation of both As(V) and As(III). Several reduction systems were used for reduction of As(V) to As(III) in the on-line arrangement. The best results were obtained using solution of 15 g KI in 100 ml of 6 M HCl at the reaction coil temperature 60 °C. A detection limit of 150 pg for As(III), 80 pg for As(III + V) and sampling rate of 25 samples per hour were reached.
Key words: Speciation; Arsenic; Gas–liquid separator; Hydride generation; AAS; FIA.

Many arsenic compounds are known to be toxic and the exposure of man and animals to arsenic remains of international concern. It is generally accepted that As(V) species are less toxic than As(III) compounds. In view of this difference between the oxidation states and in order to follow the pathways for interconversion in the environment, it is increasingly important to monitor concentrations of the individual chemical species as well as the total concentration of arsenic in the environment.

Speciation of As(III) and As(V) has been studied by many authors[1–7]. In all these papers methods distinguishing between the two forms of arsenic are used based on the fact that only As(III) can be converted to AsH_3 in weakly acidic medium[8]. Direct reduction of As(V) to the hydride never occurs in this medium. Direct reduction of As(V) to AsH_3 using $NaBH_4$ is not complete even in strongly acidic medium (low reaction rate). In the determination of As(V), it is necessary to pre-reduce As(V) to As(III) using a suitable reducing agent in strongly acidic medium. Following this step, the total arsenic content is determined by reaction with $NaBH_4$, similar to the determination of As(III). The As(V) content is found from the difference in the total As and the As(III) contents.

In the technique of generation of volatile hydrides in AAS, attention is concentrated primarily on the mechanism of hydride formation, the atomization process[9–11], study of interferences both in the liquid phase (effect of the velocity or efficiency of the hydride formation and release from solution) as well as in the gas phase (transport and atomization interference) and also on complete separation of the newly gas phase.

The separation of hydrides from the reaction mixture occurs either by flushing out by on excess hydrogen formed and the carrier gas[12] (high acid concentrations) or by the carrier gas flowing into the coupled generator–separator through a porous frit[13,14] (low acid concentrations). Another method separates the gas phase on the basis of diffusion of hydrides through the wall of a silicone tube (membrane) or PTFE microporous membrane[15,16].

On the basis of the results of a comparative study[17], a gas–liquid membrane separator with a PTFE membrane as separation interface was chosen in this work for the determination of arsenic and on-line speciation of As(V) and As(III) by the flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS). Gas–liquid membrane separators attain high measurement sensitivity, improvement in the signal-to-noise ratio and show very fast response time because of their minimum dead volumes. The following reducing systems were tested in this work for the pre-reduction of As(V) to As(III): KI/HCl system[11]; KI/ascorbic acid/HCl system[18]; $TiCl_3$/HCl system[19]; HCl/SO_3^{2-}/$S_2O_3^{2-}$/KI system[20].

EXPERIMENTAL

Apparatus

The measurements were carried out on a Varian SpectrAA 300A atomic absorption spectrometer with deuterium background correction. The radiation source was an EDL lamp for As (input power 7 W). The measurement was carried out at 193.9 nm with a spectral interval of 0.5 nm.

An eight-channel peristaltic pump (Cole–Parmer Masterflex) with tygon tubing of inner diameters 2.06 mm, 1.42 mm and 0.89 mm was used for the reagent feed. The reagent flow was switched using two three-way solenoid valves. The carrier gas (nitrogen) flow rate $q_v(N_2)$ was measured using a Cole–Parmer flow-meter. Sample injection was carried out using a six-way injection valve (RHEODYNE, Model 5020), with 30, 100, 250, 500 and 1 000 µl injection loops.

The hydrides were atomized using an absorption cell, classical quartz T-tube (length 170 mm, inner diameter 12 mm), narrowed in the centre to an inner diameter of 4 mm, with 70 mm side arm (inner diameter 2 mm), placed in the optical axis of the AA spectrometer. The quartz atomizer was heated electrically to a temperature of 950 °C (Varian Electrothermal Temperature Controller ETC-50).

The connector between the exit from the separator and the entrance into the absorption cell consisted of a 50 mm polyethylene tube (inner diameter 1.0; dead volume minimization).

Water thermostats type U-15, MLW, Medingen) were used in the reduction and reaction coil.

Membrane Gas–Liquid Separator

In the membrane separator[16,17] (Fig. 1), separation is based on diffusion of the gas through a membrane consisting of a Teflon strip (thickness 0.075 mm, width 11 mm, 1 µm pore size, Zefluor, Gel-

man Sciences). The separator consists of two blocks of poly(methyl methacrylate) with a groove in the middle of their largest sides[17]. The reaction mixture is fed through the first block with a groove of dimensions $1.0 \times 3 \times 50$ (90) mm. The hydride formed and excess hydrogen are fed into the atomizer through the second block with a groove of dimensions $3 \times 3 \times 90$ mm. Nylon grid with a thickness of 0.1 mm (100×10 mm) is used to fix the Teflon membrane. The two blocks are fitted together and sealed with a thin rubber seal fitted between the two blocks. A groove length of 90 mm corresponds to an active separation surface of only 2.7 cm^2 and a separator dead volume of 0.81 cm^3. Minimum dead volume of the separator and the whole system is the most condition for application in the FI mode.

Reagents

Standard As(III) or As(V) solutions (1.0000 g l^{-1}) were commercial (Analytika, Prague) or prepared from $Na_2HAsO_4\cdot7\ H_2O$ (Merck, Darmstadt), respectively. From them, working solutions (10 µg l^{-1} As) were prepared fresh every day.

Hydrochloric acid was Suprapure® grade (Merck, Darmstadt).

Sodium tetrahydroborate $NaBH_4$ (Merck, Darmstadt, content >96%) was always prepared fresh from the powdered substance in 0.4 wt.% NaOH.

Potassium iodide KI (Lachema, Brno), titanium chloride $TiCl_3$ (Lachema Brno), ascorbic acid (Merck Darmstadt), sodium sulfite Na_2SO_3 (Lachema Brno), sodium thiosulfate $Na_2S_2O_3$ (Lachema Brno) were of reagent grade purity.

Deionized water was prepared using the Milli Q+ deionizer from the Millipore Co., U.S.A.

The carrier gas was 99.999% pure nitrogen.

Procedure of Flow Injection Analysis

The working conditions for determining As using a membrane separator were tested with the apparatus in Fig. 2. The apparatus includes a membrane separator, peristaltic pump with tubing system, reaction coil, injection valve, flow-meter and atomizer.

The working conditions for the determination were tested on a sample of 10 ppb As(III) in 1 M HCl. The effect of the acid concentration was studied on a sample of 10 ppb As(III) in 0.01 M HCl.

After finding analytical conditions for the determination of arsenic, information was obtained for on-line speciation and determination of As(III) and As(V). The apparatus in Fig. 3 was constructed and used for the purpose.
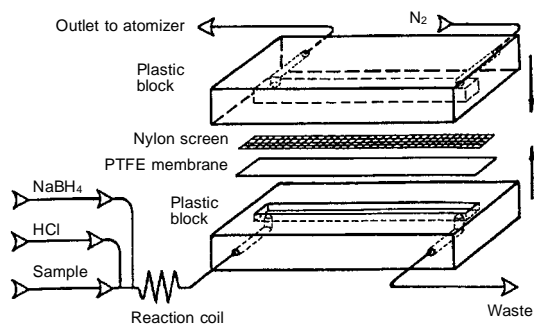

Fig. 1
Gas–liquid separator with PTFE membrane

Speciation of As(V) and As(III) requires two sample injections: As(III) is determined by injecting a sample into a stream of 0.5 M HCl; the second injection into a reducing agent stream containing 6 M HCl leads to determination of the total arsenic content in the sample (As(III) + As(V)).

Two solenoid valves simultaneously switch the channel with 0.5 M HCl and that with a reducing agent in 6 M HCl.

The total flow rate in the two branches at the sample injection site was 4.5 ml min^{-1}. The choice of two separate branches of the system with two solenoid valves is necessary because of the instability of the reducing solution in strongly acidic medium. This arrangement ensures acidification of the reducing agent immediately prior to the reduction reaction in the reaction coil. In this arrangement, the apparatus uses only one injection valve and the whole process can be automated. The injected sample first passes through the required length of the reduction coil and then enters the reaction coil where the reaction with NaBH$_4$ occurs with formation of the hydride.
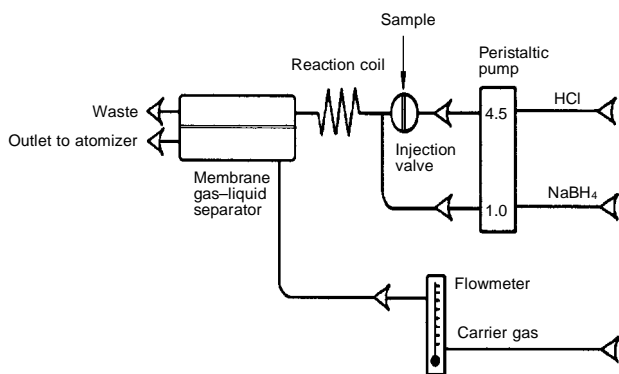

Fig. 2
Scheme of the apparatus for the FIA AAS determination of arsenic
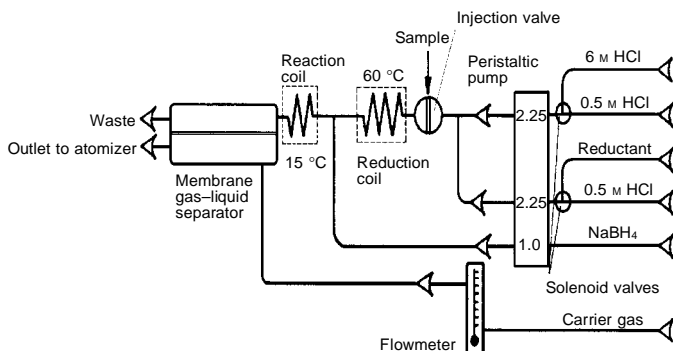

Fig. 3
Scheme of the apparatus for the speciation of As(V) and As(III)

It is necessary to ensure the same reaction conditions for the determination of As(III) and total As. Thus, the sample must pass through the reduction coil both in the determination of total As and in the determination of only As(III). This arrangement is necessary in evaluating the test signal. The gas phase is separated in the membrane separator and then enters the atomizer. Experiments associated with speciation of arsenic were evaluated on the basis of the heights of the test peaks.

RESULTS AND DISCUSSION

FI-HG-AAS Determination of As with a Membrane Phase Separator

First the working conditions were tested for generation and separation of AsH_3 in the FI mode using the given membrane separator. The parameters obtained in a comparative study were used as initial values[17]. 1.5 wt.% solution of $NaBH_4$ and flow rate $q_v(NaBH_4)$ of 1.0 ml min^{-1} were chosen as optimum.

It was found that the HCl concentration of 1 mol l^{-1} is sufficient for last hydride formation at given reagent flow rates using the described experimental arrangement and sample volume injected.

A study was also made of the appropriate flow rate of the HCl carrier stream. The graph of the peak height vs the stream flow rate passes through a maximum at a flow rate of 3–4 ml min^{-1}. As the flow rate increases, the measured peas become narrower. On the other hand, at flow rates of the carrier stream below 1 ml min^{-1}, the peaks become broader and very poorly reproducible. If the analysis is to be fast and precise with high sampling rate, then a higher medium flow rate of the carrier must be used, even at the expense of a slight decrease in the sensitivity. A carrier medium flow rate of 4.5 ml min^{-1} was chosen as optimum.

A study was also made of the effect of the amount of sample injected on the measurement sensitivity and peak shape (Fig. 4). A sample volume of 100 µl was found applicable for practical analyses. Similarly, a study of the reaction coil length was made; 2 000 mm was chosen as optimum.

A significant impact of temperature on the AsH_3 formation was demonstrated. An increase in the temperature of the reaction coil of 45 °C leads to a significant increase in the measurement sensitivity. However, a further increase above 45 °C leads to a decrease in the sensitivity. The lifetime of the separator (in particular the PTFE membrane) is low at the optimum temperature. The change in the separation efficiency is irreversible.

Because of the very small dead volume of this membrane separator (max. 0.81 cm^3), the system has a very short delay time. The hydride is transported sufficiently rapidly to the atomizer by excess hydrogen formed in the reaction of $NaBH_4$ and HCl. The introduction of further carrier gas does not improve any of the measurement parameters (sensitivity, noise). A very small carrier gas flow rate led to a decrease in the sensitivity.

Analytical conditions of the FI-HG-AAS determination with a membrane separator are: $w(NaBH_4) = 1.5$ wt.%, $q_v(NaBH_4) = 1.0$ ml min^{-1}, $c(HCl) = 1$ mol l^{-1}, q_v(carrier stream) $= 4.5$ ml min^{-1}, $q_v(N_2) = 0$ ml min^{-1}, reaction coil length 2 000 mm, injected sample volume 100 µl.

Figure 5 gives the calibration for the measured signals in the interval 0–50 ppb As(III) for an injected sample amount of 100 µl under working parameters for flow injection analysis.

The parameters of the calibration graph in peak heights attained in the FI-HG-AAS determination (Fig. 2) of arsenic with the given type of membrane gas–liquid separator
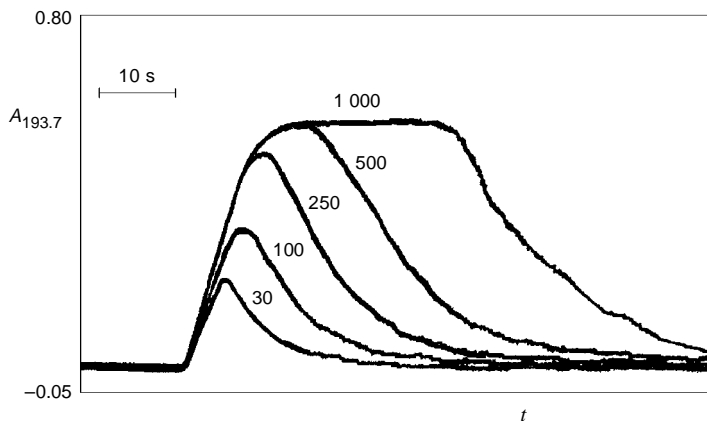

FIG. 4
Response to different volumes (in µl). ρ[As(III)] $= 10$ µg l^{-1}, q_v(carrier stream) $= 4.5$ ml min^{-1}; $c(HCl) = 1$ mol l^{-1}; $w(NaBH_4) = 1.5$ wt.%; $q_v(NaBH_4) = 1.0$ ml min^{-1}; $q_v(N_2) = 0$ ml min^{-1}; reaction coil length: 2 000 mm
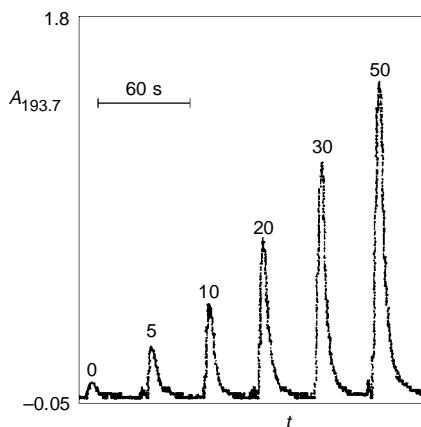

FIG. 5
Response to different contents of As (in µg l^{-1}) in injected sample. $V = 100$ µl, q_v(carrier stream) $= 4.5$ ml min^{-1}; $c(HCl) = 1$ mol l^{-1}; $w(NaBH_4) = 1.5$ wt.%; $q_v(NaBH_4) = 1.0$ ml min^{-1}; $q_v(N_2) = 0$ ml min^{-1}; reaction coil length: 2 000 mm

are: limit of detection 75 pg, reproducibility 2.4%, sensitivity of measurements (characteristic concentration) 0.03241 µg l^{-1}, linearity of calibration graph 0–20 µg l^{-1}.

As(III) and As(V) Speciation and Determination

The speciation of arsenic was tested in three solutions with the following concentrations: 10 µg l^{-1} As(III); 10 µg l^{-1} As(V); 10 µg l^{-1} As(III) + 10 µg l^{-1} As(V). Speciation was carried out in the apparatus depicted in Fig. 3.

Several systems were tested for on-line pre-reduction of As(V) to As(III): KI/HCl, KI/ascorbic acid/HCl, $TiCl_3$/HCl and HCl/SO_3^{2-}/$S_2O_3^{2-}$/$_3$KI.

The HCl/SO_3^{2-}/$S_2O_3^{2-}$/KI system cannot be used for on-line pre-reduction of As(V) to As(III), because the main reduction product SO_2 leads to high background absorption signal which completely prevents the measurement.

Because the reaction rate of the reduction of As(V) to As(III) with the given reducing agents is very slow, a study was made of the effect of the of the reduction coil and of the temperature on the efficiency of the on-line pre-reduction for the other test systems: KI/HCl, KI/ascorbic acid/HCl and $TiCl_3$/HCl.

It was found that, at laboratory temperature, 100% efficiency of the pre-reduction was not achieved for any of the test systems with a real length of the reduction coil.

A study was made of the effect of temperature in the range 25–80 °C on the rate of this pre-reduction step, using a thermostatting of the reduction coil in a water bath. A reduction coil length of 2 000 mm was chosen (compromise between a long reduction time and spreading of the zone of injected sample). The required 100% on-line pre-reduction of As(V) to As(III) under the given experimental conditions was attained only

TABLE I
Arsenic contents in field samples (in µg l^{-1} for water, in µg g^{-1} for soil) determined by AAS

Sample	FI-HG-AAS		ETA-AAS
	As(III)	As(V)	Total As(III + V)
Surface water 1[b]	n.d.[a]	3.60	3.71
Surface water 2[b]	n.d.[a]	3.01	3.12
Surface water 3[b]	n.d.[a]	3.38	3.37
Soil extract 1[c]	9.7	30.1	39.7
Soil extract 2[c]	5.7	35.8	41.5
Soil extract 3[c]	11.6	20.7	32.3

[a] Not detected; [b] surface water sample was stabilized with HCl; [c] 10 g of soil was extracted with 100 ml of 1 M HCl.

for the system containing 15 g KI in 100 g 6 M HCl at a reduction coil temperature of 60 °C. The use of this reduction system for speciation of arsenic is documented in Fig. 6, depicting the signals measured for As(III), As(V) and the As(III) + As(V) mixture for injection into a stream of reducing agent solution in 0.5 M HCl (Fig. 6a) or 6 M HCl (Fig. 6b) under the measurement conditions. Complete pre-reduction of As(V) to As(III) was not attained in the other test systems, nor at the highest temperatures used.

Under these temperature conditions (heating of the reaction coil to 60 °C), the separator membrane lifetime would be shorter (see above); thus a second thermostat set at 15 °C
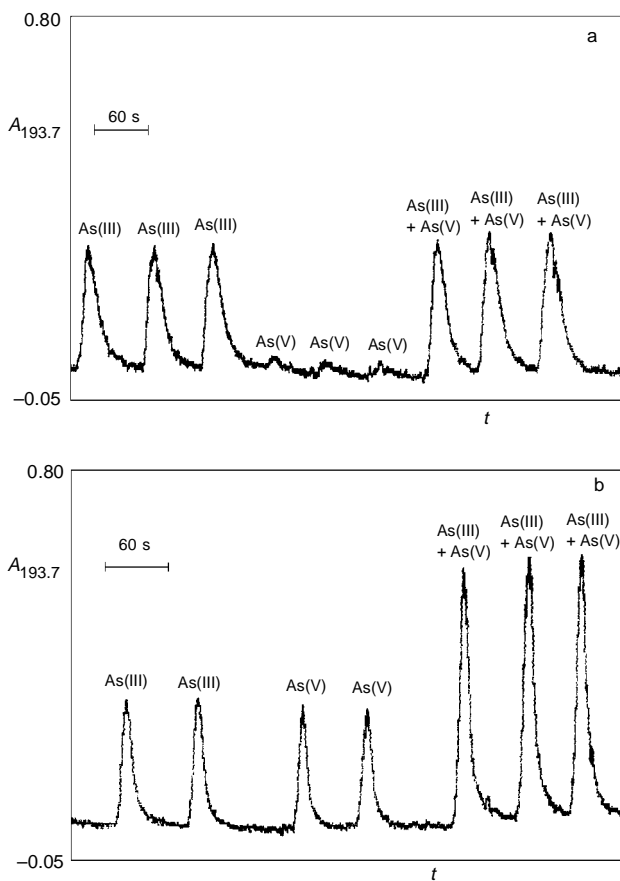

FIG. 6
Speciation of As(III) and As(V). *a*: Injection of sample [10 µg l^{-1} As(III); 10 µg l^{-1} As(V); 10 µg l^{-1} As(III) + 10 µg l^{-1} As(V)] into a stream of 0.5 M HCl. *b*: Injection of sample [10 µg l^{-1} As(III); 10 µg l^{-1} As(V); 10 µg l^{-1} As(III) + 10 µg l^{-1} As(V)] into a stream of 15 wt.% KI/6 M HCl. V = 100 µl, q_v(carrier stream) = 4.5 ml min^{-1}; w(NaBH$_4$) = 1.5 wt.%; q_v(NaBH$_4$) = 1.0 ml min^{-1}; q_v(N$_2$) = 0 ml min^{-1}; reduction coil length: 2 000 mm; reaction coil length: 2 000 mm; reduction coil temperature 60 °C

was used to decrease the temperature of the reaction mixture prior to entering the membrane separator.

A detection limit of 150 pg for As(III); 80 pg for As(III + V) (100 µl) and sampling rate of 25 samples per hour was obtained in this on-line arrangement.

This membrane phase separator and the proposed system for speciation of As(V) and As(III) using the solution of 15 g KI in 100 ml 6 M HCl reducing system was employed for the analysis of surface water and soil samples (Table I). As no reference material with certified content of As(III) and As(V) was available, we used the electrothermal atomization atomic absorption spectrometry (ETA AAS) for the determination of our own field samples. Surface-water samples were taken from the Botiç stream in Prague and soil samples were taken from areas around Prague. Water samples were stabilized with hydrochloric acid and filtered prior to treatment. Each sample was treated in triplicate. A relative standard deviation of the determination of about 5% was obtained.

REFERENCES

 1. Sperling M., Yin X., Welz B.: *Spectrochim. Acta, Part B* **1991**, *46*, 1789.
 2. Stummeyer J., Harazin B., Wippermann T.: *Fresenius' J. Anal. Chem.* **1996**, *354*, 344.
 3. El-Moll A., Heimburger R., Lagarde F., Leroy M. J. F., Mair E.: *Fresenius' J. Anal. Chem.* **1996**, *354*, 550.
 4. Slejkovec Z., Byrne A. R., Smodis B., Rossbach M.: *Fresenius' J. Anal. Chem.* **1996**, *354*, 592.
 5. Schaumloffel D., Neidhart B.: *Fresenius' J. Anal. Chem.* **1996**, *354*, 866.
 6. Pacey G. E., Straka M. R., Gord J. R.: *Anal. Chem.* **1986**, *58*, 504.
 7. Lopez A., Torralba R., Palacios M. A., Camara C.: *Talanta* **1992**, *39*, 1343.
 8. Narsito L., Agterdenbos J.: *Anal. Chim. Acta* **1987**, *197*, 315.
 9. Welz B., Schubert-Jacobs M.: *Fresenius' Z. Anal. Chem.* **1986**, *324*, 832.
10. Dedina J., Rubeska I.: *Spectrochim. Acta, Part B* **1980**, *35*, 119.
11. Welz B., Schubert-Jacobs M., Sperling M.: *Spectrochim. Acta, Part B* **1990**, *45*, 1235.
12. Brodie K., Fary B., Sturman B., Voth L.: *An Automated Vapor Generation Accessory for Atomic Absorption Analysis*. Varian Techtron Pty. Limited, Mulgrave (Australia) 1983.
13. Brindle I. D., Alarabi H., Karshman S., Lee X. C.: *Analyst* **1992**, *117*, 407.
14. Le X.-C., Cullen W. R., Reimer K. J., Brindle I. D.: *Anal. Chim. Acta* **1992**, *258*, 307.
15. Branch S., Corns W. T., Ebdon L.: *J. Anal. At. Spectrom.* **1991**, *6*, 155.
16. Chan W. F., Hon P. K.: *Analyst* **1990**, *115*, 567.
17. Krenzelok M., Rychlovsky P.: *Collect. Czech. Chem. Commun.* **1998**, *63*, 164.
18. Maher W. A.: *Anal. Chim. Acta* **1981**, *126*, 157.
19. Chung C. CH., Iwamoto E., Yamamoto M.: *Spectrochim. Acta, Part B* **1984**, *39*, 459.
20. Terada K., Matsumoto K., Inaba T.: *Anal. Chim. Acta* **1984**, *158*, 207.