In situ trapping of bismuthine in externally heated quartz tube atomizers for atomic absorption spectrometry

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A modification of the externally heated quartz tube atomizer, making possible *in situ* trapping of bismuthine, is described. The very simple experimental set-up is thus capable of lossless collection at a high preconcentration ratio. The collection/volatilization efficiency is 100 ± 2.5%. For a collection time of 300 s (sample volume of 20 ml), the preconcentration ratio and detection limit (3σ), respectively, are 530 and 3.9 pg ml^{-1}. The same approach is analytically useful also for stibine but not for arsine.

Introduction

The generation of gaseous analytes offers a route for convenient preconcentration. Besides the established technique of *in situ* trapping in graphite furnaces,[1,2] analytical applications of collecting volatile compounds in a bare quartz tube serving as a trap, interfaced with a quartz tube atomizer, have been reported.[3–5] Recently, we found that the commercially available externally heated quartz tube atomizer without any interfaced trapping device can be employed for the in-atomizer trapping of stibine under a stoichiometric excess of O_2 over H_2 and the volatilization and atomization of trapped analyte can be performed just by switching off the O_2 inlet. The preconcentration efficiency, defined as the overall efficiency of trapping and volatilization, was 100 ± 2%.[6] However, this approach did not work for other hydride forming elements. This note describes a modification of the experimental arrangement for in-atomizer trapping in the conventional quartz tube atomizer, making possible lossless trapping and subsequent analyte atomization for Bi also.

Experimental

Reagents

All reagents were of analytical reagent grade or higher purity. Deionized water was used to prepare solutions. Working Bi(III) standards were prepared from 1 mg ml^{-1} stock Bi solution (BDH Laboratory Reagents) by dilution in 1.0 mol l^{-1} HCl. The blank was 1.0 mol l^{-1} HCl. The reductant was 0.5% (m/v) solution of $NaBH_4$ (Sigma) in 0.4% (m/v) KOH (Merck) prepared daily and filtered before use.

Instrumentation

The Varian Model SpectrAA300/400 atomic absorption spectrometer with Bi hollow cathode lamp (10 mA, 223.1 nm, 0.2 nm band pass) was employed without background correction.

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An in-house made, continuous flow hydride generation system, similar to that described in refs. 6 and 7, was employed. Two T-pieces were used to merge sample flow with the reductant flow and, downstream, to merge the reaction mixture flow with the carrier argon flow. Either blank or standard solution was introduced to the sample channel. The outlet from the second T-piece was connected by a 510 mm long, 1 mm id, polytetrafluoroethylene (PTFE) tube to a 3 ml inner volume gas–liquid separator with a forced outlet. The third T-piece coupled to a 3-way valve was inserted downstream of the gas–liquid separator to introduce either auxiliary O_2 or H_2. The gas outlet from the third T-piece was connected to the inlet arm of the atomizer by a 350 mm long PTFE tube.

Sample and reductant solutions were delivered and the waste from the gas–liquid separator was removed by a peristaltic pump. Sample and reductant flow rates were 4.0 ml min^{-1} and 1.2 ml min^{-1}, respectively. The H_2 flow rate, derived from $NaBH_4$ decomposition, was calculated to be around 15 ml min^{-1}.

Atomizer

The commercial PerkinElmer externally heated quartz tube atomizer (Quartz Cell 2 for FI-MHS) without end windows was used. It was actually a plain T-tube, having a horizontal arm (aligned in the optical path of the spectrometer) with a length of 160 mm, an id of 7 mm and od of 14 mm. The length and id of the inlet arm were 90 mm and 2 mm, respectively. The atomizer was externally heated to 900 °C by a heating unit covering also the section of 15 mm of the inlet arm from the atomizer T-tube junction.

There were two atomizer inlet arm configurations employed: (i) atomizer with the bare inlet arm, and (ii) atomizer with capillary centred in the inlet arm. The configuration (i) is the normally used one: the third T-piece was connected to the bare inlet arm. In configuration (ii) a deactivated fused silica capillary (Supelco, 0.53 mm id) was centred within the inlet arm of the atomizer (sealed by a PTFE tube having an id of 0.7 mm and PTFE tape at the upstream end of the inlet arm) with its tip aligned with the downstream end of the inlet arm in the junction with the horizontal arm. The third T-piece was thus connected, by the 350 mm long PTFE tubing, to the capillary

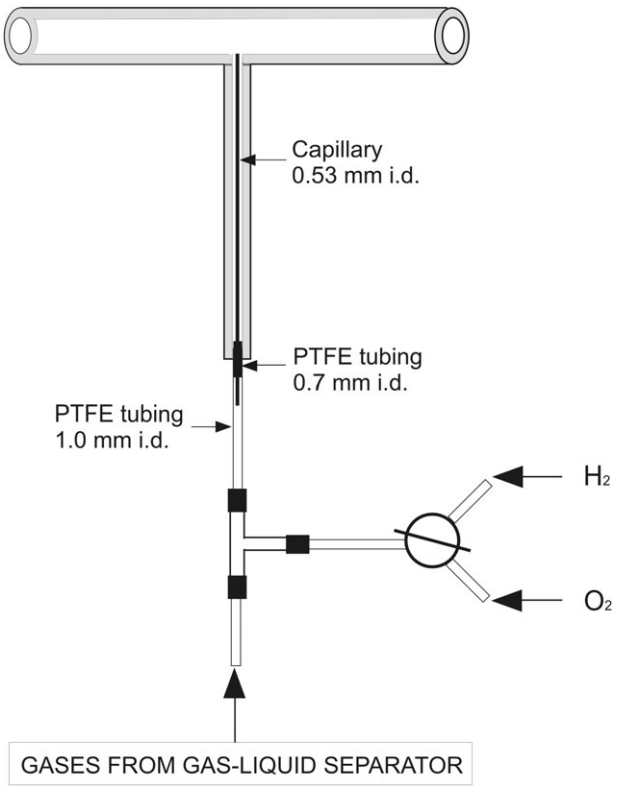

Fig. 1 Scheme of the atomizer configuration (ii).

so that all the gases flew through the capillary. See Fig. 1 for a scheme of configuration (ii).

Procedure

Measurements were performed either in the collection mode or in the direct transfer mode.

The collection mode procedure consisted of the two following steps:

Step 1-trapping: a standard was introduced to the sample channel for a given time, termed in the further text "sample introduction time". The standard was then replaced by the blank for 30 s to flush the system. The total gas flow rate introduced to the atomizer during Step 1 was 100 ml min^{-1} (75 ml min^{-1} of carrier Ar, 10 ml min^{-1} of auxiliary O_2 and 15 ml min^{-1} of H_2 evolved from $NaBH_4$). The pump was stopped at the end of Step 1.

Step 2-volatilization: O_2 flow was replaced by the H_2 flow. If not stated otherwise, the total gas flow rate introduced to the atomizer was 175 ml min^{-1} (75 ml min^{-1} of carrier Ar and 100 ml min^{-1} of auxiliary H_2). After recording the signal of volatilized analyte (peak integration time 15 s), the O_2 flow and pump were switched on and the procedure could be started again.

The direct transfer mode employs the direct transfer of hydride generated to the atomizer without introduction of O_2. After establishing the base line for blank introduction to the sample channel, an actual standard was introduced to the sample channel for 30 s. Then, the standard was replaced by the blank for 30 s. The signal obtained in the direct transfer mode was integrated for 90 s.

Results and discussion

To find the accurate value of the preconcentration efficiency of the collection mode procedure, the signals obtained were related to those in the direct transfer mode under the same conditions (gas flow rates, sample introduction time and concentration, atomizer inlet arm configuration). An Ar flow rate of 75 ml min^{-1} was found to be optimum to achieve maximum sensitivity in direct transfer mode. Increasing the H_2 flow rate from 15 ml min^{-1} (evolved from $NaBH_4$) to 100 ml min^{-1} (the total gas flow rate thus being increased from 90 to 175 ml min^{-1}) resulted in a 50% decrease in sensitivity.

For a good analytical performance of the collection mode procedure, the preconcentration efficiency should be close to 100%. Our previous reports[5,6] indicate that the only feasible way of managing the collection mode measurements in the conventional externally heated quartz tube atomizer (without any trap or additional heating device) is to use a stoichiometric excess of O_2 over H_2 in the trapping step and, subsequently, to volatilize the trapped analyte in the excess of H_2 over O_2 in the second step of the procedure. Employing a temperature difference between both steps, analogously as for the *in situ* trapping in graphite furnaces, is not feasible because the heating/cooling of the atomizer is very slow. Therefore, there is no temperature gradient in time: however, the spatial temperature distribution is not homogeneous, especially in the inlet arm of the atomizer where the temperature rises from ambient to 900 °C in the T-tube junction.

In the first step of the procedure, H_2 released from tetrahydroborate decomposition is completely burned in the flame formed in the inlet arm of the atomizer upstream of the T-tube junction. The O_2 flow rate of 10 ml min^{-1} was chosen as the sufficient excess over the flow rate of H_2 of 15 ml min^{-1} formed in the generator.

For the actual heating unit and the given temperature, the flame in the bare atomizer was not stable at an Ar flow rate of 75 ml min^{-1}: it oscillated within the inlet arm of the atomizer. The flame stability was good at the Ar flow rate of 120 ml min^{-1}, however, since the section of 15 mm of the inlet arm from the atomizer T-tube junction was covered by the heating unit, the flame was not seen and its exact position could not be specified. In contrast to the previously reported observation for Sb,[6] the overall efficiency of trapping and volatilization (preconcentration efficiency) was not satisfactory: depending on the flow rates of argon in the trapping step (75 or 120 ml min^{-1}) and H_2 (15 or 100 ml min^{-1}) in the volatilization step, the preconcentration efficiency ranged between 50 and 70%.

In principle, the low efficiency can be due to low efficiency of the trapping and/or of the volatilization. In the flame, the analyte hydride is converted most probably to oxide species. To achieve the required complete trapping, the formed analyte oxide species must be fully retained at the quartz surface in the vicinity and/or downstream of the flame. To achieve the required 100% efficiency of the second step of the procedure, retained analyte oxide species must be completely volatilized, in the excess of H_2, at the temperature of the actual section of the atomizer. The observed low preconcentration efficiency could be caused by the less efficient volatilization of analyte oxide species retained at the cooler regions of the atomizer inlet arm. To prevent analyte retention at these cooler regions,

the design of the atomizer was modified as detailed under Experimental: all gases from the hydride generator were introduced through the capillary axially centered in the inlet arm. The flame, burning during the trapping step, was thus fixed on the capillary tip aligned with the end of the inlet arm in its junction with the horizontal arm. The flame was quite stable in this arrangement, even at the Ar flow rate of 75 ml min^{-1}, in contrast to the arrangement with the bare inlet arm. However, the essential advantage of the arrangement with capillary centred in the inlet arm is that the analyte oxide species formed in the flame cannot be retained at the cooler regions of the atomizer inlet arm. The preconcentration efficiency was controlled by the flow rate of H_2 in the volatilization step: on increasing the flow rate from 15 ml min^{-1} the efficiency increased from 70% to close to 100% at 100 ml min^{-1}, remaining around the same at the flow rate up to 150 ml min^{-1}. At a flow rate of 100 ml min^{-1} the peak area corrected to blanks was 0.473 ± 0.008 s and 0.466 ± 0.007 s, for direct transfer and the collection mode, respectively, the preconcentration efficiency was thus 98.5 ± 2.3%. This proves that (1) analyte species are fully retained at the quartz surface of the atomizer horizontal arm downstream the flame, and (2) the retained analyte species are fully volatilized and atomized just by switching from the O_2 to H_2 flow rate of 100 ml min^{-1}, corresponding to 57% H_2 content in the gas. Therefore, the arrangement with capillary centered in the inlet arm and the H_2 flow rate of 100 ml min^{-1} in the volatilization step was employed for further measurements. Higher H_2 flow rates were not used because of the negative influence on sensitivity.

The sample introduction time can be increased substantially. For an introduction time of 300 s and standard concentration of 100 pg ml^{-1} (*i.e.*, for the same analyte mass of 2 ng—the same as above), the peak area corrected to blanks was 0.470 ± 0.020 s (n = 10), proving that the preconcentration efficiency was close to 100% (99.4 ± 4.6%) even for the extended sample introduction time. This suggests that there are no losses of the retained analyte species in the trapping step, *i.e.*, under excess of O_2.

According to our recent observation, Sb can be efficiently trapped and volatilized by employing the atomizer configuration with the bare inlet arm. An atomizer with the capillary centred in the inlet arm works equally well. In contrast to Bi, Sb oxide species retained in the first step of the collection procedure can be fully volatilized in the second step of the procedure at the H_2 flow rate of 15 ml min^{-1}.

The preconcentration efficiency of As was estimated under the same experimental parameters as described above for Bi. It was as low as around 1%, similar to that reported recently for the bare inlet arm configuration.[6] Even though arsine must be decomposed in the flame the resulting As species are probably not effectively trapped at the employed temperature of 900 °C.

The typical Bi signal of the collection mode is narrow with no tailing, with an FWHM (full width at half-maximum) of 0.6 ± 0.1 s. Its shape is independent of the sample introduction time. Signals in the direct transfer mode are dramatically broader than in the collection mode—their FWHM can be considered to be equal to the sample introduction time. The ratio of FWHM in the direct transfer mode to that in the collection mode can be taken as a measure of the preconcentration ratio. Consequently, the preconcentration ratio is around 53 and 530, respectively, for sample introduction times of 30 and 300 s.

The calibration function for peak area in the collection mode was linear up to 2 ng of Bi (peak height absorbance around 1.1). Peak height was linear up to absorbance around 0.5, corresponding to 0.6 ng Bi.

The precision of peak area measurements (n = 3–10), expressed as RSD, was below 4.3% in the whole calibration range for analyte mass between 0.2 and 2 ng and a sample introduction time of 300 s. The peak height precision was always slightly, but significantly, worse.

Owing to the lossless collection at high preconcentration ratio, the described procedure offers a great potential to achieve an extremely low concentration detection limit (LOD, expressed as 3σ). For a sample introduction time of 300 s (sample volume of 20 ml) the LOD of peak area measurements was 3.9 pg ml^{-1}. The actual LOD was controlled by the analyte content in blanks—5 ± 1 pg ml^{-1}. There was no attempt made to reduce contamination and, subsequently, to achieve even lower LOD. Nevertheless, the LOD is comparable to the best one achieved for *in situ* trapping in commercial graphite furnaces with subsequent AAS detection of 3.2 pg ml^{-1} reported by Sturgeon *et al.*[8] LODs given by other authors (see review[2] and refs. 9–11) are at least 6 times worse.

The repeatability of preconcentration efficiency for an analyte mass of 2 ng and a sample introduction time of 30 s, calculated from 60 measurements made during 25 days, was 100 ± 2.5% (±SD).

The data given above indicate that lossless preconcentration can be achieved for bismuth and antimony based on *in situ* trapping of respective hydrides in (only slightly modified) externally heated quartz tube atomizers. Consequently, the determination of bismuth and antimony at ultratrace levels is feasible using very simple and cheap equipment.

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References

1 J. Dědina and D. L. Tsalev, *Hydride Generation Atomic Absorption Spectrometry*, Wiley & Sons, Chichester, 1995, p. 56.
2 H. Matusiewicz and R. Sturgeon, *Spectrochim. Acta, Part B*, 1996, **51**, 377–397.
3 D. Korkmaz, N. Ertas and O. Ataman, *Spectrochim. Acta, Part B*, 2002, **57**, 571–580.
4 D. Korkmaz, C. Demir, F. Aydin and O. Y. Ataman, *J. Anal. At. Spectrom.*, 2005, **20**, 46–52.
5 D. Korkmaz, J. Dědina and O. Ataman, *J. Anal. At. Spectrom.*, 2004, **19**, 255–259.
6 J. Kratzer and J. Dědina, *Spectrochim. Acta, Part B*, 2005, **60**, 859–864.
7 T. Matoušek, M. Johansson, J. Dědina and W. Frech, *Spectrochim. Acta, Part B*, 1999, **54**, 631–643.
8 R. Sturgeon, S. Willie, G. Sproule, P. Robinson and S. Berman, *Spectrochim. Acta, Part B*, 1989, **44**, 667–682.
9 H. O. Haug and Y. P. Liao, *Fresenius' J. Anal. Chem.*, 1996, **356**, 435–444.
10 M. Elsayed, E. Bjorn and W. Frech, *J. Anal. At. Spectrom.*, 2000, **15**, 697–703.
11 C. Moscoso-Perez, J. Moreda-Pineiro, P. Lopez-Mahia, S. Muniategui-Lorenzo, E. Fernandez-Fernandez and D. Prada-Rodriguez, *Talanta*, 2003, **61**, 633–642.

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ORIGINAL PAPER

Arsine and selenium hydride trapping in a novel quartz device for atomic-absorption spectrometry

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Abstract A novel quartz device has been designed to trap arsine and selenium hydride and subsequently to volatilize the collected analyte and atomize it for atomic-absorption spectrometric detection. The device is actually the multiple microflame quartz-tube atomizer (multiatomizer) with inlet arm modified to serve as the trap and to accommodate the oxygen-delivery capillary used to combust hydrogen during the trapping step. The effect of relevant experimental conditions (trap temperature during trapping and hydrogen flow rate and trap temperature during volatilization) on collection and volatilization efficiency was investigated. Under the optimum conditions collection and volatilization efficiency for arsenic and selenium were 50 and 70%, respectively.

Keywords Arsenic and selenium hydrides · Atomic-absorption spectrometry · Multiatomizer · Hydride-trapping optimization · Quartz surface

Introduction

Determination of hydride-forming elements generally, and As and Se in particular, at trace and ultratrace levels is important for a variety of types of sample. The inherent advantage of hydride generation for atomic-absorption spectrometry (AAS) is that the analyte can be easily preconcentrated either in a special collection device (usually by cryogenic trapping [1]) or, better, directly in the atomizer. Until recently, the only approach widely used for in-atomizer trapping was in-situ trapping in commercial graphite furnaces [1, 2], although hydride trapping in a tungsten tube atomizer [3] and on the surface of a tungsten coil [4, 5] have also been reported.

Another approach to in-atomizer trapping is to collect plumbane [6], stibine [7], or volatile Cd species [8] in a bare quartz tube. Overall efficiency of trapping and volatilization in these quartz-tube traps did not exceed 70%. We recently found that a commercially available externally heated quartz-tube atomizer (conventional QTA) without any interfaced trapping device can be used for in-atomizer trapping of stibine under conditions of a stoichiometric excess of oxygen over hydrogen, and that volatilization and atomization of the trapped analyte can be performed merely by switching off the oxygen. The overall efficiency of trapping and volatilization was 100±2% [9]. Slight modification of the conventional QTA, consisting in introduction of all gases through a capillary axially centred in the inlet arm, enabled loss-less trapping and subsequent analyte atomization for Bi also [10]. Neither the unmodified nor the slightly modified conventional QTA can be used for in-atomizer trapping of hydrides of As, Se, or Te, however [9, 10].

An analytically useful device for trapping and subsequent volatilization/atomization of the most important hydride forming elements, As and Se, is described in this communication. The device incorporates the multiple microflame quartz tube atomizer (multiatomizer) [11, 12] because, in comparison with conventional QTA, it furnishes better control of the atomization process [7].

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Experimental

Reagents

All reagents were of analytical-reagent grade or higher purity. Deionized water was used to prepare solutions. Working standard solutions of As, Se, and Sb were prepared from 1 mg mL^{-1} stock solutions (BDH Laboratory Reagents) by dilution with 1.0 mol L^{-1} HCl. The blank was 1.0 mol L^{-1} HCl. The reductant was a 0.5% (*m*/*v*) solution of $NaBH_4$ (Sigma) in 0.4% (*m*/*v*) KOH (Merck) filtered after preparation and stored frozen.

Instrumentation

The Varian model SpectrAA300/400 atomic-absorption spectrometer equipped with hollow cathode lamps was used without background correction (the operating conditions used are listed in Table 1).

The flow rate of carrier gas, argon, was controlled by means of a rotameter (Cole Parmer). Mass-flow controllers (Cole Parmer) were used for all the other gases.

The continuous flow hydride generation system was made in-house and was similar to that described elsewhere [9, 13]. Two T-pieces (polyether ether ketone, 0.8 mm inner bore) were used to merge sample flow with the reductant flow and, downstream, to merge the reaction mixture flow with the carrier argon flow. Either blank or standard solution was introduced to the sample channel. The outlet from the second T-piece was connected by a 510-mm length of 1 mm i.d. polytetrafluoroethylene (PTFE) tubing to a 3-mL internal volume gas–liquid separator with a forced outlet (the gas-liquid separator is described in detail elsewhere [13]).

Sample and reductant solutions were delivered by peristaltic pump, and the waste from the gas-liquid separator was removed in the same way. In all experiments, sample and reductant flow rates were 4.0 mL min^{-1} and 1.2 mL min^{-1}, respectively. The flow rate of H_2 evolved from $NaBH_4$ decomposition was calculated to be approximately 15 mL min^{-1}.

Atomizer with integrated trap

The T-shaped device used to trap hydride and to atomize analyte (atomizer/trap device; Fig. 1) consisted of two quartz arms, horizontal and inlet.

Table 1 Spectrometer operating conditions

Element	Wavelength (nm)	Band pass (nm)	Current (mA)
As	193.7	0.5	10
Se	196.0	1	10
Sb	217.6	0.2	10

The horizontal arm (aligned in the optical path of the spectrometer) was the same as that of the multiatomizer described previously (model MM4 in Ref. [12]). It was made of two concentric tubes. The inner (optical) tube was evenly perforated with fourteen orifices. A flow of gas (outer gas) was introduced from the sides into the cavity between both tubes of the horizontal arm and then passed through the orifices into the inner tube. If not mentioned otherwise, air was employed as the outer gas and flowed at 25 mL min^{-1} continuously throughout the procedure (see section Procedure). When explicitly stated, hydrogen at a flow rate of 25 mL min^{-1} was introduced as the outer gas during the trapping step of the whole procedure (see section Procedure). A three-way valve was used to switch between air and hydrogen. The commercial heating unit, with temperature control produced by RMI (Lázně Bohdaneč, Czech Republic) was used to heat the horizontal arm to 900 °C. The 4-cm section of the inlet arm from the T-junction is covered by the heating unit.

The inlet arm served as the trap. It was a plain 8-cm length of silica tube, 2 mm i.d. and 3 mm o.d. A 6-cm length of heating coil made from 40 cm canthal wire (4.17 Ω m^{-1}, 0.65 mm diameter) covered the downstream part of the inlet arm. The mains voltage, 220 V, was reduced to 80 V by use of an autotransformer. Another autotransformer controlled the potential applied to the heating coil and the current was monitored by means of an ammeter. The gas phase temperature inside the inlet arm heated by the applied current was determined by use of a thermocouple (Cole Parmer). A current between 0 to 9 A resulted in a temperature in the range 80–1100 °C. Deactivated fused silica capillary tubing (Supelco, 0.53 mm i.d.) centred in the inlet arm served for the oxygen delivery. The end of the capillary was 2.5 cm from the upstream end of the inlet arm (Fig. 1), i.e. 5.5 cm from the atomizer T-junction. The oxygen-delivery capillary was interfaced to the inlet arm by means of a T-piece (polypropylene, 1 mm i.d.) fitted to the inlet arm. The upstream end of the oxygen-delivery capillary was fitted into the 1 mm i.d. PTFE tubing connecting the oxygen channel. All fittings were made with PTFE tape. The right arm of the T-piece (Fig. 1) served to introduce gases from the gas-liquid separator to the atomizer/trap device.

An additional T-piece (polypropylene, 1 mm i.d.) was inserted into the gas line between the gas–liquid separator and the right arm of the "oxygen channel" T-piece (Fig. 1) to introduce hydrogen from a gas container. PTFE tubing (1 mm i.d.) was used to connect the hydrogen channel to the additional T-piece. The same tubing (20 mm) was used to connect both T-pieces and 200 mm of the tubing connected the gas liquid separator with the additional T-piece.

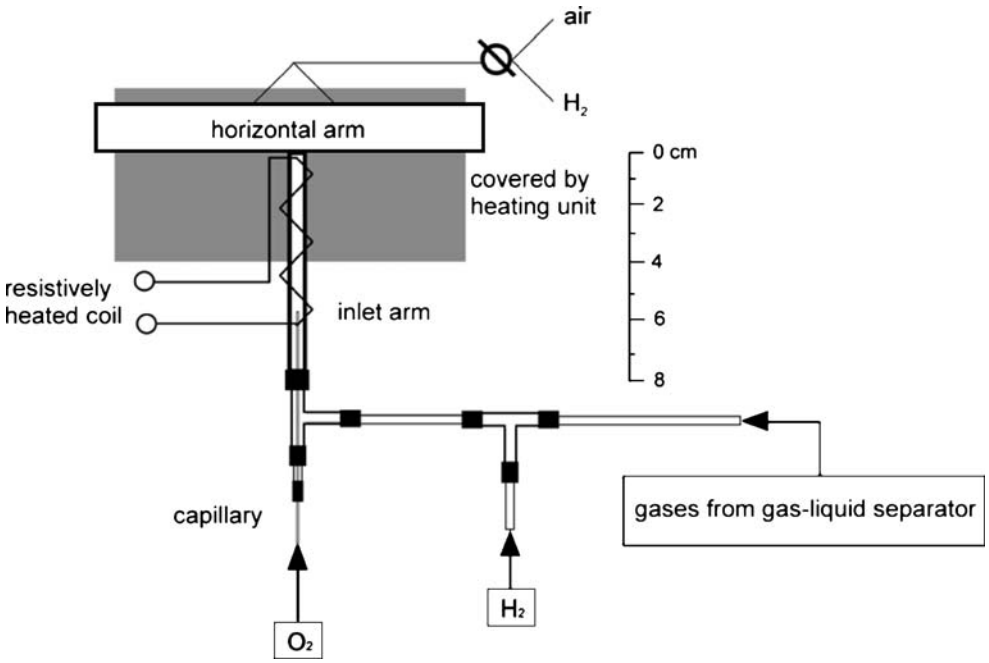

Fig. 1 Schematic diagram of the arrangement downstream of the gas–liquid separator

Procedure

Measurements were performed either in the collection mode or in the direct-transfer mode. The flow of carrier Ar (75 mL min^{-1}) was maintained throughout in both modes of operation.

The collection mode procedure consisted of two steps—trapping, in which analyte was trapped in the inlet arm of the atomizer/trap device, and volatilization, in which the trapped analyte was released and transferred into the optical arm of the atomizer/trap device and atomized there.

Trapping step

The inlet arm heating was set to the trapping temperature. It took up to 60 s to heat the inlet arm from ambient temperature. The peristaltic pump was then switched on to start hydride generation and a standard was introduced to the sample channel for 30 s. The standard was then replaced by the blank for 30 s to flush the system. The oxygen channel was opened simultaneously with switching on the pump to deliver the flow rate of 10 mL min^{-1} to the capillary. Introduction of oxygen in stoichiometric excess over 15 mL min^{-1} hydrogen, evolved from $NaBH_4$ decomposition, resulted in ignition of a flame burning at the tip of the capillary. The pump was stopped at the end of the trapping step. If explicitly stated, hydrogen at a flow rate of 25 mL min^{-1} was introduced as the outer gas into the cavity between both tubes of the horizontal arm during the trapping step and the signal of analyte breaking through the trap and atomized in the optical tube was recorded. The "breakthrough" signal integration was thus performed for 90 s beginning at the start of standard introduction.

Volatilization step

The inlet arm was heated to the volatilization temperature. The steady-state temperature was reached after 60 s. To volatilize collected analyte species the oxygen channel was closed and after 5 s delay the hydrogen channel was opened. Simultaneously with opening of the hydrogen channel the signal of volatilized analyte atomized in the optical tube was recorded and integrated for 15 s. The hydrogen channel was then closed and inlet arm heating was switched off. The volatilization step was concluded after 60 s, when the inlet arm temperature had dropped to ambient.

If explicitly stated, an additional volatilization step was introduced. The oxygen channel was opened and the inlet arm temperature was changed to 920 °C and 570 °C, respectively, for determination of As and Se. After 60 s, when the steady state temperature was reached, the volatilization procedure described above was repeated—the oxygen channel was closed, the hydrogen channel was opened with the 5-s delay time, and the signal of additionally volatilized analyte was recorded and integrated for 15 s. The hydrogen channel was then closed and inlet arm heating was switched off. The additional volatilization step was concluded after 60 s when the inlet arm temperature had dropped to ambient.

In the direct-transfer mode the inlet arm was unheated, the oxygen channel was closed, the hydrogen channel was open, the peristaltic pump was on, and the signal from

analyte atomized in the optical tube was monitored continuously. Air was always used as the outer gas. A typical measurement consisted in establishing the baseline for blank introduction to the sample channel. A standard was then introduced to the sample channel for 30 s, when it was replaced by the blank for 30 s. The signal obtained in the direct-transfer mode was integrated for 90 s beginning at the start of introduction of the standard.

Results and discussion

Preliminary observations

Previous unsuccessful attempts to use conventional QTA for in-situ trapping of As and Se [9, 10] suggested that a trap with separate temperature control, similar to that we described previously [7] for SbH_3 trapping, should be used. The arrangement used, consisting of the trap connected to the quartz tube multiatomizer by used plastic tubing, performed far from optimum, however [7].

Subsequent experiments performed with the same arrangement as in Ref. [7] (not described above in the Experimental section) indicated that a weak point of the apparatus was the temperature minimum in the plastic tubing between the trap and the atomizer—the temperature was below 200 °C. Losses of analyte volatilized from the trap had to be expected in this relatively cool section. Another source of losses could be the surface of the plastic tubing. It seemed, however, that the most serious reason for incomplete trapping and volatilization was losses of analyte in the trapping step, which were unavoidable in the presence of hydrogen developed in hydride generator. There was, for example, no loss of analyte even after 5 min at the optimum trap temperature of 680 °C in the absence of hydrogen, in contrast with substantial loss after 20 s in the presence of hydrogen, at a flow rate of 15 mL min^{-1}, from decomposition of the tetrahydroborate in the hydride generator.

Design of the atomizer/trap device

The simplest way to remove hydrogen was to combust it with a stoichiometric excess of oxygen. (This concept has been successfully used for in-situ trapping of stibine and bismuthine in conventional QTA [9, 10].) The other requirements for the experimental trap and atomizer arrangement was to remove the temperature minimum between the heated trap and the atomizer and to enable efficient atomization of analyte species in the optical path of the atomic-absorption detector. The atomizer/trap device (Experimental section) was designed to conform to all these requirements:

1. efficient atomization;
2. no temperature minimum; and
3. combustion of hydrogen.

The atomizer/trap device is actually the multiatomizer described previously [11, 12] with the inlet arm modified to serve as the trap and to accommodate the oxygen-delivery capillary used for combustion of the hydrogen.

Hydrogen radicals were proved to atomize arsine and selenium hydride at the relatively low temperatures typical of conventional QTA [1] and used for the multiatomizer [11]. Hydrogen radicals are formed at the beginning of the heated portion of the conventional QTA atomizer by reaction of hydrogen with traces of oxygen. In this way, hydride atomization in conventional QTA is facilitated by oxygen contamination of gases introduced into the atomizer [1]. Traces of oxygen in a gas containing hydrogen are removed by reaction with hydrogen at temperatures above ~500 °C, however. Consequently, the oxygen content of the gas after passing through the heated trap introduced to the conventional QTA could be too low to render the analyte atomization possible. The inherent advantage of the multiatomizer for atomization of analyte volatilized in any upstream trap is that it uses a separate supply of oxygen, in the form of air, via the outer gas inlet (Experimental section) to the atomization zone in the optical tube. The air flow rate of 25 mL min^{-1} was chosen as optimum [12]. To summarize, production of hydrogen radicals in the optical tube of the multiatomizer is controlled not by the oxygen contamination of gases introduced to the atomizer but by the supply of oxygen in the outer gas.

The other unique feature of the multiatomizer which is useful when working with excess oxygen in the trap is that hydrogen can be introduced as the outer gas to maintain excess hydrogen in the optical tube. The reason is that at temperatures typical of conventional QTA and multiatomizer (up to 1100 °C), arsine and selenium hydride cannot be atomized under conditions of stoichiometric excess of oxygen over hydrogen [1]. That free atoms are not observed under conditions of oxygen excess can be attributed to the lower production of hydrogen radicals [1] (the concentration of hydrogen radicals is thus insufficient for efficient conversion of the analyte to free atoms) and to the enhanced free analyte atom reaction with molecular oxygen resulting in the formation of analyte oxides, which cannot be converted to free analyte atoms, because the concentration of hydrogen radicals is insufficient.

Integrating the trap with the atomizer, i.e. using the inlet arm of the atomizer as the trap, avoided the need to use plastic tubing and reduced the temperature gradient. As illustrated in Fig. 2 there is no temperature minimum between the trap and the optical arm—in the central part of

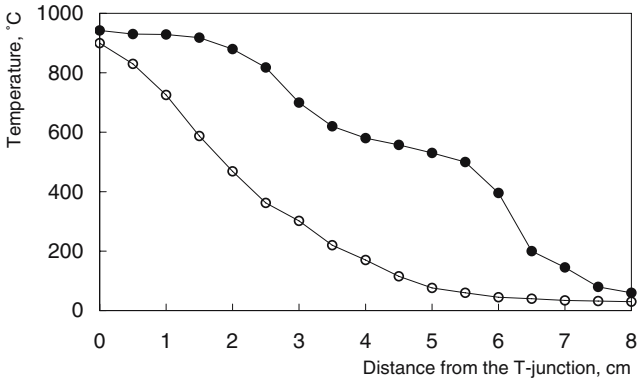

Fig. 2 Temperature in the inlet arm of the atomizer/trap device for the unheated trap (*empty circles*) and when the trap is heated to 550 °C (*filled circles*)

the trap there is 2.5-cm long temperature plateau. Temperature was measured at an Ar flow rate of 75 mL min^{-1} but neither switching off the Ar flow nor replacing Ar with hydrogen significantly affect the temperature profile shown in Fig. 2. The regular decrease of temperature with increasing distance from the optical tube should be compared with the 200 °C minimum between the separated trap and atomizer reported above [7].

The capillary arrangement of the atomizer/trap device made possible to fix the H_2/O_2 flame at the end of the oxygen-delivery capillary during the trapping step. The flame was ignited by opening the oxygen channel, irrespective of whether or not the trap was heated; if the trap temperature was low the flame was ignited in the hot optical tube and immediately flashed back to burn stably at the tip of the capillary. There was, consequently, a 5.2-cm length of inlet arm between the flame and the optical tube with a "hydrogen free" atmosphere. This inlet arm section (its temperature profile is given in Fig. 2) thus served as an efficient trap.

Direct-transfer mode

This mode is used for conventional measurements, i.e. with direct transfer of hydride generated to the atomizer [1], with the oxygen channel closed. In this mode, a carrier Ar flow rate of 75 mL min^{-1} was found to be optimum for achieving maximum sensitivity. It was therefore used for all the experiments reported below. Table 2 shows peak-area sensitivity for individual analytes. There was no flow from the hydrogen channel. The total gas flow rate to the inlet arm of the atomizer/trap device, taking into account also the flow rate of H_2 evolved from $NaBH_4$ decomposition, was thus 90 mL min^{-1}. Sensitivity decreased with increasing hydrogen flow rate for all analytes. For example, a hydrogen flow rate of 100 mL min^{-1} reduced As sensitivity to 30%. For Se, when the hydrogen flow rate was 50 mL `min^{-1} sensitivity decreased to 43%. The signal obtained in the direct-transfer mode was integrated for 90 s beginning at the start of introduction of the standard.

Table 2 Peak-area characteristic mass (m_0) for direct-transfer mode

Element	m_0 (pg)
As	7.0
Se	9.3
Sb	8.7

Direct-transfer mode was used as a reference signal for estimation of the collection mode preconcentration efficiency, defined as the overall efficiency of trapping and volatilization, and to check the short and long-range signal stability. Hydrogen flow rate was strictly kept the same in direct-transfer mode as in the volatilization step of the collection mode to enable estimation of the preconcentration efficiency by comparing respective peak areas.

Collection mode

The procedure consists of trapping and volatilization steps. As discussed above, flow of oxygen at a rate sufficient to maintain stoichiometric excess over hydrogen is required to achieve complete analyte trapping in the first step. Because the flow rate of hydrogen formed in the generator was approximately 15 mL min^{-1} (Experimental section) an oxygen flow rate of 10 mL min^{-1} was chosen. All the hydrogen is thus burned in the flame located at the end of the oxygen-delivery capillary. In the flame, the analyte hydride is most probably converted to oxide species efficiently retained on the quartz surface. The analyte species can be rapidly volatilized only in excess hydrogen and only at elevated temperatures. The excess hydrogen required makes it possible to eliminate slow heating of the trap—volatilization is initiated by the closing of the oxygen channel and, after the 5-s delay time, by opening the hydrogen channel, not before the trap reaches the selected temperature. The delay time served to flush out the atomizer/trap device to prevent non-specific absorption at wavelengths of the As and Se lines used; this is observed when traces of molecular oxygen are present in the inlet arm of the device.

In summary, the conditions which must be optimized are carrier Ar flow rate and trap temperature in the trapping step, and carrier Ar flow rate, hydrogen flow rate, and trap temperature in the volatilization step. For simplicity, the carrier Ar flow rate of 75 mL min^{-1} (the optimum for maximum sensitivity in the direct-transfer mode) was also chosen for both steps of the collection mode. Consequently, only one condition, trap temperature, had to be optimized in

the trapping step, in contrast with the volatilization step which required optimization of both hydrogen flow rate and trap temperature. Qualitatively, the efficiency and rate of volatilization increases when both of these are increased; hydrogen flow reduces sensitivity, however, and the thermal durability of quartz limits the maximum trap temperature to approximately 1150 °C. Univariate optimization searches were performed with the preconcentration efficiency as the figure of merit. The effect on breakthrough signals of trap temperature in the trapping step of collection mode (Experimental section) was checked first to estimate the optimum trapping temperature. The effect of volatilization temperature (volatilization curve) was thus determined at the optimum trapping temperature and for a hydrogen flow rate close to that previously found for Sb [7]. The signal of additional volatilized analyte (at the optimum volatilization temperatures of 920 °C and 570 °C, respectively, for determination of As and Se—Experimental section) was monitored for individual volatilization temperatures. Hydrogen flow rate was then optimized at the optimum trapping and volatilization temperatures. Finally, the effect of trapping temperature at the optimum volatilization temperature and the optimum hydrogen flow rate was determined (trapping curve).

In the volatilization step, signals of regular shape were observed; the full width of the peak at half maximum (FWHM) was, typically, 0.8 s for As and 1.0 s for Se under the optimized conditions.

Arsenic

No breakthrough signal was observed in the trap temperature range between ambient and (the maximum checked) 950 °C. The volatilization curve and the effect of volatilization temperature on the signal of additionally volatilized analyte is presented in Fig. 3. Both signals are expressed as fractions of the corresponding signal obtained in the direct-transfer mode and, therefore, the respective signal areas are expressed in Fig. 3 as the preconcentration efficiency (see above). The figure shows that a volatilization temperature of approximately 650 to 800 °C is optimum. It should be emphasized that the sum of peak areas of the signal of volatilized analyte with the signal of additionally volatilized analyte obtained for any individual volatilization temperature is 44 to 47% for volatilization temperatures between ambient and 800 °C. This shows the analyte which can be trapped, volatilized, and atomized is released from the trap in the volatilization step at temperatures of approximately 650 to 800 °C. At lower volatilization temperatures some of the analyte is retained in the trap and subsequently released and atomized in the additional volatilization step. For a maximum volatilization temperature of 950 °C, the "total efficiency" is slightly lower—40±2%. This is probably because of losses of analyte during the 5-s delay (see above reasons for the delay) between switching off the oxygen channel and opening the hydrogen channel, when the trap is heated to the volatilization temperature. The optimum hydrogen flow rate is >50 mL min^{-1} (Fig. 4). Figure 5 shows there is a broad plateau in the dependence of preconcentration efficiency on trapping temperature between ambient and approximately 800 °C. At the maximum trapping temperature of 950 °C, the efficiency decreases slightly.

All the graphs shown in Figs. 3 to 5 indicate that although all the relevant experimental conditions were optimized the preconcentration efficiency is approximately 50%. In principle, this could be because of:

1. 50% losses in the trapping step;
2. 50% atomization efficiency in the volatilization step; or
3. 50% of analyte which is not released from the trap even at the maximum volatilization temperature.

The observation of no breakthrough signals would be compatible with the first possibility only if it is assumed that 50% of the arsenic oxide species (presumably formed in the flame from arsine in the trapping step) are transported through the optical tube of the atomizer/trap device without

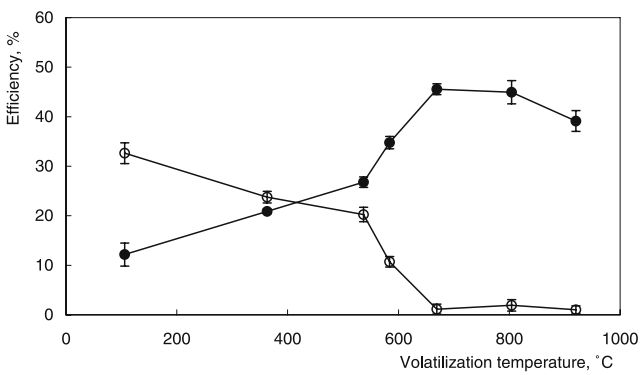

Fig. 3 Volatilization curve (*filled circles*) and additional volatilization step at 920 °C (*empty circles*) for As; trapping temperature 150 °C; volatilization hydrogen flow rate 100 mL min^{-1}

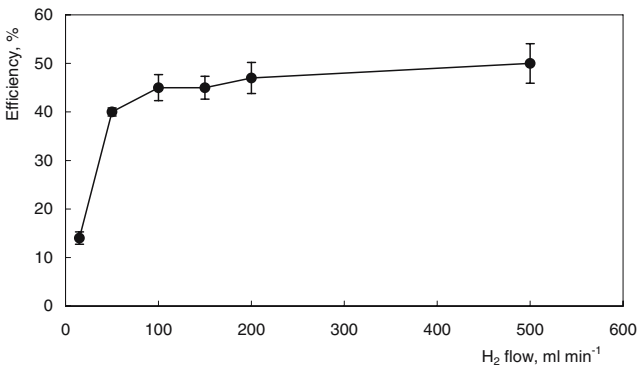

Fig. 4 Hydrogen flow optimization in the volatilization step for As; trapping temperature 150 °C; volatilization temperature 800 °C

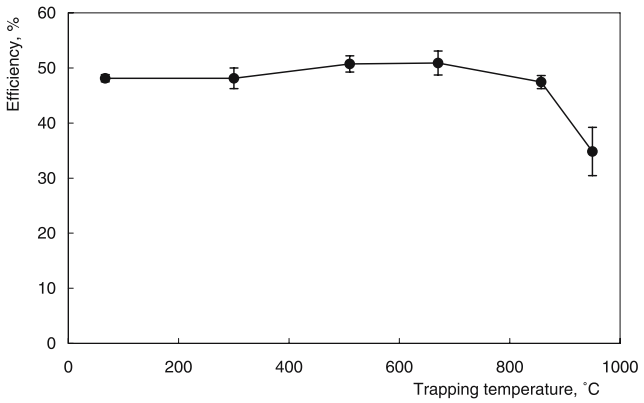

Fig. 5 Trapping curve for As; volatilization temperature 800 °C; volatilization hydrogen flow rate 100 mL min^{-1}

being atomized. Then third possibility can be discounted because no evidence of accumulation of As in the inlet arm was observed. The experimental data presented are not sufficient to decide between the first two possibilities, however.

Selenium

Although substantial breakthrough signals were observed for trap temperatures above 400 °C, a significant fraction of analyte breaks through the trap even in the "low temperature region" between ambient and 330 °C (Fig. 6). The optimum hydrogen flow rate was approximately 50 mL min^{-1}. Lower flow rates resulted in unacceptably broad peaks (full width at half maximum approx. 10 s). Increasing the flow rate to 100 mL min^{-1} did not change the preconcentration efficiency but the sensitivity decreased (see above). The volatilization curve and the effect of volatilization temperature on the signal of additionally volatilized analyte is presented in Fig. 7. The optimum volatilization temperature range was approximately 570–650 °C. The sum of peak areas of the signal of the volatilized analyte and the signal of additionally volatilized

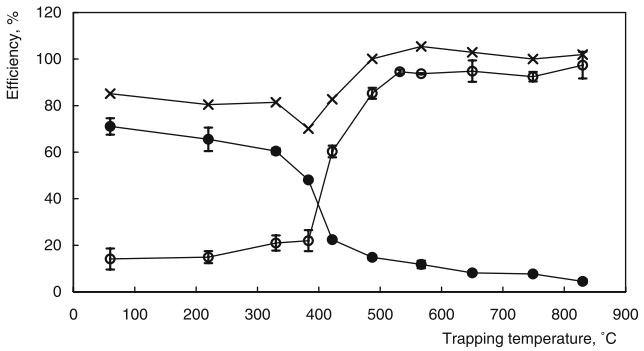

Fig. 6 Trapping curve (*filled circles*), breakthrough signal (*empty circles*), and summed signal (*crosses*) for Se; volatilization temperature 570 °C; volatilization hydrogen flow rate 50 mL min^{-1}

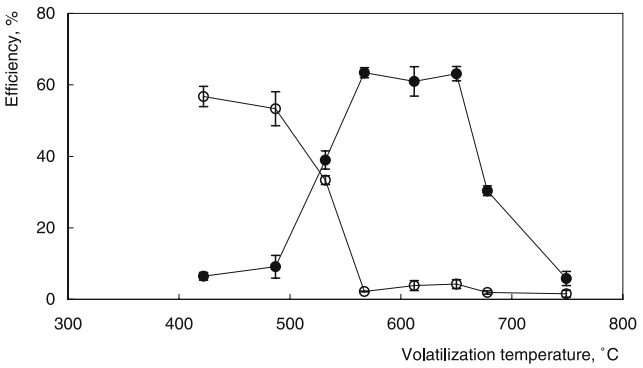

Fig. 7 Volatilization curve (*filled circles*) and additional volatilization step at 570 °C (*empty circles*) for Se; trapping temperature 80 °C; volatilization hydrogen flow rate 50 mL min^{-1}

analyte for any individual volatilization temperature was 65 to 70% for volatilization temperatures between ambient and 650 °C. This shows the analyte which can be trapped, volatilized, and atomized is released from the trap in the volatilization step at temperatures of approximately 570–650 °C. At lower volatilization temperatures some of the analyte is retained in the trap through the volatilization step to be subsequently released and atomized in the additional volatilization step. For volatilization temperatures above 650 °C the "total efficiency" decreases dramatically (Fig. 7). The reason for this decrease is the same as that discussed above for arsenic—analyte losses during the 5 s delay between switching off the oxygen channel and opening the hydrogen channel, when the trap is heated to the volatilization temperature. Figure 6 shows that even the slight trapping temperature increase, from ambient to 200 °C, negatively affects the trapping efficiency. At a trapping temperature of 650 °C, the efficiency falls below 10%.

The graphs in Figs. 6 and 7 show that the preconcentration efficiency is approximately 70% when all the relevant experimental conditions are optimized (trapping temperature 80 °C, volatilization temperature 570 °C, hydrogen flow rate 50 mL min^{-1}). Approximately one half of the 30% loss can be attributed to the analyte breaking through the trap in the trapping step (Fig. 6). The rest of the analyte (approx. 15%) is probably lost in the 5-s delay time serving to flush the atomizer/trap device of oxygen when the trap temperature is at the optimum volatilization temperature of 570 °C.

The sum of the relative peak areas of the signal of volatilized analyte and the signal of breaking through analyte obtained at trapping temperatures of 490 °C and above, when preconcentration efficiency is low, is approximately 100% (summed signals in Fig. 6). This suggests that, in contrast with the arsine trapping and As atomization discussed above, all analyte delivered to the trap is eventually transported to the optical tube and all Se species present are atomized there with efficiency approaching

100%. The decrease to 85% of the summed signals for the lower trapping temperature (Fig. 6) is because of the above mentioned loss of analyte during the 5-s delay time. This loss is not significant in the summed signals for higher trapping temperatures, because the fraction of trapped analyte is below 10% for temperatures above 600 °C when almost all analyte breaks through the trap in the collection step.

Conclusions

In the trapping step, with excess oxygen, the analyte hydrides are converted to oxides which are retained at the trap because of interaction with the quartz surface. In the volatilization step, at the elevated surface temperature of the quartz and under excess hydrogen, the interactions between the analyte oxides and the quartz surface probably become weaker and/or the analyte oxides are reduced by hydrogen. Analyte species are thus volatilized and transported to the optical arm of the multiatomizer to be atomized there.

The reasonably "flat" character, at least near the optimum settings, in the graphs shown in Figs. 3 to 7 shows that the collection-mode procedures for As and Se are fairly robust. This indicates the potential of this approach for preconcentration of arsine and selenium hydride in analytical practice. Under the optimized conditions, rapid analyte volatilization is achieved, as is apparent from the narrow peaks (FWHM 0.8 to 1.0 s—see above) comparable with recently published values for Sb and Bi (0.8 s [9] and 0.6 s [10], respectively). In addition, as illustrated in Figs. 3 and 7, respectively, carryover for arsenic and selenium is negligible under the optimized conditions. The capacity of the trap estimated from the calibration plots is not lower than 4 ng analyte which is sufficient for ultratrace analysis.

Experiments are in progress to find the explanation for and, subsequently, to improve the 50% preconcentration efficiency for As. For Se, the reasons for the 70% preconcentration efficiency were found. The objective of forthcoming experiments is to prevent losses in both the trapping and volatilization steps.

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References

1. Dědina J, Tsalev DL (1995) Hydride generation atomic absorption spectrometry. Wiley, Chichester
2. Matusiewicz H, Sturgeon RE (1996) Spectrochim Acta B 51:377–397
3. Dočekal B, Marek P (2001) J Anal At Spectrom 16:831–837
4. Barbosa F, de Souza SS, Krug FJ (2002) J Anal At Spectrom 17:382–388
5. Cankur O, Ertas N, Ataman OY (2002) J Anal At Spectrom 17:603–609
6. Korkmaz DK, Ertas N, Ataman OY (2002) Spectrochim Acta B 57:571–580
7. Korkmaz DK, Dědina J, Ataman OY (2004) J Anal At Spectrom 19:255–259
8. Korkmaz D, Demir C, Aydin F, Ataman OY (2005) J Anal At Spectrom 20:46–52
9. Kratzer J, Dědina J (2005) Spectrochim Acta B 60:859–864
10. Kratzer J, Dědina J (2006) J Anal At Spectrom 21:208–210
11. Dědina J, Matoušek T (2000) J Anal At Spectrom 15:301–304
12. Matoušek T, Dědina J, Selecká A (2002) Spectrochim Acta B 57:451–462
13. Matoušek T, Johansson M, Dědina J, Frech W (1999) Spectrochim Acta B 54:631–643

Kompaktní zařízení pro prekoncentraci a atomizaci hydridotvorných prvků pro jejich stanovení atomovou absorpční spektrometrií

Autoři

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Oblast techniky

Vynález se týká nové, kompaktní, konstrukce zařízení pro prekoncentraci prvků tvořících těkavé hydridy a následnou atomizaci analytu za účelem ultracitlivého stanovení těchto prvků atomovou absorpční spektrometrii (AAS).

Dosavadní stav techniky

Atomová absorpční spektrometrie s generováním hydridů (HG-AAS) je dobrým příkladem rutinně používané analytické metody, neboť je nenáročná na pořizovací a provozní náklady, avšak robustní, rychlá, citlivá a selektivní. Tato technika je přehledně zpracována např. v monografii [J. Dědina a D. L. Tsalev: Hydride Generation Atomic Absorption Spectrometry, Wiley, Chichester, 1995]. Navíc jsou prvky stanovitelné HG-AAS důležité z hlediska monitoringu složek životního prostředí (As, Se, Sb, Bi).

K atomizaci hydridů se obvykle používá vyhřívaného atomizátoru vyrobeného obvykle z křemene. Konvenční atomizátor je tvořen přívodním ramenem a optickou trubicí, jejíž osa je totožná s optickou osou spektrometru. Optická trubice je dlouhá 10 až 20 cm a její podstatná část je zvenčí vyhřívaná obvykle na teplotu 900 °C. Přívodní rameno je trubice přitavená k optické trubici obvykle v jejím středu v pravém úhlu. Atomizátor má pak tvar T-trubice, jejíž přívodní rameno slouží k přívodu hydridu unášeného proudem nosného plynu do vodorovně umístěné optické trubice. Konvenční atomizátory trpí závažnými nedostatky, které odstraňuje nový atomizátor hydridů - křemenný multiatomizátor popsaný v patentu [CZ Pat 287635. Dědina, J. a Matoušek, T.: Způsob atomizace těkavých sloučenin, zejména hydridů, stanovovaných prvků pro atomovou absorpční spektrometrii a zařízení k provádění tohoto způsobu. 7.11. 2000] a v článcích [Dědina, J., Matoušek, T.: J. Anal. Atom. Spectrom., 15 301-304, 2000] a [Matoušek, T., J. Dědina, A. Selecká: Spectrochim. Acta Part B, 57 451-462, 2002]. Podstata multiatomizátoru spočívá v tom, že dovnitř optické trubice konvenčního atomizátoru se mnohočetnými miniaturními proudy přivádí kontrolované množství kyslíku.

V poslední době jsou požadována stanovení čím dál nižších koncentračních hladin analytu ve vzorcích. Detekční limity současných analytických technik již nepostačují. Proto je zapotřebí zavést prekoncentrační proceduru, která by měla být pro rutinní použití jednoduchá a časově nenáročná. Inherentní výhodou generování hydridů je snadnost prekoncentrace: v prvním kroku, záchytu, prekoncentrační procedury založené na generováni hydridů je analyt ve formě těkavého hydridu uvolněn z okyseleného kapalného vzorku reakcí s roztokem tetrahydroboratu ($NaBH_4$). Generovaný hydrid je spolu s vodíkem, který je produktem rozkladu $NaBH_4$, veden proudem nosného plynu do prekoncentračního zařízení. V druhém kroku prekoncentrační procedury, uvolnění, po skončení generování hydridu ze vzorku, je analyt z prekoncentračního zařízení uvolněn a veden k atomizaci a detekci metodou AAS.

Jedním z historicky nejstarších přístupů k prekoncentraci hydridotvorných prvků bylo vymrazování v křemenné U-trubici chlazené kapalným dusíkem. Tento způsob trpí závažnými nedostatky - je časově náročný a jeho automatizace je prakticky neproveditelná. Výhodnější je provádět prekoncentraci hydridu přímo v atomizátoru. Donedávna k tomu byly používány

výhradně grafitové atomizátory. Po desetiletí je v analytické praxi široce využívána prekoncentrace hydridů v grafitových atomizátorech. I v současnosti je to nejběžnější způsob prekoncentrace při stanovení ultrastopových koncentrací hydridotvorných prvků. Avšak pořizovací i provozní náklady přístroje s grafitovým atomizátorem jsou vysoké, proto jsou hledány i alternativní přístupy k prekoncentraci hydridů.

Velmi perspektivní je nový přístup k prekoncentraci v atomizátoru: použití trubičky z křemenného skla (křemenné pasti) jako prekoncentračního zařízení pro záchyt hydridů s atomizací analytu v křemenném atomizátoru v druhém kroku prekoncentrační procedury. Byl popsán záchyt plumbanu (PbH_4) v trubičce z křemenného skla s následnou atomizací v konvenčním křemenném atomizátoru [D. Korkmaz, N. Ertas, O. Ataman, Spectrochim. Acta Part B, 57 571-580, 2002]. Tento přístup je ale nepoužitelný pro prekoncentraci většiny hydridotvorných prvků: arsen, antimon, selen, bismut, telur. Důvodem je to, že k uvolnění analytu z pasti je třeba ji zahřát na teplotu, při které jsou stopy molekulárního kyslíku v pasti odstraněny reakcí s vodíkem. Avšak atomizace těkavých forem výše uvedených prvků v konvenčním křemenném atomizátoru je bez stop molekulárního kyslíku nemožná [J. Dědina a D. L. Tsalev: Hydride Generation Atomic Absorption Spectrometry, Wiley, Chichester, 1995].

Tento problém byl vyřešen náhradou konvenčního křemenného atomizátoru multiatomizátorem [D. Korkmaz, J. Dědina, O. Ataman, J. Anal. Atom. Spectrom., 19 255-259, 2004]. Multiatomizátor byl spojený s křemennou pastí (trubičkou z křemenného skla) plastikovou hadičkou. Avšak účinnost prekoncentrace se pohybovala hluboko pod 100 %. Další studie provedené autory této patentové přihlášky prokázaly, že vodík vznikající spontánně při chemickém generování hydridu způsobuje ztráty analytu při záchytu hydridu. Z výsledků následných studií provedených autory vyplynulo, že k účinnému záchytu hydridu a tím i k prekoncentraci analytu v trubičce z křemenného skla dochází jen v nepřítomnosti vodíku. Jediným proveditelným způsobem jak toho dosáhnout je spálení vodíku v stechiometrickém nadbytku kyslíku, v plamínku hořícím na začátku té části aparatury (trubičky z křemenného skla) kde dochází k záchytu. Ke stabilnímu hoření tohoto plamínku dochází jen při této teplotě nad cca 400 °C. Hydrid analytu je za těchto podmínek rozložen a jeho rozkladné produkty, patrně oxidy, interagují s povrchem křemenného skla, kde jsou zachyceny. Po uplynutí prekoncentrační doby je zachycená forma analytu z povrchu křemenného skla uvolněna změnou složení plynné fáze (stechiometrický nadbytek vodíku vůči kyslíku v plynné fázi), např. zvýšením teploty křemenné trubičky.

V případě antimonu a bismutu jsou rozkladné produkty rozkladu jejich hydridů zachyceny na povrchu křemenného skla se 100% účinností i při teplotě nad 900°C. To umožnilo provést záchyt přímo v konvenčním křemenném atomizátoru při teplotě 900°C. K uvolnění a atomizaci analytu v druhém kroku prekoncentrační procedury stačí změnit složení plynné fáze: vypnout přívod kyslíku a zapnout přívod vodíku. Za takových podmínek bylo dosaženo 100% prekoncentrační účinnosti hydridů antimonu [J. Kratzer, J. Dědina: Spectrochim. Acta Part B, 60 859-864, 2005; J. Dědina, J. Kratzer: Způsob prekoncentrace antimonu pro jeho stanovení metodami atomové spektrometrie, PV-2004-854] a bismutu [J. Kratzer, J. Dědina: J. Anal. Atom. Spectrom., 21 208-210, 2006; J. Dědina, J. Kratzer: Způsob prekoncentrace bismutu pro jeho stanovení metodou atomové absorpční spektrometrie, PV 2005 - 761].

Tento přístup je ale nepoužitelný pro prekoncentraci nejdůležitějších hydridotvorných prvků (arsen, selen, telur, cín), protože produkty rozkladu jejich hydridů nejsou při teplotě křemenného atomizátoru zachycené na povrchu křemenného skla. K prekoncentraci těchto hydridotvorných prvků je proto nutné použít obdobné uspořádání jako to popsané ve výše citované práci [D. Korkmaz, J. Dědina, O. Ataman, J. Anal. Atom. Spectrom., 19 255-259,

2004]: křemennou past, oddělenou od multiatomizátoru, jejíž teplotu lze ovládat nezávisle na teplotě multiatomizátoru.

Podstata vynálezu

Experimentální studie provedené autory prokázaly, že produkty, vzniklé rozkladem hydridů některých z nejdůležitějších hydridotvorných prvků (arsen, selen, telur, cín) v plamínku, nejsou zachycené na povrchu křemenného skla ani při teplotě cca 400 °C. Toto určitě platí v případe selenu. Předběžné experimenty nevyloučily, že by to mohl být i případ jiných výše uvedených hydridotvorných prvků. Pro účinný záchyt analytu v křemenné pasti v prvním kroku prekoncentrační procedury je proto třeba zajistit i, kromě výše zdůvodněného odstranění vodíku, aby teplota pasti byla v tomto kroku co nejnižší, nejlépe aby odpovídala laboratorní teplotě. Dále bylo prokázáno, že kvůli bezeztrátovému transportu analytu v druhém kroku prekoncentrační procedury je žádoucí, aby past byla co nejblíže optické trubici multiatomizátoru a aby teplotní profil mezi pastí a vyhřívanou optickou trubicí multiatomizátoru nevykazoval minimum.

Požadavky shrnuté v předchozím odstavci jsou splněny konstrukcí kompaktního zařízení pro prekoncentraci a atomizaci, jehož podstata spočívá v tom, že (1) jako pasti je využito vstupní rameno multiatomizátoru a v tom, že (2) kyslík, nutný pro spálení vodíku v prvním kroku prekoncentrační procedury, je přiváděn na začátek pasti kapilárou o vnitřním průměru 0,53 mm nebo méně.

Využití vstupního ramene multiatomizátoru jako pasti (a) zkracuje na minimum vzdálenost mezi pastí a optickou trubicí multiatomizátoru a (b) odstraňuje v druhém kroku prekoncentrační procedury teplotní minimum mezi pastí a vyhřívanou optickou trubicí multiatomizátoru.

Přivádění kyslíku kapilárou na začátek pasti v prvním kroku prekoncentrační procedury vede k tomu, že na vyústění této kapiláry hoří kyslíko-vodíkový plamínek. Pro teploty pasti nižší než 400-500 °C dojde v optické trubici multiatomizátoru, která je stabilně vyhřívána na atomizační teplotu 900 °C, ke vznícení směsi vodíku a kyslíku a plamínek proskočí na vyústění křemenné kapiláry. Plamínek nutný pro rozložení hydridu analytu a pro spálení vodíku zde hoří stabilně a při jakékoliv teplotě pasti, i v případě, že past není zvenku vyhřívána. Úsek vstupního ramene multiatomizátoru mezi plamínkem a optickou trubicí multiatomizátoru pak slouží jako velice účinná past, jejíž teplota může být regulována a to i v prvním kroku prekoncentrační procedury, kdy na začátku pasti hoří plamínek, v širokých mezích: od laboratorní teploty až po 1000 °C.

Výhodou popsaného kompaktního zařízení pro prekoncentraci a atomizaci je flexibilita a univerzálnost. Flexibilita spočívá v možnosti ovládat teplotu pasti v širokých mezích v obou krocích prekoncentrační procedury a to při zachování nutné podmínky pro účinný záchyt v prvním kroku: spálení vodíku. Univerzálnost spočívá v tom, že na rozdíl od výše citovaných postupů a zařízení, které jsou vhodné pro prekoncentraci jen některých hydridotvorných prvků, kompaktního zařízení pro prekoncentraci a atomizaci lze v principu použít pro prekoncentraci všech hydridotvorných prvků. Předběžné experimenty prokázaly, použitelnost této aparatury pro As, Se, Sb a Bi.

Oproti běžně používané prekoncentraci hydridů v grafitovém atomizátoru je metoda prekoncentrace v aparatuře podle vynálezu jednodušší a pořizovací i provozní náklady jsou desetkrát až stokrát nižší a očekávané detekční limity výrazně lepší.

Příklady provedení vynálezu

Příklad provedení vynálezu je blíže osvětlen pomocí výkresu, na kterém je schematicky znázorněno kompaktní zařízení pro prekoncentraci a atomizaci. Konstrukce zařízení podle vynálezu je založena na multiatomizátoru s modifikovaným vstupním ramenem. Modifikované vstupní rameno slouží jako past pro záchyt hydridů v prvním kroku prekoncentrační procedury a pro uvolnění analytu v druhém kroku. Zařízení je vyrobeno z křemenného skla a sestává se z přívodního ramene (1), do něhož je vložena křemenná kapilára (2) a z optické trubice (3), jejíž osa je totožná s optickou osou spektrometru.

Centrální část (4) optické trubice (3), dlouhá 150 mm, je tvořena dvěma koncentrickými trubicemi, vnitřní (5) (vnitřní průměr 6 mm, délka 150 mm) a vnější (6) (vnější průměr 14 mm, délka 185 mm). Vnitřní koncentrická trubice (5) má na svém obvodu sedm párů protilehlých otvorů (7) o průměru 0,5 mm uspořádaných jak zobrazeno na výkresu. Vzdálenost mezi jednotlivými páry je 15 mm. Mezi oběma koncentrickými trubicemi (5,6) je dutina (8), do které vedou přívody (9). Okrajové části (10) optické trubice (vnitřní průměr 17 mm, délka 17 mm) mají jednoduchou stěnu. Přívody (9) slouží pro dávkování vzduchu do mezikruží mezi vnější a vnitřní optickou trubici. Vzduch pak vstupuje otvory ve vnitřní optické trubici do její vnitřní části, kterou prochází záření ze zdroje AAS spektrometru. Centrální část optické trubice multiatomizátoru je vyhřívána elektrickou odporovou pícku na atomizační teplotu 900 °C.

Přívodní rameno multiatomizátoru (1) o světlosti 2 mm, vnějším průměru 4 mm a délce 80 mm je přitaveno k optické trubici (3) v jejím středu v pravém úhlu. Část přívodního ramene v délce 60 mm od jeho spojení s optickou trubicí je krytá spirálkou z odporového drátu (11) (kanthal, délka ca 400 mm, 4,17 Ω m^{-1}, průměr drátu 0,65 mm). Volbou napětí 0-80 V je v přívodním rameni dosažena teplota v intervalu 25-1100 °C. Do podélné osy přívodního ramene (1) atomizátoru je vložena křemenná kapilára (2) o světlosti 0,5 mm, jejíž konec je vzdálen 55 mm od spojení přívodního ramene a optické trubice, tj. část konce kapiláry v délce 5 mm je již kryta odporově vyhřívanou spirálou (11). Tato křemenná kapilára (2) je vycentrována v přívodním rameni (1) pomocí polypropylenové T- spojky (12). Kapilára (2) je připojena k přívodu kyslíku z tlakové láhve (13). Přívodní kanál (14) připojený pomocí T-spojky (12) slouží buď k zavádění plynů z generátoru hydridů v kroku záchytu prekoncentrační procedury, nebo k přívodu vodíku z tlakové láhve v druhém kroku (uvolnění).

Funkce zařízení:

V kroku záchytu je nejprve nastavena teplota přívodního ramene zvolená pro záchyt. Nejdéle za 60 s se teplota ustálí na zvolené hodnotě. Pak je spuštěno kontinuální generování hydridu a současně je do kapiláry (2) přiváděn kyslík z tlakové láhve (13) o průtoku 10 $ml.min^{-1}$. Generovaný hydrid analytu v proudu argonu (75 $ml.min^{-1}$) s příměsí vodíku (z rozkladu tetrahydroboratu, cca 15 $ml.min^{-1}$) je veden z generátoru kanálem (14). Stechiometrickému poměru kyslíku odpovídá 7,5 $ml.min^{-1}$, zvolený průtok kyslíku 10 $ml.min^{-1}$ tedy bezpečně zaručuje stechiometrický nadbytek kyslíku vůči vodíku v přívodním rameni (1). Za těchto podmínek hoří plamínek na konci kapiláry (2) pro jakoukoli zvolenou teplotu přívodního ramene (25-1100 °C). Při teplotách přívodního ramene (1) 25-400 °C dojde k zažehnutí plamínku v optické trubici vyhřívané na 900 °C a k jeho okamžitému proskočení na konec kapiláry (2) přivádějící kyslík a jeho stabilnímu hoření na tomto místě. Krok záchytu je ukončen vypnutím generování hydridu. Tím je ukončen i proud vodíku a plamínek zhasne.

V druhém kroku prekoncentrační procedury je nastavena teplota přívodního ramene pro uvolnění analytu. Nejdéle za 60 s se teplota ustálí na zvolené hodnotě. Zachycený analyt je z přívodního ramene uvolněn uzavřením přívodu kyslíku (13) a následným otevřením přívodu vodíku kanálem (14). Tím je analyt zachycený v přívodním rameni (1) najednou uvolněn a

transportován do vnitřní optické trubice (5), kde je atomizován. Ideální atomizační podmínky jsou zajištěny přívodem 25 $ml.min^{-1}$ vzduchu do přívodů (9).

Popsané kompaktní prekoncentrační a atomizační zařízení bylo použito k prekoncentraci prvků, které nelze prekoncentrovat v konvenčním křemenném atomizátoru, t.j. arsenu a selenu. Pro arsen byly nalezeny tyto optimální podmínky: teplota záchytu 80-700 °C, teplota uvolnění 650-800 °C, průtok vodíku v kroku uvolnění 100 $ml.min^{-1}$. V případě selenu byly nalezeny tyto optimální podmínky: teplota záchytu 80-300 °C, teplota uvolnění 550-650 °C, průtok vodíku v kroku uvolnění 50 $ml.min^{-1}$. Prekoncentrační účinnost se pohybovala kolem 50 % pro As a 70 % pro Se. Popsané kompaktní prekoncentrační a atomizační zařízení - past integrovaná s multiatomizátorem lze použít i pro prekoncentraci antimonu a bismutu.
Pro antimon byly nalezeny tyto optimální podmínky: teplota záchytu 600-1100 °C, teplota uvolnění 900-1100 °C, průtok vodíku v kroku uvolnění 15 $ml.min^{-1}$. V případě bismutu byly optimální tyto podmínky: teplota záchytu 700 -1000 °C, teplota uvolnění rovněž 700-1000 °C, průtok vodíku v kroku uvolnění 100 $ml.min^{-1}$. V obou případech byla účinnost prekoncentrace 100%.

Průmyslová využitelnost

Kompaktní zařízení pro prekoncentraci a atomizaci podle vynálezu lze použít pro ultracitlivé AAS stanovení prvků tvořících těkavé hydridy, zejména As, Sb, Se, Sn, Pb, Te a Bi ve všech typech vzorků, např. klinických, potravinářských, životního prostředí a průmyslových.

PATENTOVÉ NÁROKY

Zařízení pro prekoncentraci a atomizaci hydridotvorných prvků za účelem jejich stanovení atomovou absorpční spektrometrií na principu multiatomizátoru **vyznačující se** tím, že past pro záchyt hydridů a uvolnění analytu je tvořena vstupním ramenem (1) multiatomizátoru, do něhož je v podélné ose vložena křemenná kapilára (2) pro přívod kyslíku, přičemž vyústění kapiláry je ve vzdálenosti 50 až 100 mm od optické trubice (3) multiatomizátoru.

Anotace

Kompaktní zařízení pro prekoncentraci a atomizaci hydridotvorných prvků pro jejich stanovení atomovou absorpční spektrometrií

Zařízení pro prekoncentraci a atomizaci hydridotvorných prvků za účelem jejich stanovení atomovou absorpční spektrometrií. Konstrukce zařízení je založena na multiatomizátoru s modifikovaným vstupním ramenem do něhož je vložena křemenná kapilára. Na vyústění kapiláry hoří v prvním kroku prekoncentrační procedury plamínek spalující vodík v přebytku kyslíku. Úsek vstupního ramene za plamínkem slouží jako velice účinná past pro záchyt rozkladných produktů hydridů, jejíž teplota může být regulována v širokých mezích od laboratorní teploty výše. V druhém kroku prekoncentrační procedury je zachycený analyt bezeztrátově uvolněn a transportován do části zařízení sloužící pro atomizaci.

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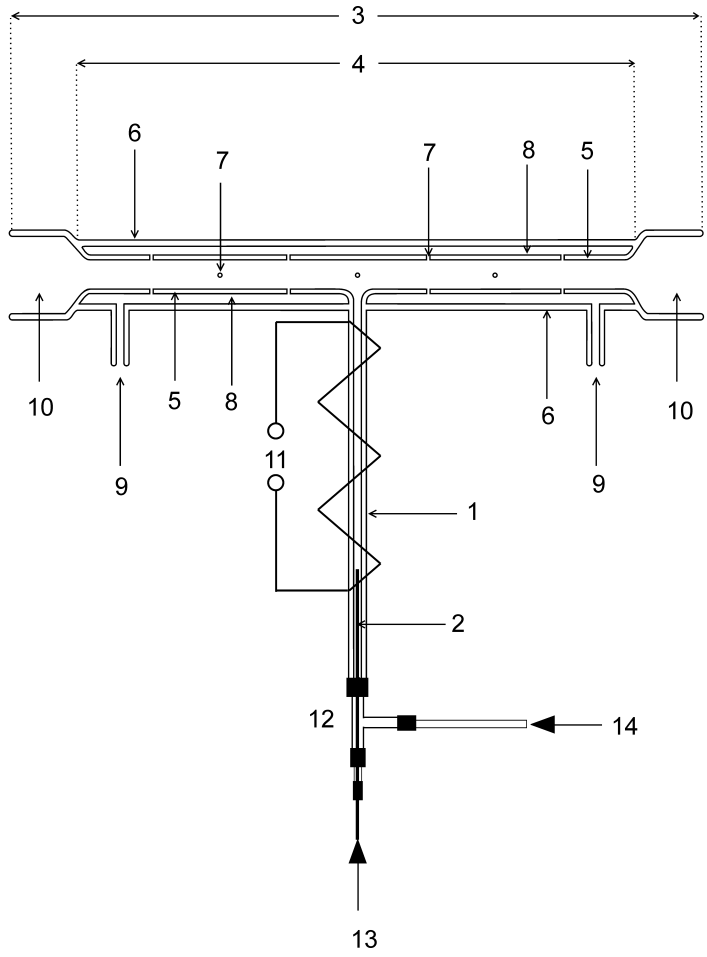
Obrázek:



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Stibine and bismuthine trapping in quartz tube atomizers for atomic absorption spectrometry — Method optimization and analytical applications ☆

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ABSTRACT

The compact trap-and-atomizer device was employed to trap stibine and bismuthine, and subsequently to volatilize collected analyte and atomize it for atomic absorption spectrometric detection. The device is actually the multiple microflame quartz tube atomizer (multiatomizer) with inlet arm modified to serve as the trap and to accommodate the oxygen delivery capillary employed for burning out hydrogen during the trapping step. The optimization of Sb and Bi collection in the device is presented based on a study of the influence of relevant experimental parameters on preconcentration efficiency of both analytes. The parameters studied were: (1) trap temperature during trapping and (2) hydrogen flow rate and (3) trap temperature during volatilization and (4) the stability of the trapped analyte species. Under optimized conditions, the preconcentration efficiency was 100% for both analytes. The trap-and-atomizer device can be replaced by the simple conventional externally heated quartz tube atomizer without any trap as demonstrated on the ultratrace antimony determination in groundwater reference material and mineral water samples. The interference of other hydride forming elements on Bi in-situ collection in the conventional externally heated quartz tube atomizer was investigated.

1. Introduction

Hydride generation coupled to atomic absorption detector (HG-AAS) [1] is due to its simplicity, selectivity and sensitivity a powerful and favorite analytical technique for the trace determination of many important analytes such as As, Se, Sb, Bi, Pb, Sn, etc. Analyte conversion to the gaseous hydride has two advantages — firstly, analyte is separated from the matrix and secondly, analyte can be preconcentrated from the gaseous phase. Employing the preconcentration step, the HG-AAS detection limit can be pushed down to meet the requirements of the ultratrace analysis being often inevitably requested for hydride forming elements either by law regulations or by the customers.

The analyte hydride can be easily preconcentrated either in a special collection device (usually by cryogenic trapping) or directly in the atomizer. Cryogenic trapping is time consuming and considerable effort is involved [1]. In contrast, in-atomizer trapping of hydrides is the most convenient way of analyte collection. It can take place on the surface of the atomizer segment that is aligned in the optical path of the instrument. Then the terminology "in-situ" collection, suggested in one of the first papers on in-atomizer collection in graphite furnaces [2], accurately reflects the nature of the process. Until recently, the only widely used approach to in-atomizer collection was in-situ collection in graphite furnaces [3] but then procedures based on collection on metal [4–7] and quartz [8–11] surfaces emerged.

An analytically useful compact quartz trap-and-atomizer device for hydride trapping and subsequent analyte volatilization/atomization of two important analytes — As and Se has been described recently [12]. The device is actually the multiple microflame quartz tube atomizer (multi-atomizer) [13,14] with its inlet arm modified to serve as the trap and to accommodate the oxygen delivery capillary employed for burning out hydrogen during the trapping step. Since the trapping zone (inlet arm) is not in the optical arm of the instrument but it is an integral part of the atomizer, the process should be termed "in-atomizer collection". The aim of the current contribution was (1) to find the optimum collection parameters for Sb and Bi in the trap-and-atomizer device and to compare the parameters with those found previously for As and Se in the same setup, (2) to employ the optimum parameters for Sb and Bi hydride trapping in conventional quartz tube atomizers (QTA) for routine analytical applications; the reason is better availability of QTA compared to the trap-and-atomizer device.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade or higher purity. Deionized water (Ultrapure, Watrex, USA) was used to prepare solutions.

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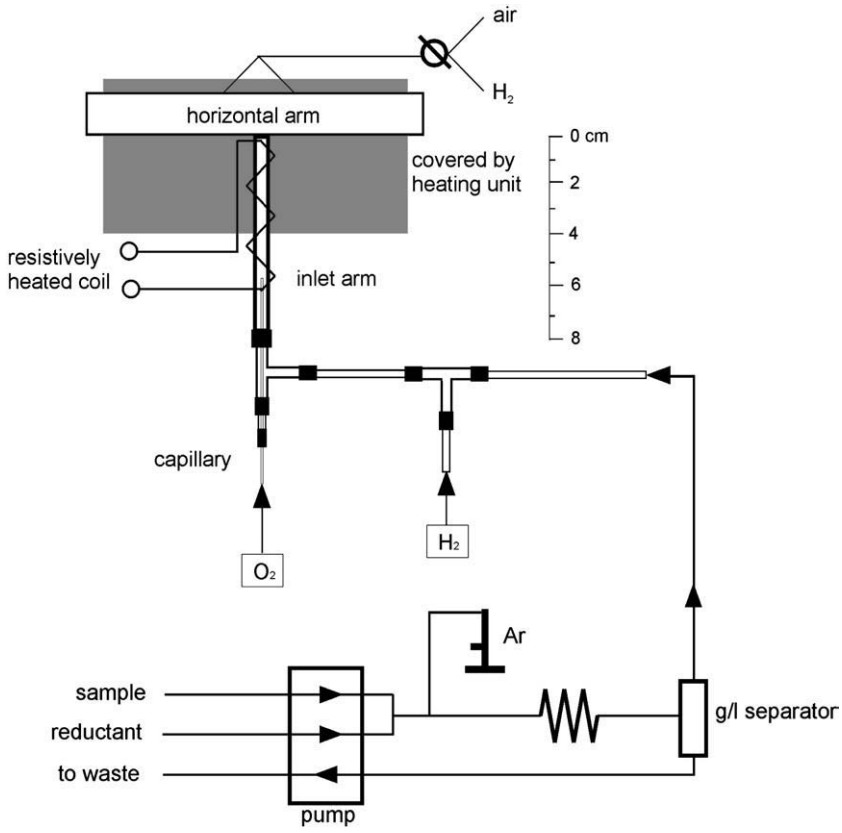

Fig. 1. Schematic diagram of the apparatus.

Working 2 ng ml^{-1} Sb and 1.5 ng ml^{-1} Bi standards were prepared from 1 mg ml^{-1} stock solutions (BDH Laboratory Reagents) by dilution in 1.0 mol l^{-1} HCl (Merck). The blank was 1.0 mol l^{-1} HCl. The reductant was 0.5% (m/v) solution of $NaBH_4$ (Sigma) in 0.4% (m/v) KOH (Merck) filtered after preparation and stored frozen.

For interference studies, the As(III), Se(IV), Te(IV), Sb(III), Sn(II), Pb(II) and Ge(IV) 1 mg ml^{-1} stock solutions (BDH Laboratory Reagents) were used to prepare the working solutions in 1 mol l^{-1} HCl and containing always 1 ng ml^{-1} Bi as analyte and from 10 to 10 000 ng ml^{-1} of the interferent.

Groundwater reference material (trace elements/metals) Grumo-K (Eurofins, Denmark) with certified content of 0.54 ± 0.19 ng ml^{-1} Sb and mineral water were used as testing materials. The standard and sample were prepared in 1 mol l^{-1} HCl and pre-reduced 30 min before the analysis by adding solid KI (p.a., Lachema Brno, Czech Republic) and ascorbic acid (p.a., Farmakon Olomouc, Czech Republic) to reach their final 8% and 0.5% (m/v), respectively, content in the sample solution.

2.2. Spectrometer and hydride generator

The Varian model SpectrAA300/400 atomic absorption spectrometer equipped with hollow cathode lamps was employed without background correction. An in-house made, continuous flow hydride generation system similar as described in ref. [15] was employed (see Fig. 1 for the schema of the hydride generator). A 3 ml inner volume gas–liquid separator with a forced outlet (see ref. [15] for detailed description) was used. Flow rate of carrier argon was controlled by a rotameter (Cole Parmer). Mass flow controllers (Cole Parmer) were used for all the other gases (see Table 1 for spectrometer, pump and gas controllers operation parameters).

Table 1
Operation parameters

Spectrometer			Pump flow rates	(ml min^{-1})
Band pass (nm)		0.2	Sample	4.0
Lamp current (mA)		10	Reductant	1.2
Wavelength (nm)	Sb	217.6	Waste	6.0
	Bi	223.1		
Gas flow rates		(ml min^{-1})	Temperature program	(optimum, °C)
Carrier Ar in both steps		75	Trapping step	870
Outer gas (air or H_2) in the trapping step		25	Volatilization step	870
Outer gas (air) in the volatilization step		25	Additional volatilization step	870
O_2 in the trapping step (capillary)		10		
H_2 in the volatilization step	for Sb	75		
	for Bi	100		

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Either the blank or the standard solution was introduced to the sample channel. The flow rate of H_2 evolved from $NaBH_4$ decomposition was calculated to be around 15 ml min^{-1}. The flow rate of the Ar carrier was kept constant at 75 ml min^{-1} in all experiments.

2.3. Trap-and-atomizer device

The trap-and-atomizer device was the modified T-shaped multiatomizer (see Fig. 1 for the schema of the device and hydride generator). The horizontal arm of the device was made of two concentric tubes: the inner (optical) one was evenly perforated with 14 holes. A flow of gas (outer gas) was introduced from the sides into the cavity between the two tubes of the horizontal arm and then passed through the holes into the optical tube. If not mentioned otherwise 25 ml min^{-1} air was employed as the outer gas flowing continuously throughout the whole procedure (see Section 2.4 Procedure). When explicitly stated, 25 ml min^{-1} of hydrogen was introduced as the outer gas during the trapping step of the whole procedure (see Section 2.4). The commercial heating unit with temperature control produced by RMI (Lázně Bohdaneč, Czech Republic) was used for heating the horizontal arm to 900 °C.

The inlet arm of the device, resistively heated independently of the horizontal arm and allowing to reach temperature inside the inlet arm from 80 to 1100 °C, served as the trap. A deactivated fused silica capillary (Supelco, 0.53 mm i.d.) centered within the inlet arm served for the oxygen delivery in the first (trapping) step of the collection procedure (see Section 2.4). For more detailed description of the apparatus see Ref. [12].

The trap temperature was measured when the oxygen channel (Fig. 1) was closed, i.e. in the absence of the microflame, by a thermocouple approximately 5 cm from the T-junction, close to the tip of the oxygen delivery capillary. The influence of the carrier gas composition and flow rate in the employed range on the trap temperature was negligible. The microflame burning in the trap during the trapping step (see below) did not influence the temperature considerably as illustrated by the (outer) surface temperature of the trap being well below 100 °C for trap externally unheated and microflame burning.

2.4. Procedure

Measurements were performed either in the collection mode or in the direct transfer mode. The exact description of the both procedure modes can be found in Ref. [12].

The *collection mode* procedure consisted of two steps: trapping – analyte is trapped in the inlet arm of the trap-and-atomizer device; volatilization – trapped analyte is released and transferred into the optical arm of the trap-and-atomizer device and atomized there.

Trapping step:

The inlet arm heating was set to the actual trapping temperature. It took up to 60 s to heat the inlet arm up from the ambient temperature. 10 ml min^{-1} O_2 was delivered through the oxygen channel to the capillary in the inlet arm. A standard was introduced to the sample channel of the hydride generator for 30 s then it was replaced by the blank for 30 s to flush the system. The reason for 30 s flushing of the hydride generator by the blank was to ensure all the analyte from the apparatus was delivered into the trap. The introduction of oxygen in the stoichiometric excess over 15 ml min^{-1} hydrogen, evolved from $NaBH_4$ decomposition, resulted in an ignition of a flame burning at the tip of the capillary. The pump was stopped at the end of trapping step. If explicitly stated, hydrogen at the flow rate of 25 ml min^{-1} was introduced as the outer gas into the cavity between both tubes of the horizontal arm during the trapping step and the signal of analyte breaking through the trap and atomized in the optical tube was recorded. Although there is the oxygen excess over hydrogen in the inlet arm, employing hydrogen as the outer gas enables to reach hydrogen excess over oxygen in the optical arm. This is necessary to detect the "breakthrough" signal by AAS. The "breakthrough" signal integration was thus performed for 90 s beginning at the start of the standard introduction.

Volatilization step:

The inlet arm heating was changed to the actual volatilization temperature. After 60 s the steady state temperature was reached. To volatilize collected analyte species, the oxygen channel was closed and the hydrogen channel was opened immediately. Simultaneously with opening the hydrogen channel, the signal of volatilized analyte atomized in the optical tube was recorded and integrated for 15 s. There was no change in the flow rate of outer gas.

If explicitly stated, an additional volatilization step was introduced: The oxygen channel was opened and the inlet arm temperature was changed to 870 °C. After 60 s when the steady state temperature was reached, the volatilization procedure described above was repeated and the signal of additionally volatilized analyte was recorded and integrated for 15 s. It took up to 60 s to cool down the inlet arm to the ambient temperature.

In the *direct transfer mode*, the inlet arm was unheated, the oxygen channel was closed, the hydrogen channel was open, the peristaltic pump was on and the signal of analyte atomized in the optical tube was continuously monitored. Air was employed as the outer gas. Direct transfer mode was used as a reference signal for estimation of the preconcentration efficiency of the collection mode. Standard solution concentration, sample introduction time as well as the hydrogen flow rate were strictly kept the same in both, the direct transfer mode and volatilization step of the collection mode to enable estimation of the preconcentration efficiency by comparing respective peak areas. The preconcentration efficiency (efficiency) E, defined as the overall efficiency of trapping, volatilization and atomization, is calculated as the ratio of the peak area obtained in the volatilization step of the collection mode to the peak area obtained in the direct transfer mode.

Analogously, the "breakthrough" signal can be quantified employing the direct transfer mode. The inlet arm was heated to the actual trapping temperature, the oxygen channel was open, the hydrogen channel was closed, the peristaltic pump was on and the signal of analyte atomized in the optical tube was continuously monitored. 25 ml min^{-1} H_2 was employed as the outer gas. The "breakthrough" efficiency B is calculated as the ratio of peak areas obtained under the same gas flows in the trapping step of the collection procedure to the peak area obtained in the direct transfer mode with hydrogen as outer gas and inlet arm unheated. Assuming the lossless volatilization, following equation holds: $E+B=1$.

2.5. Routine applications in conventional externally heated quartz atomizer

The commercial quartz tube atomizer without any trap (Perkin Elmer Quartz Cell 2 for FI-MHS) operated without end windows was used to demonstrate routine application of the proposed approach. See Refs. [16,17] for detailed atomizer description. The hydride generator was the same as described in Section 2.2 and spectrometer parameters employed as that summarized in Table 1.

To determine the total Sb content in groundwater reference material and mineral water samples, the samples were pre-reduced by KI/ascorbic acid 30 min before the analysis. The sample introduction time was 30 s followed by 30 s introduction of the blank. Gas

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composition in the trapping step was: 120 ml min^{-1} carrier Ar + 15 ml min^{-1} H_2 evolved from hydride generator + 10 ml min^{-1} O_2 through the auxiliary gas channel to burn the hydrogen in the trapping step. The analyte was trapped in-situ in the optical arm of the atomizer heated to 900 °C. Subsequently, the oxygen flow was switched off and the trapped analyte species were volatilized, atomized and detected by adding 75 ml min^{-1} H_2 to 75 ml min^{-1} carrier Ar. See Ref. [16] for detailed description of the procedure.

To investigate interferences of other hydride forming elements on Bi in-situ collection the atomizer was modified as follows: a deactivated fused silica capillary (Supelco, 0.53 mm id) was centered within the inlet arm of the atomizer. The tip of the capillary was aligned with the downstream end of the inlet arm in the junction with the optical arm. The sample introduction time was 30 s followed by 30 s introduction of the blank. The sample in 1.0 mol l^{-1} HCl contained always 1 ng ml^{-1} Bi as analyte and from 10 to 10 000 ng ml^{-1} of the interferent. Gas composition in the trapping step was: 75 ml min^{-1} carrier Ar + 15 ml min^{-1} H_2 evolved from hydride generator + 10 ml min^{-1} of auxiliary O_2 added through the capillary to burn out the hydrogen in the trapping step. The analyte was trapped in-situ in the optical arm of the atomizer heated to 900 °C. Subsequently, in the volatilization step, the oxygen flow was switched off and the trapped analyte species were volatilized, atomized and detected by adding 100 ml min^{-1} H_2 through the auxiliary gas channel to 75 ml min^{-1} of carrier Ar. See Ref. [17] for detailed description of the apparatus and procedure.

3. Results and discussion

3.1. Antimony

There was no breakthrough signal observed in the whole trap temperature range studied (between 220 °C and 950 °C) using the hydrogen as outer gas. Fig. 2 shows the dependence of preconcentration efficiency on the trapping temperature between 220 and 950 °C. This is very much different from the trapping curve reported in Ref.[9] for stibine trapping in a similar quartz trap but without burning out hydrogen during the trapping step. The very sharp maximum at around 650 °C in the curve, corresponding to efficiency of 65% [9], should be accounted mainly to hydrogen-induced analyte losses rising with temperature of the trapping step [12]. The present broad plateau corresponding to efficiency of around 100% clearly demonstrates excellent function of the present trap-and-atomizer device.

There are significant (around 10%) analyte losses below trap temperature of 400 °C. As shown below, there are no analyte losses either in the period between the trapping and volatilization step or in the volatilization step (if optimum volatilization temperature 870 °C is used). Thus, loss of analyte in the trapping step is the most probable explanation in spite of the above reported absence of the breakthrough signal. However, the missing 10% of analyte transported to the optical arm during the whole 30 s trapping step corresponds to the flow of analyte continuously generated from a sample of 0.2 ng ml^{-1} Sb. Corresponding signal is near the detection capability of the multiatomizer with hydrogen as outer gas (around 0.1 ng ml^{-1} Sb) so that it would be hardly detectable.

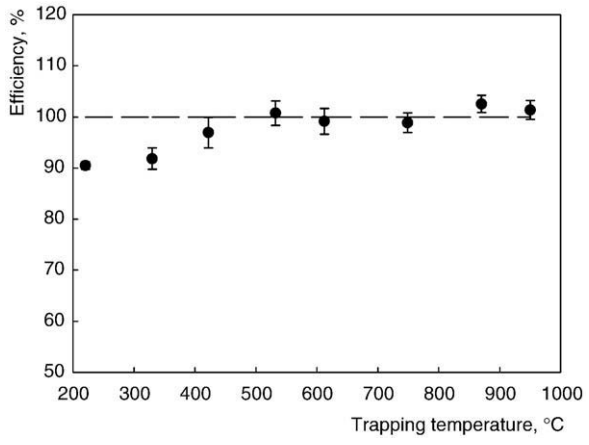

Fig. 2. Trapping curve for Sb (trapped analyte amount 4 ng); volatilization temperature 870 °C, volatilization hydrogen flow rate 75 ml min^{-1}. Uncertainty expressed as SD (n=3).

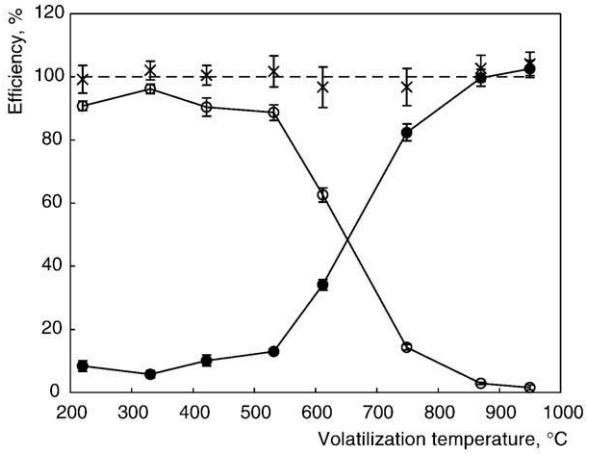

Fig. 3. Volatilization curve for Sb (trapped analyte amount 4 ng) (filled circles) and additional volatilization step at 870 °C (empty circles), totally volatilized analyte in volatilization and additional volatilization step (crosses); trapping temperature 870 °C, volatilization hydrogen flow rate 75 ml min^{-1}. Uncertainty expressed as SD (n=3).

The volatilization curve and the influence of volatilization temperature on the signal of additionally volatilized analyte are presented in Fig. 3. Moreover, also the "sum of volatilized analyte" is displayed in Fig. 3 as the sum of the analyte volatilized in the volatilization step at the examined volatilization temperature and the analyte volatilized in the additional volatilization step always done at 870 °C. The fact that the total efficiency of the volatilization and additional volatilization step fluctuates around 100% (see Fig. 3) proves that all the trapped analyte species were released either in the volatilization or in the additional volatilization step after it.

Fig. 3 shows that all the trapped antimony is released and atomized at volatilization temperature of 870 °C and above. The temperature of

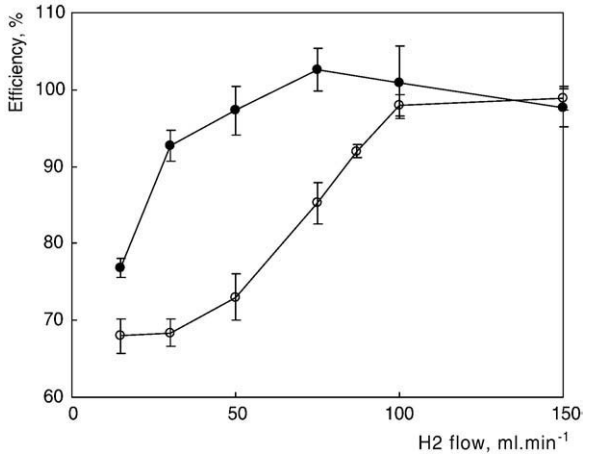

Fig. 4. Hydrogen flow rate optimization in the volatilization step for Sb and Bi; Sb (filled circles, trapped analyte amount 4 ng); trapping temperature 870 °C, volatilization temperature 870 °C; Bi (empty circles, trapped analyte amount 3 ng); trapping temperature 870 °C, volatilization temperature 870 °C. Uncertainty expressed as SD (n=3).

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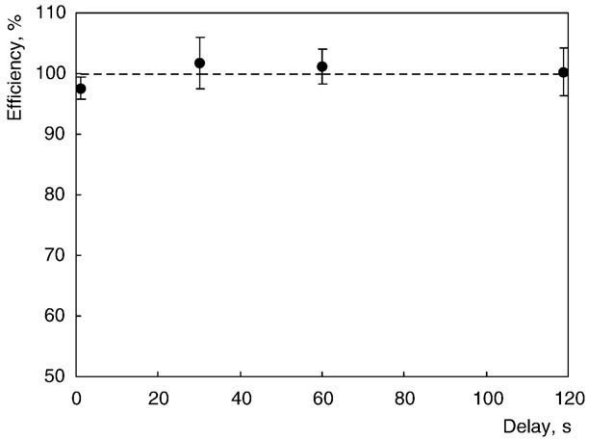

Fig. 5. Trapped Sb species stability (trapped analyte amount 4 ng) — effect of the time delay between the trapping and volatilization step (O_2 flow switched off immediately after the trapping step); trapping temperature 870 °C, volatilization temperature 870 °C, volatilization hydrogen flow rate 75 ml min^{-1}. Uncertainty expressed as SD (n=3).

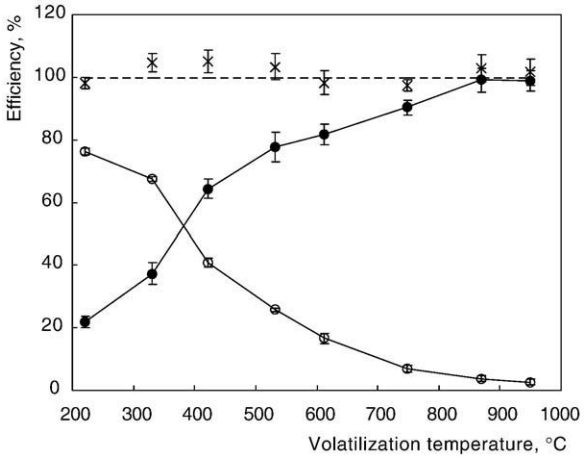

Fig. 7. Volatilization curve for Bi (trapped analyte amount 3 ng) (filled circles) and additional volatilization step at 870 °C (empty circles), totally volatilized analyte in volatilization and additional volatilization step (crosses); trapping temperature 870 °C, volatilization hydrogen flow rate 100 ml min^{-1}. Uncertainty expressed as SD (n=3).

870 °C was chosen as optimum. For volatilization temperature lower than 800 °C, a fraction of analyte is retained in the trap to be subsequently released and atomized in the additional volatilization step. Around 90% of the trapped analyte is retained in the trap if the volatilization temperature is below 500 °C. When increasing the volatilization temperature from 500 to 750 °C, the retained analyte fraction rapidly decreases from 90 to 15%.

75 ml min^{-1} H_2 was chosen as the optimum hydrogen flow rate for the volatilization (see Fig. 4). However, the maximum is very flat and H_2 flow rate as low as only 30 ml min^{-1} results in 93% efficiency. Hydrogen flow rate appears to be dependent on the actual apparatus design since 15 ml min^{-1} H_2 was sufficient for 100% release of trapped antimony species in the conventional externally heated quartz tube atomizer [16].

A stability study of the trapped analyte species in the presence of oxygen and in its absence was carried out for Sb and Bi. The trapping step was done under oxygen excess over hydrogen as described (see Section 2.4 Procedure) employing the optimum trapping temperature 870 °C. Then in the first set of experiments (I) the oxygen flow was switched off immediately after the trapping step. The trapped analyte was volatilized after the delay of 0–120 s by adding the 75 and 100 ml min^{-1} H_2 through the auxiliary gas channel, respectively, for Sb and Bi. In the second set of experiments (II), the oxygen flow was kept on after the trapping step till the volatilization step was accomplished after the time delay of 0–120 s. The volatilization step was again realized by adding the 75 and 100 ml min^{-1} H_2 through the auxiliary gas channel, respectively for Sb and Bi. In both sets of experiments (I and II) 75 ml min^{-1} carrier Ar and 25 ml min^{-1} outer air was used during the whole procedure. Thus, the only difference between the sets (I) and (II) is the absence or presence of the oxygen flow, respectively, during the delay time between the trapping and volatilization step. Results for the first set of experiments (I) and antimony are depicted in Fig. 5. No analyte losses were observed even for the delay of 120 s. It means that the trapped Sb species are stable at the quartz surface even at 870 °C and in the absence of oxygen. Similar results, without any losses, were obtained for the second set of experiments (II) in the presence of oxygen.

3.2. Bismuth

Employing hydrogen as outer gas (see Section 2.4 Procedure), no breakthrough signal was observed during the trapping step in the whole studied temperature range (between 220 and 950 °C). In accordance with this observation, the trapping efficiency was around 100% in the

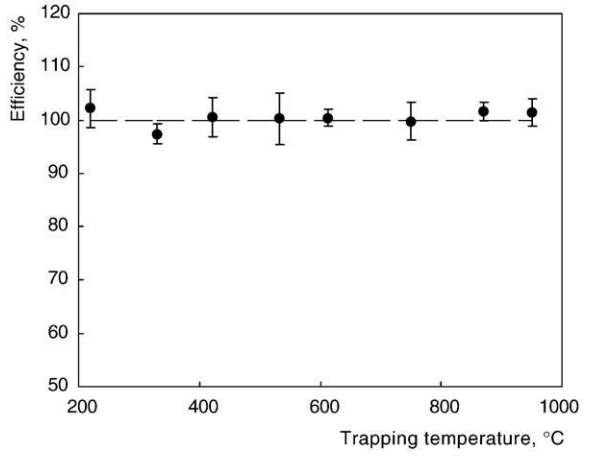

Fig. 6. Trapping curve for Bi (trapped analyte amount 3 ng); volatilization temperature 870 °C, volatilization hydrogen flow rate 100 ml min^{-1}. Uncertainty expressed as SD (n=3).

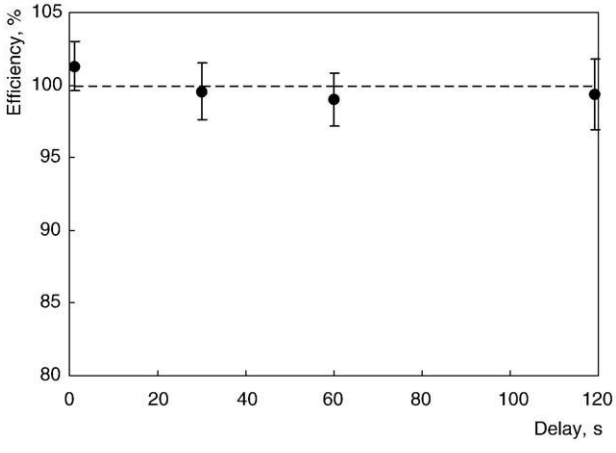

Fig. 8. Trapped Bi species stability (trapped analyte amount 3 ng) — effect of the time delay between the trapping and volatilization step (O_2 flow switched off immediately after the trapping step); trapping temperature 870 °C, volatilization temperature 870 °C, volatilization hydrogen flow rate 100 ml min^{-1}. Uncertainty expressed as SD (n=3).

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whole temperature range (see Fig. 6). It can be concluded, that Bi behaves likewise Sb in the trapping step (compare Figs. 2 and 6).

The influence of volatilization temperature on the signal obtained in additional volatilization step, and the "sum of volatilized analyte" is presented in Fig. 7. As explained above, the fluctuation of the preconcentration efficiency after volatilization and additional volatilization step around 100% (see Fig. 7) proves that all the trapped analyte species were released either in the volatilization step or after it — in the additional volatilization step.

Fig. 7 shows that volatilization is complete above 800 °C, 90% volatilization efficiency is reached at 750 °C. Comparing the results obtained for Sb and Bi it is obvious that the trapped Bi species are more easily volatilized (compare Figs. 3 and 7). Whereas 90% antimony fraction is retained in the quartz inlet arm serving as a trap employing the volatilization temperature of 500 °C, the non-volatilized fraction for bismuth and 500 °C is only 26%. It should be pointed out that the decrease of the retained analyte fraction at the quartz surface with increasing volatilization step is not so steep for bismuth as it is for antimony.

The optimum hydrogen flow rate is above 100 ml min^{-1} (Fig. 4). Using the lower hydrogen flow rate for volatilization results in significant decrease in the efficiency.

The stability of trapped Bi species was verified analogously as described above for antimony (see Section 3.1). The results for the first set of experiments (I) are depicted in Fig. 8. No analyte losses were observed for both sets of experiments (I and II) indicating the stability of the Bi species trapped at the quartz surface at 870 °C.

The stability of trapped analyte is crucial for prolonging the trapping step to reduce the detection limit. 5 min preconcentration period was tested for both, Sb and Bi and no losses were observed.

3.3. Comparison of collection of As, Sb, Bi and Se in the trap-and-atomizer device

To date four analytes have been investigated in the trap-and-atomizer device, besides Sb and Bi (see above), As and Se were treated in ref. [12]. The analytes fall into two groups: (1) As and Se and (2) Sb and Bi. Analytes of the first group are more volatile as illustrated by losses at trapping temperatures above 800 °C and 300 °C, respectively, for As and Se [12]. This should be compared to the above reported (Figs. 2 and 6) lossless trapping of Sb and Bi hydrides up to the maximum feasible temperature of 950 °C. Volatilization shows the same trend. Optimum volatilization temperature ranges between 600–800 °C and 550–650 °C, respectively, for As and Se [12]. On the contrary, optimum volatilization temperature for both Sb and Bi is above 800 °C (Figs. 3 and 7). Even more marked illustration of volatility of As and Se is that they are partially lost within the 60 s period at elevated temperatures (As at 800 °C and Se at 570 °C) even under stoichiometric excess of oxygen over hydrogen [12]. This contrasts with negligible Sb and Bi losses after 120 s even at 870 °C and in absence of oxygen (see Sections 3.1 and 3.2 and Figs. 5 and 8).

Although the exact mechanisms of the trapping and volatilization remain unknown, the above described observations correspond well with the physical–chemical properties of the studied analytes [18]. The analytes from the first group show significantly lower boiling points compared to the second group. Whereas the boiling points of As and Se are 613 °C and 685 °C, respectively, Sb has boiling point 1750 °C and Bi 1560 °C. The same trend holds for their oxides. The boiling points for As_2O_3 and SeO_2 are 460 °C and 350 °C (sublimation), respectively; much higher values are reported for Sb_2O_3 (1550 °C) and Bi_2O_3 (1890 °C).

The nature of the trapped and volatilized species as well as the description of the interaction of analyte species with the quartz surface remains unclear. It is only reasonable to assume that in the trapping step the analyte hydride is converted to oxide form(s) and stabilized by an interaction with the quartz surface.

Table 2
Determination of antimony in water samples (a calibration curve technique used), sample introduction time 30 s, trapping temperature 870 °C, volatilization temperature 870 °C, volatilization hydrogen flow rate 75 ml min^{-1}

Sample	Sb (ng ml^{-1})	Certified Sb (ng ml^{-1})
Grumo-K	0.39±0.01*	0.54±0.19
Mineral water	0.28±0.02*	–

* Standard deviations from 5 measurements.

Table 3
Interference extent [a]

Interferent concentration (μg ml^{-1})	Signal suppression (%) due to given concentration of interferent[b]						
	As	Se	Te	Sb	Sn	Pb	Ge
0.01	0	0	0	2	0	0	0
0.1	0	0	0	21	0	0	0
1	0	8	–	36	1	0	0
10	3	13	3	52	11	0	2

[a] Sample introduction time 30 s, standard concentration 1.5 ng ml^{-1}.
[b] Uncertainty (expressed as SD calculated from five measurements) was 3% or lower.

3.4. Analytical applications

The above reported results show very high temperature stability of antimony and bismuth species trapped at the quartz surface in oxygen or argon atmosphere. In the volatilization step, all trapped analyte is rapidly volatilized under excess of hydrogen. Furthermore, 100% preconcentration efficiency, i.e. lossless trapping and volatilization, can be achieved without changing trap temperature between trapping and volatilization steps: for trap temperature above 800 °C and 870 °C, respectively, in the case of Sb and Bi. Than the only difference between both steps is that oxygen flow which is on in the trapping step is switched to hydrogen flow in the volatilization step. This means that there is no need for a trap. This is the explanation for recently published observations on in-situ collection of Sb [16] and Bi [17] in the optical tube of conventional externally heated quartz tube atomizers.

Using the trap-and-atomizer device the peak area characteristic mass (m_0) for Sb and Bi was, 25 and 22 pg, respectively. m_0 of 9 pg found for Sb in multiatomizer recently [12] — is in reasonable agreement with the present results since much lower hydrogen flow rate (15 ml min^{-1}) was employed in Ref. [12]. Using the same gas flow rate and composition and employing the conventional QTA, m_0 of 19 pg Bi was found recently [17]. This corresponds well with the m_0 of 22 pg Bi found in the trap-and-atomizer device in this work.

The detection limits (LODs) for the sample introduction time of 30 s in the trap-and-atomizer device were 13 and 11 pg ml^{-1}, respectively, for Sb and Bi. Taking into account that analyte content in blanks was below LOD, substantial improvement in LODs should be expected for longer sample introduction time — similar as observed for the sample introduction time of 300 s in the conventional QTA (2.8 [16] and 3.9 pg ml^{-1} [17], respectively, for Sb and Bi. Additional measurements were performed to demonstrate the routine application of the optimized Sb and Bi collection in the simple conventional externally heated quartz tube atomizers.

The antimony determination in a reference material and mineral water with 30 s sample introduction time is summarized in Table 2.

To test the resistance of the collection mode procedure to interferences the influence of concentration of other hydride forming elements in the sample on the observed Bi signal (standard 1.0 ng ml^{-1} Bi, corresponding to trapped analyte mass of 2 ng Bi) was determined (see Table 3). Antimony is the strongest interferent — 0.1 μg ml^{-1} Sb corresponding to co-trapped interferent mass of 0.2 μg Sb causes the 20% suppression of Bi signal. 10 μg ml^{-1} Sn or Se (corresponding to co-

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trapped interferent mass of 20 μg) caused ca 10% Bi signal suppression. The resistance of bismuth to the interference of other hydride forming elements in the collection mode can be compared with previously published [16] resistance of antimony (standard 1.0 ng ml^{-1} Sb, corresponding to trapped analyte mass of 2 ng Sb) to the interference of other hydride forming elements. Bi and Sn were found as the strongest interferents to antimony. Their 1.0 μg ml^{-1} concentration in solution caused 77% and 18% signal suppression of the Sb signal. 20 μg of co-trapped As, Ge, Se or Pb resulted in 10–20% suppression of antimony signal.

To summarize, Sb is the strongest interferent to Bi determination in the collection mode and vice versa. Literature data [1] suggest that interferences during hydride generation and transport are negligible and that the observed signal suppressions are due to interferences in the atomizer during the collection, volatilization or atomization step. Sb and Bi are, undoubtedly, co-trapped in the trapping step and also volatilized together because of their very similar preconcentration conditions. Thus, atomization interferences may arise. Fortunately, the interference extent is not serious considering concentrations of the interferents in real samples.

4. Conclusions

The collection of Sb and Bi in quartz atomizers is a very promising technique for ultratrace analysis. This approach requires only simple and cheap equipment and also the operation costs are low. The inherent advantages of the trap-and-atomizer device should be highlighted: besides allowing an independent control of trapping and atomization temperatures, it enables to monitor the breakthrough signal and to control the atomization conditions (in terms of sufficient air/oxygen supply). Thus, it is ideally suited for optimization and/or mechanistic studies. These studies make possible to find the simplest possible setup for routine applications.

The flat character of the trapping curves in the trap-and-atomizer device for both, Sb and Bi, shows the robustness of the trapping step. The stability of trapped analyte species under excess of oxygen at temperature up to 900 °C indicates a strong interaction between analyte forms and quartz surface. In contrast, under excess of hydrogen and at surface temperature around 900 °C, the trapped analyte species are completely and fast released from the quartz surface. As a result, apparatus for routine use can be simplified employing the in-situ trapping of Sb and Bi directly in the optical arm of the conventional QTA.

The observation that the conventional QTA is fully sufficient for in-atomizer trapping of Sb and Bi may attract more routine laboratories to use this challenging hydride trapping approach in analytical praxis. The detection limits for hydride trapping are comparable in both, the conventional QTA and trap-and-atomizer design. Higher tolerance limits for interferents in the trap-and-atomizer device compared to the conventional QTA should be expected, however, the tolerance limits found in the conventional QTA are good enough for ultratrace analysis of typical environmental samples.

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References

[1] J. Dědina, D.L. Tsalev, Hydride Generation Atomic Absorption Spectrometry, Wiley & Sons, Inc., Chichester, 1995.
[2] R.E. Sturgeon, S.N. Willie, S.S. Berman, Hydride generation-atomic absorption determination of antimony in seawater with in situ concentration in a graphite furnace, Anal. Chem. 57 (1985) 2311–2314.
[3] J. Dědina, Atomization of volatile compounds for atomic absorption and atomic fluorescence spectrometry: on the way towards the ideal atomizer, Spectrochim. Acta Part B 62 (2007) 846–872.
[4] B. Dočekal, S. Gucer, A. Selecká, Trapping of hydride forming elements within miniature electrothermal devices. Part I. Investigation of collection of arsenic and selenium hydrides on a molybdenum foil strip, Spectrochim. Acta Part B 59 (2004) 487–495.
[5] P. Krejčí, B. Dočekal, Z. Hrušovská, Trapping of hydride forming elements within miniature electrothermal devices. Part 3. Investigation of collection of antimony and bismuth on a molybdenum foil strip following hydride generation, Spectrochim. Acta Part B 61 (2006) 444–449.
[6] X. Guo, X. Guo, Determination of ultra-trace amounts of selenium by continuous flow hydride generation AFS and AAS with collection on gold wire, J. Anal. At. Spectrom. 16 (2001) 1414–1418.
[7] O. Cankur, N. Ertas, O.Y. Ataman, Determination of bismuth using on-line preconcentration by trapping on resistively heated W coil and hydride generation atomic absorption spectrometry, J. Anal. At. Spectrom. 17 (2006) 603–609.
[8] D.K. Korkmaz, N. Ertas, O.Y. Ataman, A novel silica trap for lead determination by hydride generation atomic absorption spectrometry, Spectrochim. Acta Part B 57 (2002) 571–580.
[9] D.K. Korkmaz, J. Dědina, O.Y. Ataman, Stibine preconcentration in a quartz trap with subsequent atomization in the quartz multiatomizer for atomic absorption spectrometry, J. Anal. At. Spectrom. 19 (2004) 255–259.
[10] D.K. Korkmaz, C. Demir, F. Aydin, O.Y. Ataman, Cold vapour generation and on-line trapping of cadmium species on quartz surface prior to detection by atomic absorption spectrometry, J. Anal. At. Spectrom. 20 (2005) 46–53.
[11] I. Menemenlioglu, D.K. Korkmaz, O.Y. Ataman, Determination of antimony using a quartz atom trap and electrochemical hydride generation atomic absorption spectrometry, Spectrochim. Acta Part B 62 (2007) 40–47.
[12] J. Kratzer, J. Dědina, Arsine and selenium hydride trapping in a novel quartz device for atomic absorption spectrometry, Anal. Bioanal. Chem. 388 (2007) 793–800.
[13] J. Dědina, T. Matoušek, Multiple microflame — a new approach to hydride atomization for atomic absorption spectrometry, J. Anal. At. Spectrom. 15 (2000) 301–304.
[14] T. Matoušek, J. Dědina, A. Selecká, Multiple microflame quartz tube atomizer — further development towards the ideal hydride atomizer for atomic absorption spectrometry, Spectrochim. Acta Part B 57 (2002) 451–462.
[15] T. Matoušek, M. Johansson, J. Dědina, W. Frech, Spatially resolved absorption measurement of antimony atom formation and dissipation in quartz tube atomizers following hydride generation, Spectrochim. Acta Part B 54 (1999) 631–643.
[16] J. Kratzer, J. Dědina, In situ trapping of stibine in externally heated quartz tube atomizers for atomic absorption spectrometry, Spectrochim. Acta Part B 60 (2005) 859–864.
[17] J. Kratzer, J. Dědina, In situ trapping of bismuthine in externally heated quartz tube atomizers for atomic absorption spectrometry, J. Anal. At. Spectrom. 21 (2006) 208–210.
[18] R.C. Weast, Handbook of Chemistry and Physics, 64th editionCRC Press, Florida, 1983–1984.

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Communication

In situ trapping of stibine in externally heated quartz tube atomizers for atomic absorption spectrometry

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Abstract

An evaluation of an extremely simple method for antimony preconcentration based on the novel experimental approach, in situ trapping of stibine in externally heated quartz tube atomizers, is presented. The only difference to the set-up employed for the conventional operation mode is that a flow of oxygen (at stoichiometric excess over hydrogen) is introduced just upstream of the atomizer in the trapping step of the procedure. The volatilization of the trapped analyte can be performed just by switching off the oxygen inlet. The collection/volatilization efficiency (±S.D.) is 100±2%. For the collection time of 300 s (sample volume of 20 ml), the preconcentration ratio and detection limit (3σ), respectively, is 400 and 2.8 pg ml^{-1}. A possible way of further improvement of the detection limit is suggested. The same approach can be analytically useful also for bismuthine (efficiency 55±2%) but not for arsine, selenium hydride and tellurium hydride.

Keywords: Stibine generation; Atomic absorption spectrometry; Preconcentration; In situ trapping; Quartz tube atomizers

1. Introduction

The fact that hydrides can be easily preconcentrated makes hydride generation an extremely valuable tool for the trace and ultratrace analysis. The most convenient way of hydride preconcentration is in-atomizer trapping. Until recently, the only widely used approach to that was in situ trapping in graphite furnaces [1,2]. There is another, very recent, approach to in-atomizer trapping—to collect plumbane [3], stibine [4] or volatile Cd species [5] in a bare quartz tube. The limitation of the present quartz-tube traps is that they require an additional heating device with temperature control of the trapping step and the volatilization step. Moreover, the trapping was incomplete; published efficiencies did not exceed 70% which made the sensitivity and, mainly, repeatability worse.

The aim of this work was to extend our investigation of stibine trapping in quartz tube traps [4] to stibine collection (and subsequent analyte atomization) in conventional quartz tube atomizers. The intention was to employ the simplest possible experimental arrangement: just the commercially available externally heated quartz tube atomizer without any trap or additional heating device.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade or higher purity. Deionized water was used to prepare solutions. Working standards were prepared by dilution of the respective stock standard solutions in 1.0 mol l^{-1} HCl. The blank was 1.0 mol l^{-1} HCl. The reductant was 0.5% (m/v) solution of $NaBH_4$ (Sigma) in 0.4% (m/v) KOH (Merck) prepared daily and filtered before use.

2.2. Atomic absorption spectrometer

The Varian SpectrAA300/400 model with Sb hollow cathode lamp (10 mA, 217.6 nm, 0.2 nm band pass) was employed without background correction.

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2.3. Hydride generator

An in-house made, continuous-flow hydride generation system similar as described in Ref. [6] was employed (see Fig. 1). Two T-pieces (PEEK-polyether ether ketone, 0.8 mm inner bore) were used to merge sample flow with the reductant flow and downstream to merge the reaction mixture flow with the carrier argon flow. Either blank or standard solution was introduced to the sample channel. The outlet from the second T-piece was connected by a 510-mm-long, 1-mm-i.d. polytetrafluoroethylene (PTFE) tubing to a 3-ml inner volume gas–liquid separator with a forced outlet (see Ref. [6] for a detailed description of the gas–liquid separator). Another PEEK, 0.8-mm inner bore T-piece was inserted downstream of the gas–liquid separator to introduce auxiliary O_2 (see below). The gas outlet from the gas–liquid separator was connected to the inlet arm of the atomizer (see below) by a 350-mm-long PTFE tubing. If not explicitly stated otherwise, PTFE tubings (1.0 mm i.d. for gases and 0.5 mm i.d. for liquids) and Rheodyne 1/16-in. flangeless fittings were used for the hydride generator and also to connect the atomizer.

Sample and reductant solutions were delivered and the waste from the gas–liquid separator was removed by a peristaltic pump. In all experiments, sample and reductant flow rates were 4.0 ml min^{-1} and 1.2 ml min^{-1}, respectively. The flow rate of H_2 that evolved from $NaBH_4$ decomposition was calculated to be around 15 ml min^{-1}.

2.4. Atomizer

It was a Perkin Elmer electrically heated quartz (plain) T-tube with the horizontal arm length of 160mm and i.d. of 7mm. The length and i.d. of the inlet arm was 90 mm and 2 mm, respectively.

2.5. Procedure

Measurements were performed either in the collection mode or in the direct transfer mode.

The collection mode procedure consisted of the following two steps:

Step 1 Trapping: At the start of Step 1, a standard was introduced to the sample channel for a given time, termed in the further text as "sample introduction time." The standard was then replaced by the blank for 30 s to flush the system. The total gas flow rate introduced to the inlet arm of the atomizer during Step 1 was 145 ml min^{-1} (120 ml min^{-1} of carrier Ar, 10 ml min^{-1} of auxiliary oxygen, around 15 ml min^{-1} of H_2 evolved from $NaBH_4$ decomposition).

Step 2 Volatilization: The carrier Ar flow rate was decreased to 75 ml min^{-1} (to reach maximum sensitivity, see below). To volatilize the collected analyte species, the oxygen flow was switched off. The total gas flow rate introduced to the inlet arm of the atomizer was 90 ml min^{-1} (75 ml min^{-1} of carrier Ar and 15 ml min^{-1} of H_2 evolved from $NaBH_4$ decomposition). After recording the signal of volatilized analyte (peak integration time 15 s), the oxygen flow was switched on and the procedure could be started again.

The pump was still on during the whole collection mode procedure.

In the direct transfer mode, the gas flow rates introduced to the inlet arm of the atomizer were the same as in the volatilization step of the collection mode. After establishing the baseline for blank introduction to the sample channel, an actual standard was introduced to the sample channel for 30 s. Then the standard was replaced by the blank for 30 s. The signal obtained in the direct transfer mode was integrated for 90 s.

3. Results and discussion

3.1. Preliminary observations

In our recent study of SbH_3 trapping in a quartz tube interfaced by a plastic tubing to a quartz tube multiatomizer,

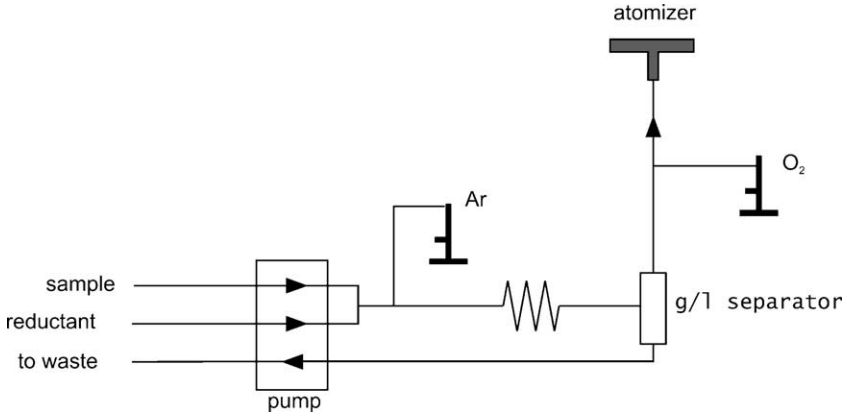

Fig. 1. Schema of the hydride generator.

we found a preconcentration efficiency, defined as the overall efficiency of trapping and volatilization, of around 60% [4]. Our subsequent experiments indicated that the incomplete trapping/volatilization was due to trapping losses which were unavoidable in the presence of hydrogen developed in the hydride generator. It appeared that the solution was to burn hydrogen out in a stoichiometric excess of oxygen. Thus, the antimony species could be efficiently collected in a quartz tube trap even at temperatures typical for hydride atomization (800–1000 °C). Such a temperature is sufficient to release the collected antimony species in the absence of oxygen. This suggested that conventional externally heated quartz tube atomizers, without any trap, could be employed for stibine collection and subsequent analyte atomization.

3.2. Direct transfer mode

This mode is used for conventional measurements, i.e., with direct transfer of hydride generated to the atomizer without introduction of oxygen [1]. In this mode, Ar flow rate of 75 ml min^{-1} was found to be optimum to achieve maximum sensitivity. Atomizer temperature of 900 °C, recommended by the atomizer manufacturer, was employed. The typical signal is shown in Fig. 2. For Ar flow rate of 120 ml min^{-1}, sensitivity decreased by around 35%.

3.3. Collection mode

The procedure consists of trapping and volatilization steps. To achieve the complete analyte trapping in the first step, the flow of oxygen securing stoichiometric excess over hydrogen is required. Since the flow rate of hydrogen formed in the generator is around 15 ml min^{-1} (see Experimental), the oxygen flow rate of 10 ml min^{-1} was chosen. All hydrogen released from tetrahydroborate decomposition is thus burned in the flame formed upstream of the horizontal arm of the atomizer. The position, as well as the stability, of the flame is obviously controlled by the gas flow rates and by the inner profile of the apparatus downstream the oxygen inlet and by the temperature distribution there. In the flame, the analyte hydride is converted most probably to oxide species efficiently retained at the quartz surface. The analyte species can be volatilized only in the excess of hydrogen and only at elevated temperatures. It is therefore essential to keep the flame stable in the section of the atomizer inlet arm which is heated to sufficiently high temperature. In the employed atomizer and heating unit, the flame was not stable with Ar flow rate of 75 ml min^{-1}; however, it was stable at Ar flow rate of 120 ml min^{-1}. Since the section of 15 mm of the inlet arm from the atomizer T-tube junction is covered by the heating unit, the flame is not seen and its exact position cannot be specified.

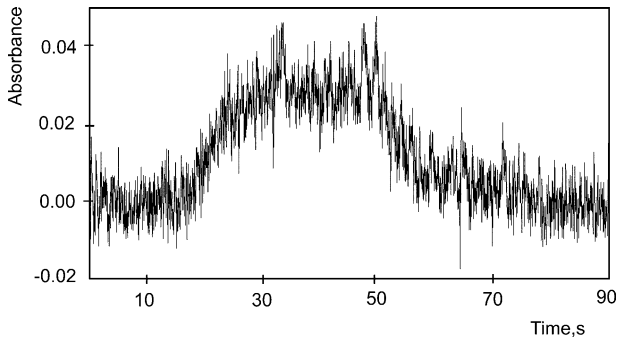

Fig. 2. The typical signal shape observed in direct transfer mode; standard concentration 1 ng ml^{-1}.

In principle, optimum settings Ar flow rate, atomizer temperature and hydrogen flow rate in the volatilization step may differ from those in the trapping step. Since the imperative of the present work was to make the operation as simple as possible, the atomizer temperature was kept the same (900 °C) in both steps and the flow of hydrogen required for a reasonably fast analyte volatilization in the second step was provided from tetrahydroborate decomposition (15 ml min^{-1}). It made possible to work without additional channel for hydrogen introduction. The volatilization of trapped analyte was performed just by switching off the flow of oxygen. The carrier Ar flow rate was decreased to 75 ml min^{-1} (which is optimum to achieve the maximum sensitivity). When accepting around 35% lower sensitivity at the argon flow rate of 120 ml min^{-1} (see above), the volatilization of trapped analyte could be performed just by switching off the flow of oxygen.

3.4. Preconcentration efficiency and ratio

The signal obtained in the collection mode (Fig. 3) should be compared with that for the direct transfer mode under the same analyte concentration (1 ng ml^{-1}) and the same sample introduction time of 30 s (Fig. 2). Areas of both signals do not differ significantly, demonstrating complete trapping and volatilization: the average (±S.D.) for 10 measurements were 0.970 ± 0.018 s and 0.973 ± 0.025 s, respectively, for the collection and direct transfer mode. In contrast, widths of both signals (Figs. 2 and 3) differ dramatically: FWHM (full width at half-maximum) are 0.8 s and 32 s, respectively, in the collection and direct transfer mode. The ratio of FWHM (around 40) can be taken as a measure of the preconcentration ratio.

The sample introduction time can be increased substantially. For a time of 300 s and standard concentration of 0.1 ng ml^{-1} (i.e., for the same analyte mass of 2 ng as in Figs. 2 and 3), the peak area corrected to blanks was 0.963 ± 0.021 s (±S.D., $n = 10$), proving that the preconcentration efficiency was around 100% even for the extended sample introduction time. It should be emphasized that signal FWHM in the collection mode is independent of the sample introduction time. Since the signal FWHM in the direct transfer mode is roughly equal to the sample introduction time, the preconcentration ratio can be enhanced proportionally to the

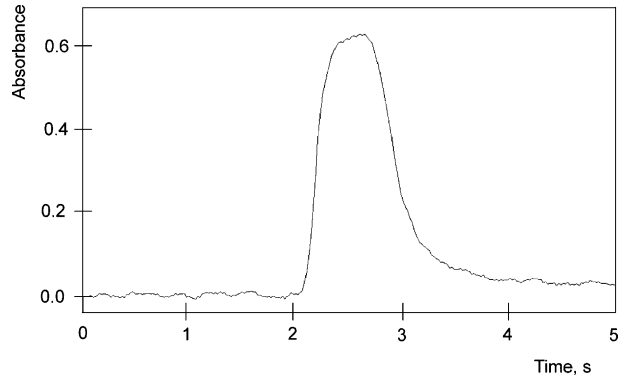

Fig. 3. The signal observed for the collection mode; sample introduction time 30 s, standard concentration 1 ng ml^{-1}.

sample introduction time reaching a value around 400 for 300 s.

3.5. Signal characteristics and limit of detection

The peak shape for the collection mode was not significantly influenced by sample introduction time in the tested range between 30 and 300 s. The peak area was given only by the total analyte mass. The calibration functions for peak area as well as peak height were linear up to 1.5 ng Sb (Sb concentration of 75 pg ml^{-1} for the standard solution introduction time 300 s).

Precision of peak area and height measurements did not differ markedly: e.g., for analyte mass between 0.5 and 2 ng, R.S.D. ($n=3$) was below 2.5% and 3.1%, respectively, for sample introduction time 30 and 300 s.

Reproducibility of preconcentration efficiency for analyte mass of 2 ng and sample introduction time 30 s, calculated from 75 measurements made during 20 days was 100±2% (±S.D.).

Due to the lossless collection at high preconcentration ratio, the described procedure offers a great potential to achieve extremely low concentration detection limit (LOD, always expressed as 3 σ) by employing either peak area or peak height measurements.

For a sample introduction time of 300 s (sample consumption 20 ml), the LOD achieved for peak area measurements was 2.8 pg ml^{-1}. The actual LOD was controlled by the analyte content in blanks −11±1 pg ml^{-1}. There was no attempt made to reduce contamination and, subsequently, to achieve even lower LOD. Even so, the LOD is the same as the best ones achieved for in situ trapping in commercial graphite furnaces with subsequent AAS detection: 2.9 and 3 pg ml^{-1}, respectively, reported by Sturgeon et al. [7] and by Kalahne et al. [8]. LODs given by other authors [9–11] are three to seven times worse.

3.6. Interferences in the atomizer in the collection mode

To test the resistance of the collection mode procedure to interferences, the influence of concentration of other hydride-forming elements in the sample on the observed signal was determined (see Table 1). In analogy to mutual interferences of other hydride-forming elements [1,12–14], it can be assumed that interferences during hydride generation and transport are negligible and that the observed signal suppressions are due to interferences in the atomizer. The observed interference extent can be compared with the literature data on interferences to Sb determination using the direct transfer mode and externally heated quartz tube atomizers [8,15–22]. The most pronounced interferents observed in this work are Sn and Bi (Table 1). Their interference extent corresponds to that reported in the literature [15,16,18,20,21]. However, interference magnitude of As, Se, Te, Pb and Ge is typically at least one order of magnitude lower compared to the literature data [8,15–22].

In principle, interferences due to other hydride-forming elements can take place either in the trapping step (reduction of a trapping capacity of the atomizer surface) or in the volatilization one. Because of the high surface area of the employed atomizer, the observed interferences probably originate in the volatilization step—due to interferents trapped together with the analyte. Interferences in the volatilization step have to be the same as atomization interferences in the direct transfer mode in externally heated quartz tube atomizers—their mechanism was extensively studied and understood [1,12]. Their extent is one to two orders of magnitude less pronounced in the new-generation hydride quartz tube atomizer–multiatomizer [13,14]. Consequently, the extent of observed interferences should be substantially reduced when replacing the employed externally heated quartz tube atomizer by the multiatomizer.

3.7. Other figures of merit

Reproducibility was tested as a peak area of 1 ng ml^{-1} standard for sample introduction time of 30 s. Within 30 days, all values obtained fell within the range 0.72–1.0 s. The average, expressed as the peak area characteristic mass, was 10.2 pg. Sample throughput: 10 samples per hour for a sample introduction time of 300 s.

Table 1
Interference extent[a]

Interferent concentration (μg ml^{-1})	Signal suppression (%) due to given concentration of interferent[b]						
	As	Se	Te	Bi	Sn	Pb	Ge
0.01	0	0	0	0	0	0	0
0.1	0	0	4	0	0	0	0
1	7	0	–	77	18	4	1
10	27±3	12	8	–	44	12	22±4

[a] Sample introduction time 30 s, standard concentration 1 ng ml^{-1}.
[b] Uncertainty (expressed as S.D. calculated from five measurements) was, if not given otherwise, 2% or lower.

3.8. Applicability to other hydride-forming elements

Preconcentration efficiency of As, Bi, Se and Te was estimated under the same experimental parameters as described above for Sb. Bi can be preconcentrated with the efficiency of 55±2%, efficiency for As was as low as around 1%. No significant preconcentration of Se and Te was observed. It appears that even though hydrides of the other elements must be decomposed in the flame, the resulting analyte species are not efficiently either trapped or volatilized/atomized. Changing gas flow rates in the trapping step and temperature of the atomizer did not yield significant improvement.

4. Conclusions

There is no doubt that other designs of externally heated quartz tube atomizers are suited for in situ trapping of stibine and bismuthine with the same efficiency as described above for the employed atomizer design. The only critical requirement to be fulfilled is to keep the flame stable in the section of the atomizer inlet arm which is heated to sufficiently high temperature. The experimental parameters (namely, gas flow rate and atomizer temperature) must be thus chosen to conform with this requirement. The disadvantage of this solution is that hydride generation with blank introduced to the sample channel of the hydride generator must be on also in the volatilization step of the procedure. This presents a contribution to the noise observed and can negatively influence the resulting LOD.

The data given above indicate the potential of this novel experimental approach, in situ trapping of hydrides in externally heated quartz tube atomizers, for determination of Sb and perhaps also Bi. Obviously, to make the full use of the potential, i.e., to reach even lower LOD than the achieved 2.8 pg ml^{-1} (which compares well with the best values reported for in situ trapping in commercial graphite furnaces; see above), analyte concentration in the blank must be kept as low as possible. There is an additional option to improve LOD—by changing the experimental procedure in the volatilization step: instead of providing the flow of hydrogen (required for reasonably fast analyte volatilization) from tetrahydroborate decomposition, an additional channel for hydrogen introduction from the gas container can be incorporated. This would reduce the observed blank noise, but the procedure (as well as the experimental set-up) would be slightly more complicated.

Also, other figures of merit, besides LOD, compare favorably with those either for direct transfer of hydride generated to the externally heated quartz tube atomizer [1] or for the in situ trapping of hydride in a commercial graphite furnace [1,2]. It should be emphasized that all the promising results, mainly the fundamental attribute of the procedure (100% collection/volatilization efficiency), were obtained with the very simple and cheap equipment.

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References

[1] J. Dědina, D.L. Tsalev, Hydride Generation Atomic Absorption Spectrometry, Wiley and Sons Inc, Chichester, 1995.
[2] H. Matusiewicz, R.E. Sturgeon, Atomic spectrometric detection of hydride forming elements following in situ trapping within a graphite furnace, Spectrochim. Acta Part B 51 (1996) 377–397.
[3] D.K. Korkmaz, N. Ertas, O.Y. Ataman, A novel silica trap for lead determination by hydride generation atomic absorption spectrometry, Spectrochim. Acta Part B 57 (2002) 571–580.
[4] D.K. Korkmaz, J. Dědina, O.Y. Ataman, Stibine preconcentration in a quartz trap with subsequent atomization in the quartz multiatomizer for atomic absorption spectrometry, J. Anal. Atom. Spectrom. 19 (2004) 255–259.
[5] D. Korkmaz, C. Demir, F. Aydin, O.Y. Ataman, Cold vapour generation and on-line trapping of cadmium species on quartz surface prior to detection by atomic absorption spectrometry, J. Anal. Atom. Spectrom. 20 (2005) 46–52.
[6] T. Matoušek, M. Johansson, J. Dědina, W. Frech, Spatially resolved absorption measurement of antimony atom formation and dissipation in quartz tube atomizers following hydride generation, Spectrochim. Acta Part B 54 (1999) 631–643.
[7] R.E. Sturgeon, S.N. Willie, G.I. Sproule, P.T. Robinson, S.S. Berman, Sequestration of volatile element hydrides by platinum group elements for graphite-furnace atomic-absorption, Spectrochim. Acta Part B 44 (1989) 667–682.
[8] R. Kalahne, G. Henrion, A. Hulanicki, S. Garbos, M. Walcerz, Comparison of AAS with hydride concentration in a graphite furnace with other spectrometric techniques, Spectrochim. Acta Part B 52 (1997) 1509–1516.
[9] P. Niedzielski, M. Siepak, Determination of Sb(III) and Sb(V) in water samples by hydride generation atomic absorption spectrometry with in-situ trapping in a graphite tube, Anal. Lett. 36 (2003) 971–986.
[10] H. Matusiewicz, M. Mikolajczak, Determination of As, Sb, Se, Sn and Hg in beer and wort by direct hydride generation sample introduction-electrothermal AAS, J. Anal. Atom. Spectrom. 16 (2001) 652–657.
[11] H.O. Haug, Y.P. Liao, Investigation of the automated determination of As, Sb and Bi by flow injection hydride generation using in-situ trapping on stable coatings in graphite furnace atomic absorption spectrometry, Fresenius' J. Anal. Chem. 356 (1996) 435–444.
[12] A. D'Ulivo, J. Dědina, Interferences in hydride atomization studied by atomic absorption and atomic fluorescence spectrometry, Spectrochim. Acta Part B 51 (1996) 481–498.
[13] J. Dědina, T. Matoušek, Multiple microflame—a new approach to hydride atomization for atomic absorption spectrometry, J. Anal. Atom. Spectrom. 15 (2000) 301–304.
[14] T. Matoušek, J. Dědina, A. Selecká, Multiple microflame quartz tube atomizer—further development towards the ideal hydride atomizer for atomic absorption spectrometry, Spectrochim. Acta Part B 57 (2002) 451–462.
[15] L.H. Lajunen, T. Merkkiniemi, H. Hayrynen, Influence of volatile hydride-forming elements on Sb determination by atomic-absorption spectrometry with hydride-generation, Talanta 31 (1984) 709–713.
[16] M. Yamamoto, M. Yasuda, Y. Yamamoto, Hydride-generation atomic absorption spectrometry coupled with flow injection analysis, Anal. Chem. 57 (1985) 1382–1385.

[17] K. Dittrich, R. Mandry, Investigations into the improvement of the analytical application of the hydride technique in atomic absorption spectrometry by matrix modification and graphite furnace atomization: Part I. Analytical results, Analyst 111 (1986) 269–275.
[18] K. Petrick, V. Krivan, Interferences of hydride forming elements and of mercury in the determination of antimony, arsenic, selenium and tin by hydride-generation AAS, Fresenius Z. Anal. Chem. 327 (1987) 338–342.
[19] A. Hulanicki, E. Bulska, M. Walcerz, Twin-channel flow system for the investigation of gas- and liquid-phase interferences in hydride generation atomic absorption spectrometry, Fresenius Z. Anal. Chem. 332 (1988) 176–177.
[20] S. Mcintosh, Z. Li, G.R. Carnrick, W. Slavin, The determination of tin in steel samples by flow injection hydride generation atomic absorption spectroscopy, Spectrochim. Acta Part B 47 (1992) 897–906.
[21] E. Krakovska, D. Mackovych, Mutual interferences of hydride-forming elements in gaseous phase, Chem. Pap.-Chem. Zvesti 50 (1996) 121–124.
[22] N. Erdem, E. Henden, Inter-element interferences in the determination of arsenic and antimony by hydride generation atomic absorption spectrometry with a quartz tube atomizer, Anal. Chim. Acta 505 (2004) 59–65.

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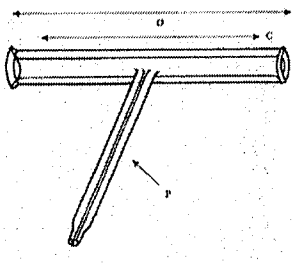
(54) Název přihlášky vynálezu:

Způsob prekoncentrace antimonu pro jeho stanovení metodami atomové spektrometrie

(57) Anotace:

Způsob prekoncentrace antimonu založený na generování stibanu, jeho záchytu v křemenné pasti a následném uvolnění zachyceného analytu, jeho atomizaci a detekci některou z metod analytické atomové spektrometrie. V kroku záchytu je do nosného plynu obsahujícího generovaný hydrid a vodík (vzniklý rozkladem tetrahydroboratu) přidán kyslík v nadstechiometrickém množství vůči přítomnému vodíku. V křemenné pasti, tvořené trubičkou o vnitřním průměru několik milimetrů zevně ohřívanou na teplotu mezi 500 a 1100 °C, hoří plamínek, ve kterém je vodík spálen v přebytku kyslíku. Hydrid je v pasti rozložen a analyt zachycen. Po skončení generování hydridu je prostým uzavřením přívodu kyslíku analyt z pasti najednou uvolněn a proudem nosného argonu transportován k atomizaci a detekci. Teplotu pasti není potřeba měnit. Pokud je pro stanovení Sb prekoncentrovaného metodou podle řešení zvolena AAS. lze pro záchyt i atomizaci analytu využít konvenční vyhřívaný křemenný atomizátor bez jakékoliv úpravy.



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Způsob prekoncentrace antimonu pro jeho stanovení metodami atomové spektrometrie

Oblast techniky

Vynález se týká metody prekoncentace antimonu v křemenné trubici za účelem stanovení jeho stopových a ultrastopových koncentrací některou z metod analytické atomové spektrometrie.

Dosavadní stav techniky

Stopové a ultrastopové koncentrace antimonu lze ve vzorcích stanovovat různými instrumentálními metodami, nejčastěji spektrometrickými. Detekční limit lze dále snížit předřazením prekoncentračního kroku. K prekoncentraci se nejlépe hodí generování hydridů. Tato technika je přehledně zpracována např. v monografii [J. Dědina a D. L. Tsalev: Hydride Generation Atomic Absorption Spectrometry, Wiley, Chichester, 1995]. Analyt je ve formě těkavého hydridu uvolněn z kapalného vzorku reakcí s roztokem tetrahydroboratu v kyselém prostředí. Generovaný hydrid je veden do prekoncentračního zařízení. Po skončení generování hydridu ze vzorku je analyt z prekoncentračního zařízení uvolněn a veden k atomizaci a detekci některou z metod analytické atomové spektrometrie - nejčastěji atomovou absorpční spektrometrií (AAS), nebo atomovou fluorescenční spektrometrií, nebo metodou atomové emisní spektrometrie s indukčně vázanou plazmou (ICP-AES), případně metodou hmotnostní spektrometrie s indukčně vázanou plazmou (ICP-MS).

K prekoncentraci se může použít křemenné U-trubice chlazené kapalným dusíkem, v které je zachycen generovaný hydrid. Ten je po skončení generování uvolněn zahřátím U-trubice. Tento způsob prekoncentrace trpí závažnými nedostatky - je časově náročný a jeho automatizace je prakticky neproveditelná.

Výhodnější je provádět prekoncentraci hydridu přímo v atomizátoru. Donedávna k tomu byly používány výhradně grafitové atomizátory. Generovaný hydrid je zachycen v atomizátoru, který je vyhříván na 200 - 600 °C. Povrch grafitového atomizátoru je krytý modifikátorem. Po skončení generování hydridu ze vzorku je atomizátor zahřát na teplotu kolem 2500 °C, čímž je veškerý zachycený analyt atomizován a detekován, obvykle AAS. K detekci lze však použít i jiné metody analytické atomové spektrometrie. Nevýhodami prekoncentrace v grafitovém atomizátoru jsou vysoké pořizovací i provozní náklady grafitového atomizátoru. Nicméně tento způsob prekoncentrace je v současnosti v analytické praxi velice široce

využíván a patří k nejobvyklejším přístupům ke stanovení stopových a ultrastopových koncentrací hydridotvorných prvků. V literatuře publikované detekční limity pro prekoncentraci antimonu v grafitovém atomizátoru s následným stanovením AAS se pohybují řádově v jednotkách až desítkách pg ml^{-1}. Nejlepší publikovaný detekční limit je 3 $pg.ml^{-1}$.
V literatuře byla nedávno popsána prekoncentrace stibanu ve speciálním prekoncentračním zařízení - vyhřívané křemenné pasti, která byla předřazena před vyhřívaný křemenný atomizátor. Analyt byl zachycen v atmosféře argonu s obsahem jednotek % obj. vodíku. K uvolnění zachyceného analytu došlo zvýšením teploty pasti a dávkováním argonu s obsahem desítek % obj. vodíku do pasti. [Korkmaz, D. K.; Dědina, J.; Ataman, O. Y: Anal. Atom. Spectrom.19:2, 255-259 (2004)]. Výhodou tohoto způsobu prekoncentrace je jednoduchost konstrukce i provozu křemenné pasti a z toho vyplývající minimální pořizovací i provozní náklady. Zásadním nedostatkem takto prováděné prekoncentrace je nedostatečná účinnost celého procesu zachycení a uvolnění analytu (ztráty se pohybují v desítkách procent) a s tím související neuspokojivá reprodukovatelnost analytických signálů.

Podstata vynálezu

Experimentální studie provedené autory prokázaly, že výše zmíněná nedostatečná účinnost celého procesu zachycení hydridu a uvolnění analytu při provádění prekoncentrace ve vyhřívané křemenné pasti doposud známým způsobem je způsobena tím, že stabilita analytu v pasti při záchytu závisí kromě teploty pasti především na složení plynné fáze, konkrétně na obsahu vodíku v plynné fázi. Vzhledem k tomu, že vodík je produktem rozkladu tetrahydroboratu, je jeho přítomnost v pasti při záchytu neodvratná. Podstatou vynálezu je spalování molekulárního vodíku v pasti při záchytu přidáním stechiometrického přebytku kyslíku.
Metoda vychází z běžného způsobu generování hydridů [Dědina, J.; Tsalev, D. L.: Hydride Generation Atomic Absorption Spectrometry, Wiley, Chichester, 1995], který je modifikován tak, že je rozdělen do dvou kroků: (1) záchyt a (2) uvolnění:
(1) Do nosného plynu obsahujícího generovaný hydrid a vodík vzniklý rozkladem tetrahydroboratu je pomocným kanálem přidán kyslík v nadstechiometrickém množství vůči přítomnému vodíku. V křemenné pasti, tvořené tenkostěnnou trubičkou o vnitřním průměru několik milimetrů zevně ohřívanou na teplotu mezi 500 a 1100 °C, hoří plamínek, ve kterém je spalován molekulární vodík ve stechiometrickém přebytku kyslíku. Hydrid je v pasti rozložen a analyt zachycen. Průtok nosného plynu aparaturou je třeba optimalizovat tak, aby

plamínek vznikající hořením vodíku v stechiometrickém nadbytku kyslíku hořel stacionárně na začátku pasti.

(2) Po skončení generování hydridu ze vzorku je nutné udržet obsah vodíku proudícího v plynné fázi pastí na úrovni odpovídající průtoku minimálně jednotkám $ml.min^{-1}$. Pak je prostým uzavřením přívodu kyslíku analyt z pasti najednou uvolněn a proudem nosného argonu transportován k atomizaci a detekci. Teplotu pasti není potřeba měnit. Odstraněním (spálením) vodíku v stechiometrickém nadbytku kyslíku v kroku záchytu se dosáhne úplného záchytu. Účinnost uvolnění analytu je také 100%. To vede k výborné reprodukovatelnosti analytických signálů. Je nežádoucí, aby úsek aparatury mezi pastí a atomizátorem/detektorem byl výrazně chladnější než 600°C, jinak dochází ke snížení účinnosti prekoncentrační procedury a ke zhoršení reprodukovatelnosti.

Příklady provedení vynálezu

Pokud je pro stanovení Sb prekoncentrovaného metodou podle vynálezu zvolena AAS, lze pro záchyt i atomizaci analytu využít konvenční vyhřívaný křemenný atomizátor bez jakékoliv úpravy. Viz např. monografii [J. Dědina a D. L. Tsalev: Hydride Generation Atomic Absorption Spectrometry, Wiley, Chichester, 1995] pro podrobný popis jednotlivých typů konvenčních vyhřívaných křemenných atomizátorů.

Příklad provedení vynálezu pro stanovení Sb metodou AAS je blíže osvětlen pomocí výkresu, na kterém je schematicky znázorněn jeden z typů konvenčních vyhřívaných křemenných atomizátorů. Atomizátor je vyroben z křemene a sestává se z přívodního ramene P a z optické trubice O o světlosti 7 mm a délce 160 mm, jejíž osa je totožná s optickou osou spektrometru. Přívodní rameno P o světlosti 2 mm a délce 90 mm je přitaveno k optické trubici O v jejím středu v pravém úhlu. Centrální část C optické trubice O, dlouhá 125 mm, je vyhřívána elektrickou odporovou pícko u na teplotu 900°C.

V kroku záchytu je do přívodního ramene P přiváděn generovaný stiban v proudu argonu s příměsí vodíku (z rozkladu tetrahydroboratu) a kyslíku v nadstechiometrickém množství vůči přítomnému vodíku (kyslík přidáván pomocným kanálem). Generování probíhá v kontinuálním režimu, kdy jsou do generátoru hydridů přiváděny kontinuální průtoky vzorku v 1 M HCl (průtok 4,3 $ml.min^{-1}$) a roztoku tetrahydroboratu (průtok 1,1 $ml.min^{-1}$). Za těchto podmínek se z tetrahydroboratu uvolňuje 15 $ml.min^{-1}$ vodíku. Stechiometrickému poměru kyslíku odpovídá 7,5 $ml.min^{-1}$, byl zvolen průtok kyslíku 10 $ml.min^{-1}$. Při průtocích Ar pod 100 $ml.min^{-1}$ dochází, podle aktuálního průtoku Ar, buď k "zpětným rázům" plamínku až do

místa, kde je proud kyslíku připojen k proudu argonu s vodíkem a generovaným stibanem, nebo k nestacionární reakci v přívodním rameni P atomizátoru. Proto byl zvolen průtok nosného Ar 120 $ml.min^{-1}$. Za těchto podmínek hoří plamínek klidně ve spojnici přívodního ramene P s optickou trubicí O. Střed optické trubice slouží v tomto uspořádání v kroku záchytu jako past pro záchyt analytu. Po skončení generování hydridu ze vzorku je proud vzorku do generátoru nahrazen proudem 1 M HCl o stejném průtoku.

V kroku uvolnění je, beze změny teploty atomizátoru, jen uzavřen přívod kyslíku. Tím je analyt zachycený ve středu optické trubice najednou uvolněn a atomizován. Za účelem zvýšení citlivosti měření lze v kroku uvolnění před uzavřením přívodu kyslíku snížit průtok nosného Ar (ze 120 $ml.min^{-1}$ nutných ke stabilizaci plamínku v kroku záchytu na 50 až 100 $ml.min^{-1}$ Ar).

Popsaná metoda byla využita pro stanovení obsahu antimonu v pitné vodě. V kroku záchytu byl přiváděn kontinuální průtok vzorku po dobu 5 min. Pak byl nahrazen průtokem 1 M HCl. V kroku uvolnění byl nejprve snížen průtok nosného Ar na 75 $ml.min^{-1}$ a pak byl jen uzavřen přívod kyslíku. Tím byl analyt zachycený ve středu optické trubice uvolněn a atomizován. Obsah antimonu ve vzorku byl změřen tímto postupem jak metodou kalibrační křivky, tak technikou standardního přídavku. Výsledky získané oběma metodami se od sebe statisticky významně nelišily. Kalibrační křivka pro stanovení antimonu s prekoncentrační dobou 5 min je lineární v oblasti 0 - 75 $pg.ml^{-1}$ Sb. Mez detekce (podle definice IUPAC) byla 3 $pg.ml^{-1}$ Sb.

Průmyslová využitelnost

Metodu lze použít pro prekoncentraci antimonu před jeho stanovením některou z metod analytické atomové spektrometrie, zejména AAS, atomovou fluorescenční spektrometrií, ICP-AES, nebo ICP-MS.

Oproti v literatuře nedávno popsané prekoncentraci stibanu ve vyhřívané křemenné pasti (viz odstavec Dosavadní stav techniky) je metoda prekoncentrace podle vynálezu jednodušší, protože není třeba měnit teplotu pasti a hlavně tato metoda vede k podstatně lepší reprodukovatelnosti analytických signálů.

Oproti běžně používané prekoncentraci hydridu v grafitovém atomizátoru (viz odstavec Dosavadní stav techniky) je metoda prekoncentrace podle vynálezu jednodušší a pořizovací i provozní náklady jsou desetkrát až stokrát nižší. Detekční limit prekoncentrace podle vynálezu s následným stanovením AAS je na úrovni v literatuře uvedeného nejlepšího

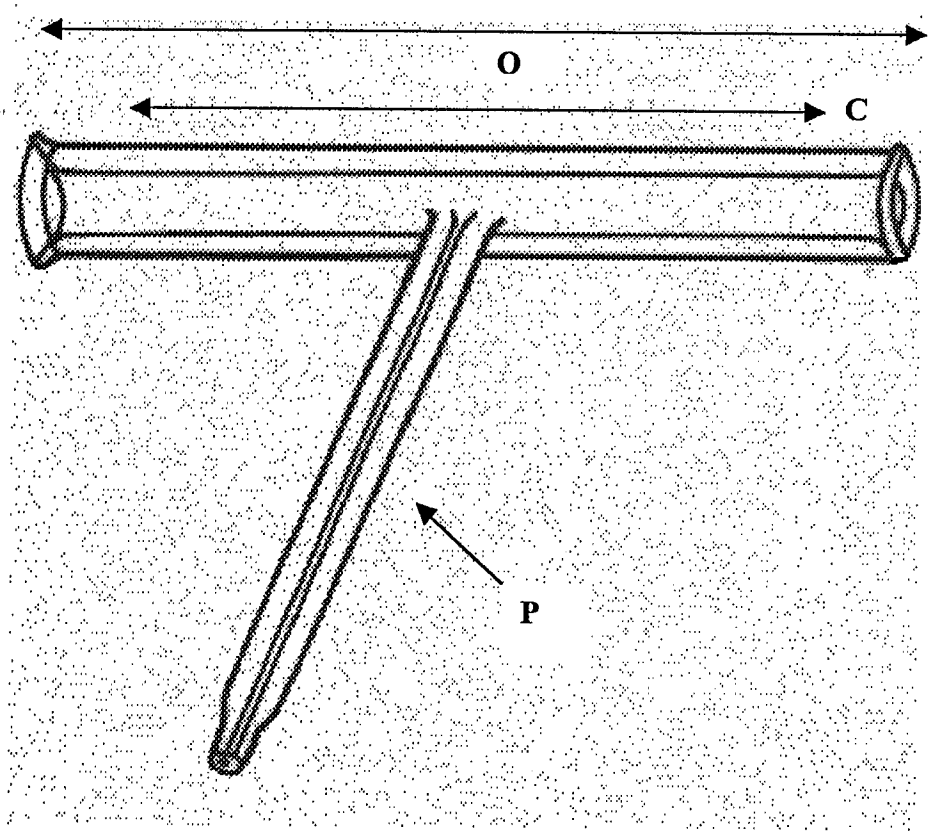
detekčního limitu pro záchyt v grafitovém atomizátoru s následným stanovením AAS (viz výše).

PATENTOVÉ NÁROKY

1. Způsob prekoncentrace analytu pro stanovení stopových a ultrastopových koncentrací antimonu metodami analytické atomové spektrometrie **vyznačující se** tím, že záchyt se provádí v křemenné trubičce ve které je spalován molekulární vodík ve stechiometrickém přebytku kyslíku, zevně ohřívané na teplotu mezi 500 a 1100°C a při obsahu vodíku v plynné fázi proudící křemennou trubičkou odpovídajícím průtoku minimálně jednotkám $ml.min^{-1}$, se provede uvolnění zachyceného analytu pouhým uzavřením přívodu kyslíku.

2. Způsob podle nároku 1. **vyznačující se** tím, že detekce se provádí pomocí atomové absorpční spektrometrie a záchyt se provádí pomocí konvenčního křemenného atomizátoru vyhřívaného na teplotu 900 °C.

Obr.1



PŘIHLÁŠKA VYNÁLEZU

zveřejněná podle § 31 zákona č. 527/1990 Sb.

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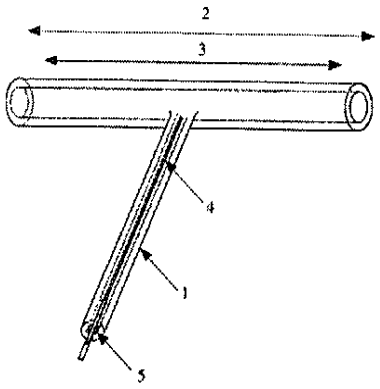
(74) Zástupce:
Středisko společných činností AV ČR, v.v.i. Patentové a licenční služby, Národní 1009/3, Praha 1, 11000

(54) Název přihlášky vynálezu:

Způsob prekoncentrace bismutu pro jeho stanovení metodou atomové absorpční spektrometrie



(57) Anotace:

Způsob prekoncentrace bismutu je založen na generování bismutanu, jeho záchytu v konvenčním vyhřívaném křemenném atomizátoru, modifikovaném vložením křemenné kapiláry do přívodního ramene atomizátoru, jejíž konec dosahuje až na začátek optické trubice atomizátoru, jeho atomizaci a detekci metodou AAS. V kroku záchytu je do nosného plynu obsahujícího generovaný hydrid a vodík (vzniklý rozkladem tetrahydroboratu) přidán kyslík v nadstechiometrickém množství vůči přítomnému vodíku. Na konci křemenné kapiláry hoří plamínek, ve kterém je vodík spálen v přebytku kyslíku. Hydrid je v plamínku rozložen a analyt zachycen. Po skončení generování hydridu je uzavřením přívodu kyslíku a spuštěním proudu vodíku analyt najednou uvolněn a atomizován. Atomizátor pro provádění tohoto způsobu je modifikován tak, že v podélné ose přívodního ramene (1) atomizátoru je umístěna křemenná kapilára (4) o vnitřním průměru od 0,3 do 0,7 mm dosahující na začátek optické trubice (2) atomizátoru.

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Způsob prekoncentrace bismutu pro jeho stanovení metodou atomové absorpční spektrometrie

Oblast techniky

Vynález se týká metody prekoncentace bismutu v modifikovaném konvenčním zvnějšku vyhřívaném křemenném atomizátoru za účelem stanovení jeho stopových a ultrastopových koncentrací metodou atomové absorpční spektrometrie (AAS).

Dosavadní stav techniky

Stopové a ultrastopové koncentrace bismutu lze ve vzorcích stanovovat různými instrumentálními metodami, nejčastěji spektrometrickými. Detekční limit lze dále snížit předřazením prekoncentračního kroku. K prekoncentraci se nejlépe hodí generování hydridů. Tato technika je přehledně zpracována např. v monografii [J. Dědina a D. L. Tsalev: Hydride Generation Atomic Absorption Spectrometry, Wiley, Chichester, 1995]. V prvním kroku prekoncentrační procedury je analyt ve formě těkavého hydridu uvolněn z okyseleného kapalného vzorku reakcí s roztokem tetrahydroboratu. Generovaný hydrid je spolu s vodíkem, který je produktem rozkladu tetrahydroboratu, veden do prekoncentračního zařízení. V druhém kroku prekoncentrační procedury, po skončení generování hydridu ze vzorku, je analyt z prekoncentračního zařízení uvolněn a veden k atomizaci a detekci některou z metod analytické atomové spektrometrie - nejčastěji AAS.

K prekoncentraci se může použít křemenné U-trubice chlazené kapalným dusíkem, ve které je generovaný hydrid zachycen. Ten je po skončení generování uvolněn zahřátím U-trubice. Tento způsob prekoncentrace trpí závažnými nedostatky - je časově náročný a jeho automatizace je prakticky neproveditelná.

Výhodnější je provádět prekoncentraci hydridu přímo v atomizátoru. Donedávna k tomu byly používány výhradně grafitové atomizátory. Generovaný hydrid je v prvním kroku procedury zachycen v atomizátoru, který je vyhříván na 200 - 600 °C. V druhém kroku prekoncentrační procedury, po skončení generování hydridu ze vzorku, je atomizátor zahřát na teplotu kolem 2500 °C, čímž je veškerý zachycený analyt atomizován a detekován, obvykle AAS. K detekci lze však použít i jiné metody analytické atomové spektrometrie. Nevýhodami prekoncentrace v grafitovém atomizátoru jsou vysoké pořizovací i provozní náklady grafitového atomizátoru.

Nicméně tento způsob prekoncentrace je v současnosti v analytické praxi velice široce využíván a patří k nejobvyklejším přístupům ke stanovení stopových a ultrastopových koncentrací hydridotvorných prvků. V literatuře publikované detekční limity pro prekoncentraci bismutu v grafitovém atomizátoru s následným stanovením AAS se pohybují řádově v jednotkách až desítkách pg ml^{-1}. Nejlepší publikovaný detekční limit je 4 pg ml^{-1}.

Nedávno byla podána patentová přihláška na způsob prekoncentrace antimonu založený na záchytu stibanu v křemenné pasti a následném uvolnění zachyceného analytu, jeho atomizaci a detekci některou z metod analytické atomové spektrometrie (Jiří Dědina, Jan Kratzer: Způsob prekoncentrace antimonu pro jeho stanovení metodami atomové spektrometrie, PV-2004-854).

Pro záchyt i atomizaci analytu lze využít konvenční vyhřívaný křemenný atomizátor bez jakékoli úpravy. Tento atomizátor se obvykle sestává z optické trubice o světlosti kolem 5 až 10 mm, jejíž osa je totožná s optickou osou spektrometru a z přívodního ramene o světlosti minimálně 2 mm přitaveného k optické trubici v jejím středu v pravém úhlu. Centrální část optické trubice je zevně vyhřívána na teplotu 900 °C. Analytická procedura prekoncentrace antimonu je rozdělena do dvou kroků: (1) záchyt a (2) uvolnění:

(1) Do nosného plynu (argonu) obsahujícího generovaný hydrid a vodík vzniklý rozkladem tetrahydroboratu je přidáván kyslík v nadstechiometrickém množství vůči přítomnému vodíku. Veškeré plyny (argon, hydrid, vodík a kyslík) jsou přiváděny do přívodního ramene atomizátoru. Na jeho konci hoří plamínek, ve kterém je spalován molekulární vodík ve stechiometrickém přebytku kyslíku. Hydrid je v tomto plamínku rozložen a analyt kvantitativně zachycen. Průtok nosného plynu aparaturou je třeba optimalizovat tak, aby plamínek vznikající hořením vodíku v stechiometrickém nadbytku kyslíku hořel stacionárně na konci přívodního ramene.

(2) Po skončení generování hydridu ze vzorku je nutné v plynné fázi proudící pastí udržet obsah vodíku odpovídající průtoku minimálně jednotkám ml min^{-1}. Pak je prostým uzavřením přívodu kyslíku analyt najednou kvantitativně uvolněn a atomizován.

Zásadním nedostatkem takto prováděné prekoncentrace je její nepoužitelnost pro prekoncentraci bismutu. Jak bylo uvedeno nedávno v literatuře (Jan Kratzer, Jiří Dědina: Spectrochim. Acta Part B, 60 859-864, 2005), důvodem je nedostatečná účinnost uvolnění bismutu, 55%, a s tím související neuspokojivá reprodukovatelnost analytických signálů.

Podstata vynálezu

Experimentální studie provedené autory prokázaly, že výše zmíněná nedostatečná účinnost uvolnění bismutu při provádění prekoncentrace v konvenčním vyhřívaném křemenném atomizátoru způsobem používaným pro prekoncentraci antimonu je způsobena tím, že část analytu je zachycena v místech přívodního ramene atomizátoru, kde je povrchová teplota významně nižší nežli 900 °C. V druhém kroku procedury tato teplota nestačí k účinnému uvolnění analytu.

Uvedený nedostatek odstraňuje způsob prekoncentrace bismutu pro jeho stanovení metodou AAS, jehož podstata spočívá v tom, že do přívodního ramene konvenčního křemenného atomizátoru, zevně vyhřívaného na teplotu 900 °C, je v podélné ose přívodního ramene vložena křemenná kapilára, jejíž konec dosahuje až na začátek optické trubice atomizátoru, přičemž veškeré plyny jsou přiváděny do této vložené křemenné kapiláry.

V prvním kroku analytické procedury prekoncentrace bismutu, tj. při záchytu, je do nosného plynu (argonu) obsahujícího generovaný hydrid a vodík vzniklý rozkladem tetrahydroboratu přidáván kyslík v nadstechiometrickém množství vůči přítomnému vodíku. Veškeré plyny (argon, hydrid, vodík a kyslík) jsou přiváděny do vložené křemenné kapiláry. Na jejím konci hoří plamínek, ve kterém je spalován molekulární vodík ve stechiometrickém přebytku kyslíku. Hydrid je v tomto plamínku rozložen a analyt je kvantitativně zachycen na povrchu atomizátoru.

Po skončení generování hydridu, v druhém kroku procedury, t.j. při uvolnění, je uzavřením přívodu kyslíku analyt najednou uvolněn proudem vodíku a atomizován. Účinnost uvolnění analytu je 100%. To vede k výborné reprodukovatelnosti analytických signálů.

Oproti běžně používané prekoncentraci hydridu v grafitovém atomizátoru je metoda prekoncentrace podle vynálezu jednodušší a pořizovací i provozní náklady jsou desetkrát až stokrát nižší. Detekční limit prekoncentrace podle vynálezu s následným stanovením AAS je na úrovni v literatuře uvedeného nejlepšího detekčního limitu pro záchyt v grafitovém atomizátoru s následným stanovením AAS .

Příklady provedení vynálezu

Pro stanovení Bi prekoncentrovaného metodou podle vynálezu lze využít širokou škálu konvenčních vyhřívaných křemenných atomizátorů, viz např. monografii [J. Dědina a D. L. Tsalev: Hydride Generation Atomic Absorption Spectrometry, Wiley, Chichester, 1995] pro

podrobný popis jednotlivých typů konvenčních vyhřívaných křemenných atomizátorů. Jedinou nutnou úpravou je vložení křemenné kapiláry o světlosti 0,5 mm do přívodního ramene atomizátoru.

Příklad provedení vynálezu pro stanovení Bi je blíže osvětlen pomocí výkresu, na kterém je schematicky znázorněn jeden z typů konvenčních vyhřívaných křemenných atomizátorů. Atomizátor je vyroben z křemene a sestává se z přívodního ramene 1 a z optické trubice 2 o světlosti 7 mm a délce 160 mm, jejíž osa je totožná s optickou osou spektrometru. Přívodní rameno 1 o světlosti 2 mm a délce 90 mm je přitaveno k optické trubici 2 v jejím středu v pravém úhlu. Centrální část 3 optické trubice 2, dlouhá 125 mm, je vyhřívána elektrickou odporovou pícko u na teplotu 900 °C. Do podélné osy přívodního ramene 1 atomizátoru je vložena křemenná kapilára (Supelco) 4 o světlosti 0,5 mm, jejíž konec dosahuje až na začátek optické trubice 2. Kapilára 4 je v přívodním rameni 1 utěsněna těsněním 5 sestávajícím z teflonové hadičky o světlosti 0,7 mm a z teflonové pásky.

V kroku záchytu je do kapiláry 4 přiváděn generovaný bismutan v proudu argonu (75 ml.min^{-1}) s příměsí vodíku (z rozkladu tetrahydroboratu, cca 15 ml.min^{-1}) a kyslíku (10 ml.min^{-1}) přidávaného pomocným kanálem v nadstechiometrickém poměru vůči vodíku). Generování probíhá v kontinuálním režimu, kdy jsou do generátoru hydridů přiváděny kontinuální průtoky vzorku v 1 M HCl (průtok 4,3 ml.min^{-1}) a roztoku tetrahydroboratu (průtok 1,1 ml.min^{-1}). Za těchto podmínek se z tetrahydroboratu uvolňuje 15 ml.min^{-1} vodíku. Stechiometrickému poměru kyslíku odpovídá 7,5 ml.min^{-1}, byl zvolen průtok kyslíku 10 ml.min^{-1}. Za těchto podmínek hoří plamínek na konci kapiláry 4. Střed optické trubice slouží v tomto uspořádání v kroku záchytu jako past pro záchyt analytu. Po skončení generování hydridu ze vzorku je proud vzorku do generátoru nahrazen proudem 1 M HCl o stejném průtoku.

V kroku uvolnění je, beze změny teploty atomizátoru, uzavřen přívod kyslíku a pomocným kanálem přiveden proud vodíku o průtoku 100 ml.min^{-1}. Tím je analyt zachycený ve středu optické trubice najednou uvolněn a atomizován.

Průmyslová využitelnost

Metodu lze použít pro prekoncentraci bismutu před jeho stanovením AAS.

PATENTOVÉ NÁROKY

1. Způsob prekoncentrace analytu pro stanovení stopových a ultrastopových koncentrací bismutu metodou atomové absorpční spektrometrie, kdy se do nosného plynu obsahujícího analyt ve formě hydridu a vodík přidává kyslík v nadstechiometrickém množství vůči přítomnému vodíku a molekulární vodík se spaluje ve stechiometrickém přebytku kyslíku a uvolnění zachyceného analytu se provede uzavřením přívodu kyslíku, **vyznačující se** tím, že plyny se přivádí do křemenné kapiláry vložené do přívodního ramene atomizátoru, který je zevně vyhříván na atomizační teplotu, tj. na teplotu mezi 700 °C a 1000°C, molekulární vodík se spaluje ve stechiometrickém přebytku kyslíku v plameni hořícím na konci této kapiláry, načež se zachycený analyt uvolní uzavřením přívodu kyslíku a spuštěním proudu vodíku.

2. Atomizátor pro prekoncentraci bismutu stávající se z optické trubice a přívodního ramene, **vyznačující se** tím, že v podélné ose přívodního ramene (1) atomizátoru je umístěna křemenná kapilára(4) o vnitřním průměru od 0,3 do 0,7 mm dosahující na začátek optické trubice (2) atomizátoru.

Obrazek