CHARLES UNIVERSITY IN PRAGUE

FACULTY OF SCIENCE

Department of Analytical Chemistry

PRECONCENTRATION OF HYDRIDE FORMING ELEMENTS IN QUARTZ ATOMIZERS FOR ATOMIC ABSORPTION SPECTROMETRY

Synopsis of the PhD Thesis

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CONTENTS

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4. Stanovení stopových koncentrací hydridotvorných prvků technikou HG-AAS, FRVŠ č. 1011/2006, 2006. (***principal investigator***)

5. Development and optimization of quartz preconcentration devices and atomizers for ultratrace determination of hydride forming elements by AAS, GA UK 306/2006/B-CH/PrF, 2006-2008. (***principal investigator***)

List of publications

Articles in impacted journals

1. KRATZER J., DĚDINA J.: In situ trapping of stibine in externally heated quartz tube atomizers for atomic absorption spectrometry. Spectrochim. Acta Part B 60 (2005) 859-864.

2. KRATZER J., DĚDINA J.: In situ trapping of bismuthine in externally heated quartz tube atomizers for atomic absorption spectrometry. J. Anal. Atom. Spectrom 21 (2006), 208-210.

3. KRATZER J., DĚDINA J.: Arsine and selenium hydride trapping in a novel quartz device for atomic absorption spectrometry. Anal. Bioanal. Chem. 388 (2007), 793-800.

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3. DĚDINA J., KRATZER J.: Compact Preconcentration and Atomization Device for the Determination of Hydride Forming Elements by Atomic Absorption Spectrometry. Patent application applied to Industrial Property Office of the Czech Republic, PV 2007-112, 13.2. 2007.

The articles and patent applications are supplements of the thesis.

List of conference contributions

Oral contributions

1. DĚDINA J., KORKMAZ D., KRATZER J., ATAMAN Y.: Hydride preconcentration on the quartz surface with subsequent atomization in the quartz multiatomizer. In: Colloquium Spectroscopicum Internationale XXXIII, (Fernandéz J., Pérez J., Eds.), Granada, Spain, 7.-12. September 2003, p. 162, ISBN 84-338-3017-1

2. KRATZER J., DĚDINA J., RYCHLOVSKÝ P.: Prekoncentrace antimonu na křemenném povrchu po generování stibanu. In: 7. ročník soutěže o nejlepší studentskou práci v oboru analytická chemie „O cenu firmy Merck“, (Barek J., Ventura K., Eds.) Ostrava, 4.-5. 2. 2004, vydala ČSCH, Praha, 2004, str. 40-46, ISBN 80-86238-38-5

3. KRATZER J., DĚDINA J., RYCHLOVSKÝ P.: A new approach to stibine preconcentration: *in-situ* trapping in quartz tube atomizer for atomic absorption spectrometry. In: 6th Joint Seminar of Young Scientists, 24.5. 2004, p.13, Prague.
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5. DĚDINA J., KRATZER J.: Hydride Trapping in Quartz Tube Atomizers. In: 2. Ulusal Analitik Kimya Kongresi, Malatya, Turkey, 2.-4. September 2004

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7. DĚDINA J., KRATZER J.: Hydride trapping in quartz tube atomizers. In: CSI XXXIV - Colloquium Spectroscopicum Internationale, Antwerpen, Belgium, 5.-9.9. 2005, p. 297

8. DĚDINA J., KRATZER J.: A new approach to preconcentration of hydride forming elements: hydride trapping in quartz tube atomizers for atomic absorption spectrometry. In: IV. International conference on inorganic environmental analysis, Pardubice, 18.-22.9. 2005, p. 22.

9. KRATZER J., DĚDINA J.: Hydride trapping at the quartz surface for AAS: A powerful tool for ultratrace analysis. In: IV. International conference on inorganic enviromental analysis. Pardubice, 18.-22.9. 2005, p. 127-128.

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16. KRATZER J., VOBECKÝ M., RYCHLOVSKÝ P., DĚDINA J.: Hydride Trapping in Quartz Atomizers for Atomic Absorption Spectrometry: Radiotracer Study and Routine Applications. In: CSI XXXV- Colloquium Spectroscopicum Internationale, Xiamen, China, 23.-27.9. 2007, p. 34
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Poster contributions

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5. KRATZER J., VOBECKÝ M., RYCHLOVSKÝ P., DĚDINA J.: As and Se Hydride Trapping at the Quartz Surface. In: CANAS´07 - Colloquium Analytische Atomspektroskopie, Konstanz, Germany, 18.-21.3. 2007, p. P16

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1. BAREK J., KONEČNÁ B., KRATZER J., HRUŠKOVÁ M., NAVRÁTIL T.: Voltammetric determination of cytostatics using silver solid amalgam electrode. [stať ve sborníku] In: Moderní elektrochemické metody. Praha, Česká společnost chemická 2003, 16-19. ISBN 80-86238-29-6. MSM 113100002, GAUK 253/2001/B-Ch/PrF.
2. MUSIL S., KRATZER J., VOBECKÝ M., RYCHLOVSKÝ P., MATOUŠEK T.: Chemical Vapour Generation of Silver as a Method for Sample Introduction for Atomic Absorption Spectrometry, In: 4th International Student Conference „Modern Analytical Chemistry“, Book of Proceedings, Prague, 28.-29.1. 2008, ISBN 978-80-903103-2-2, p. 113-117

Abstract

The use of quartz atomizers to preconcentrate hydride forming elements for their ultratrace determination by atomic absorption spectrometry is studied in this work. The inlet arm of the quartz multiatomizer served as the trap in optimization studies. The advantage of in-atomizer trapping in the quartz atomizer is compact and simple apparatus design, low atomizer cost as well as low measurement noise. The advantage of the quartz trap is its temperature control, which is independent of the atomization temperature control.

Collection and volatilization conditions (surface temperature, gas composition) as well as atomization conditions (oxygen content in the atomizer influencing the amount of hydrogen radicals) were optimized for all the four analytes tested (As, Sb, Bi, Se). Analytical methods based on in-situ trapping of Sb and Bi hydrides in the conventional quartz tube atomizer and in-atomizer trapping of As and Se hydrides in the quartz multiatomizer were developed and validated. Novel collection approach under oxygen excess over hydrogen enables to reach 100% collection efficiency. The overall preconcentration efficiency reaches 100 % for Sb and Bi. The preconcentration efficiency for As and Se is also satisfactory reaching 50 % and 70 %, respectively. The applicability of the methods was demonstrated using real samples. Detection limits in the low pg ml^{-1} range were reached for 5 min preconcentration (sample consumption 20 ml).

The collection and volatilization efficiency for Bi and As was investigated also by independent radiotracer study.

Additional experiments were carried out to clarify the mechanisms of the processes during collection, volatilization and atomization.

1 Ultratrace analysis of hydride forming elements

Determination of analyticaly important elements at ultratrace concentration levels is nowadays one of the most challenging tasks of instrumental analytical chemistry, not only due to increased interest in element speciation[1]. Low detection limits are often required by law regulations, especially in case of toxic (such as arsenic, mercury, cadmium) or essential (such as selenium) elements. A suitable routine analytical method should meet following requirements: low detection limit, low operational and investment costs and it also should not be laborious for the operator. The method might be also robust and provide both precise and accurate results for different sample matrix because the analyte may be determined in a variety of sample types (food, environment, etc.).

To reach the corresponding sensitivity, it is either necessary to equip the laboratory by an expensive instrumentation or to employ a preconcentration step prior the analysis. Spectrometric methods, especially atomic absorption spectrometry (AAS)[2] seem to be suitable detectors for element analysis meeting all the requirements put on ultratrace element analysis - except for sufficiently low detection limit. Hydride generation atomic absorption spectrometry (HG-AAS)[3] is favourably used to determine elements that form volatile hydrides such as arsenic, selenium, antimony and bismuth. This method minimizes the risk of interferences. Moreover, analyte can be preconcentrated from gaseous phase - that might be advantageous in some cases. The hydride is usually atomized in simple quartz tube atomizers. Unfortunately, HG-AAS without employing any preconcentration step does not reach the detection limit low enough for ultratrace analysis.

The number of scientific works exploring materials suitable for hydride trapping with subsequent AAS detection has increased significantly in last decade. The reasons for that might be the popularity of AAS as the detection technique, permanent effort to decrease the detection limits of analytical techniques employed in element analysis as well as the high investment and operation costs of the sufficiently sensitive techniques such as ICP-MS. The surface materials tested can be divided into three groups[4] – graphite[5], metal[6-9] and quartz[10-13].

2 Objectives of the Thesis

This dissertation was elaborated at the Institute of Analytical Chemistry of the ASCR, v.v.i. under the framework of a long time research in the Laboratory of Trace Element Analysis in Prague, which aim is to develop highly sensitive methods for determination and speciation of analyticaly important hydride forming elements.

The main idea of this work was to further develop the novel approach to hydride trapping based on hydride collection in quartz atomizers. The objectives were:

- Development of a compact and all-purpose conection of the quartz preconcentration device with the quartz atomizer to investigate the optimum trapping conditions.

- Optimization of collection and volatilization conditions for As, Sb, Bi a Se at the quartz surface (collection temperature, volatilization temperature, gaseous phase composition).

- Proposal and validation of the analytical methods for the determination of As, Sb, Bi and Se at ultratrace concentration levels (trapping efficiency, limit of detection, repeatability, interference).

- Contribution to the explanation of the collection and volatilizaton mechanisms.

The thesis consists of 4 scientific articles published in international impacted journals and 3 patent applications that were applied to the Industrial Property Office of the CR. Furthermore, the results were presented as 22 contributions (6 invited lectures, 11 oral presentations and 5 posters) either at international or domestic conferences.

3 Experimental

3.1 Apparatus

A multiple microflame quartz tube atomizer (multiatomizer), which had been developed in our laboratory by Dědina and Matoušek[14,15], was modified and used to study and optimize the individual steps of the preconcentration procedure.

The inlet arm of the multiatomizer (having a length of 80 mm, inner diameter 2 mm and outer diameter 3 mm), served as a trap (in atomizer trapping). A 6 cm long heating coil made from ca 40 cm Ni-Cr canthal wire (4.17 Ω m^{-1}, 0.65 mm in diameter) covered the downstream part of the inlet arm. The heating coil allowed heating the inlet arm from 100 up to 1100 °C independently of the horizontal (optical) arm. The horizontal arm was continually heated to 900 °C.

Employing two auxiliary gas channels, the apparatus design enables to introduce hydrogen and oxygen gas flows into the inlet arm of the multiatomizer. The gas flow rates can be controlled acuratelly by the mass flow controllers. Oxygen is delivered through a silica capillary, whereas other gases are introduced through a concentric teflon tube around this capillary. Either air or hydrogen gas flow was introduced into the horizontal arm of the multiatomizer as the outer gas.

The schema of the apparatus is depicted in Fig.1.

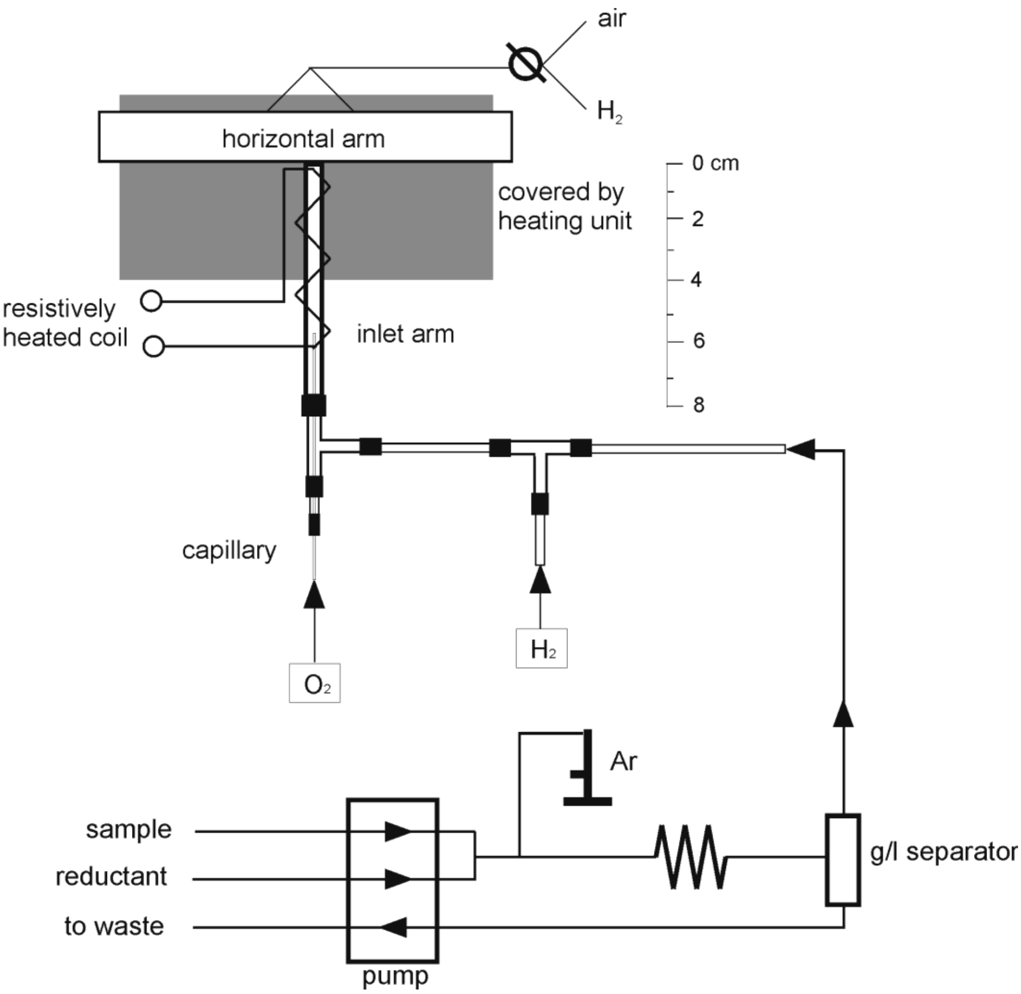

Fig. 1 – Schematic diagram of the apparatus for in-atomizer trapping

3.2 Procedure

The proposed collection procedure consists of two steps – **trapping** and **volatilization**.

In the trapping step, analyte is retained in the inlet arm under the stoichiometric oxygen excess over hydrogen. Cca 15 ml min^{-1} of hydrogen is evolved from decomposition of $NaBH_4$ which is employed as a reductant to generate hydrides. Since hydrogen is responsible for analyte losses in the trapping step, it must be removed. It is realized in an oxygen-hydrogen flame burning at the tip of the oxygen delivery capillary.

The apparatus setup enables to monitor the **breakthough signal** during the trapping step, i.e. to detect the non-collected analyte breaking through into the atomizer. To detect signal by AAS, hydrogen excess over oxygen must be maintained in the optical arm. However, there is oxygen excess over hydrogen in the inlet arm during the trapping step. Consequently, hydrogen must be introduced to the optical arm as the outer gas.

Trapped analyte is volatilized, atomized and detected in the **volatilization** step. Hydrogen presence in the inlet arm during the voaltilization step was proved to be essential. Signal of the volatilized analyte is monitored employing air as outer gas.

Trapping and volatilization temperature can vary within the range 100-1100 °C. A **cleanout step** followed after the volatilization step in the optimization study, in which the trap was heated to a temperature sufficient to remove the non-volatilized analyte fraction.

Optimization study was performed as univariate. The parameters studied were: trapping and volatilization temperature as well as the hydrogen flow rate in the volatilization step.

The efficiency of the whole preconcentration period can be estimated taking into account the analyte signals measured in the trapping (including the breakthrough signal), volatilization and additional volatilization (cleanout) step. The overall efficiency of the collection procedure can be quantified when comparing the signals measured in the collection mode with those obtained without preconcentration (on-line atomization), but otherwise under the same experimental conditions.

Tab. 1 Apparatus conditions during the optimization study

parameter	**trapping step**	reaching volatilization conditions	**volatilization step**	reaching cleanout conditions	**cleanout step**	reaching trapping conditions
time (s)	60	60	15	60	15	60
Ar (ml min^{-1})	75	75	75	75	75	75
O_2 (ml min^{-1})	10	10	0	10	0	0
$H_2(BH_4^-)$ (ml min^{-1})	15	0	0	0	0	0
pump on/off	ON	OFF	OFF	OFF	OFF	OFF
signal reading	YES	NO	YES	NO	YES	NO
outer gas (25 ml min^{-1})	H_2	air	air	air	air	air

3.3 Detection by atomic absorption spectrometry

Atomic absorption spectrometer VarianAA 300

(Varian, Australia)

Tab. 2 Operation paramaters of the hollow cathode lamps

	Element			
Parameter	As	Sb	Bi	Se
λ (nm)	193.7	217.6	223.1	196.0
slit (nm)	0.5	0.2	0.2	1.0
I (mA)	10.0	10.0	10.0	10.0

3.4 Measurements with the radiotracers

Besides AAS, radiotracers were employed to study the trapping behavior of bismuth and arsenic.

The trapping and volatilization efficiency, respectively, was quantified employing the scintillation NaI(Tl) well-type detector (Minaxi 5000, Packard).

The spatial distribution of the radiotracer was invesigated by image plate autoradiography. The radiograms were evaluated using a Fuji BAS 5000 laser scanner.

Tab. 3 Characteristic of the radiotracers used

Isotope	$T_{1/2}$	$E_{\gamma, window}$ (keV)	m (g kBq^{-1})	preparation
^{73}As	80.30 d	30-200	$1.2.10^{-13}$	Ge_{nat}(p, x n)
^{74}As	17.78 d	30-1300	$2.7.10^{-13}$	
^{205}Bi	15.3 d	80-1800	$6.5.10^{-13}$	Pb_{nat}(p, x n)
^{206}Bi	6.24 d	80-1100	$2.7.10^{-13}$	

$T_{1/2}$ – half-life, d-days, nat-natural, x = 1,2, m-estimated mass of the radiotracer having activity of 1 kBq, $E_{\gamma, window}$ – range of the energy measured

4 Results and discussion

Quartz was chosen as the material for the preconcentration (trap-and-atomizer) device in this work because quartz atomizers are usually used for hydride atomization. Optimization studies were performed in a preconcentration device that was an integral part of the inlet arm of the multiatomizer. This setup enables to control the trapping and volatilization conditions independently of those for atomization. Even though, the trap-and-atomizer device design remains compact and simple. Conditions for hydride generation were taken from the literature or from the procedures routinely used in the laboratory. However, the approach to preconcentration based on the hydride collection under excess of oxygen, making possible a complete collection, is completely original. Collection and volatilization conditions (surface temperature, gas composition) were optimized for all four analytes studied (As, Sb, Bi, Se). Also the atomization of the volatilized analyte species was optimized (oxygen content in the atomizer that controls H radical production). Analytical methods employing in-situ trapping of Sb and Bi in the conventional quartz tube atomizer and in-atomizer trapping of As and Se in quartz multiatomizer were developed and validated subsequently.

4.1 Optimization of the preconcentration conditions by AAS

The proposed apparatus setup (Fig. 1) as well as the developed procedure (chapter 3.2) is ideal to study preconcentration conditions of all hydride forming elemets. The apparatus setup is due to its compact design, simplicity and universality the best one among other designs studied previously in our laboratory.

100% overall preconcentration efficiency was reached for Sb and Bi, whereas 50% analyte losses were observed for As between the trapping and volatilization step. 15% breakthrough signal during the trapping step and subsequently, 15% losses between the trapping and volatilization step were found for Se.

Tab. 4 Optimum conditions founded for collection at the quartz surface

parameter		**trapping step**	**volatilization step**
Trap temperature (°C)			
	As	100-700	600-800
	Sb	500-950	800-950
	Bi	100-950	800-950
	Se	100-300	550-650
H_2 flow (ml min-1)			
	As		100
	Sb		75
	Bi		100
	Se		50

4.2 Routine applications

Because the optimum trapping, volatilization and atomization temperatures for Sb and Bi overlap, these analytes can be preconcentrated without use of any special trap. The trapping, volatilization and atomization processes proceed at the same temperature; being controlled only by the composition of gaseous phase. The collection procedure can be simplified for routine applications, the analyte is trapped directly in the horizontal arm of the conventional quartz tube atomizer, no multiatomizer is required.

The detection limits (300 s preconcentration period) were found to be 2.8 pg.ml^{-1} and 3.9 pg.ml^{-1}, respectively, for Sb and Bi. The accuracy of the developed routine method was checked by Sb reference material (trace elements in water) – see Tab. 5. The interference extent of other hydride forming elemets on the determination of Sb and Bi was found to be comparable for the novel collection method and HG-AAS without the collection mode.

Tab. 5 Determination of Sb in reference material and mineral water

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	-

4.3 Radiotracer study

Bismuth

Complete bismuth trapping as well as subsequent volatilization were confirmed by radiotracer method. Efficiency of (96±5)% and (98±2)% was found, respectively, for trapping and volatilization (n=5). Image plate autoradiography proved that the trapping area is increasing when trapping temperature is elevated. The trapping area for unheated trap was 1.5 cm (Fig. 2A), whereas it was 4 cm in the trap heated to 900 °C (Fig. 2B). However, the trapping efficiency remains to be 100 % in the whole temperature range studied.

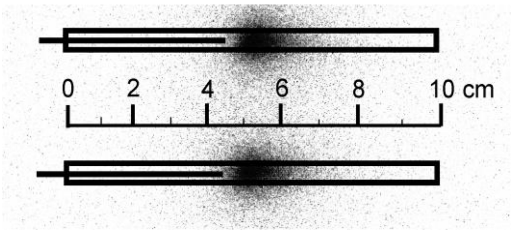

Fig. 2 A – autoradiography of the trapped Bi trap unheated (n=2)

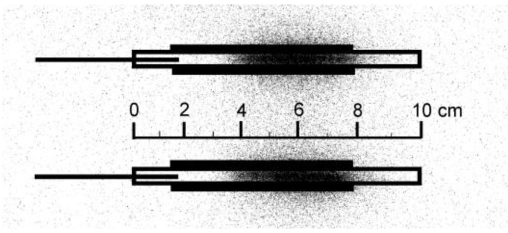

Fig. 2 B – autoradiography of the trapped Bi trap heated to 900 °C (n=2)

Arsenic

Employing the radiotracer, 93±4 % arsenic trapping efficiency was found. Only 4±3 % (n=5) of trapped arsenic species were retained at the quartz surface after the volatilization step indicating the nearly complete volatilization.

Arsenic was found to be lost between the trapping and volatilization step, during the 60 s interval, in which the trap temperature is increased from 100 °C (optimum for trapping) to 800 °C (optimum for volatilization). Analyte losses during this period were estimated to reach 50 %, which explains why 50 % overall efficiency was observed previously with AAS detection. Unfortunately, using the resistive heating of the inlet arm, it is not possible to reach 800 °C equilibrium temperature of the inner quartz surface faster than in 60 s interval. Losses of the trapped arsenic species were found to be less significant under the oxygen presence in the carrier argon gas.

4.4 Mechanistic study

The identification of the trapped and volatilized form would require the use of mass spectrometry as a detector. Nevertheless, none of the experiments performed is against our theory based on the radical mechanism. The analyte hydride seems to be decomposed in the oxygen-hydrogen microflame and converted probably to its oxide. The analte oxide is retained at the quartz surface. Two factors are needed to volatilize the trapped analyte form – (1) hydrogen presence and (2) elevated temperature of the quartz surface.

A mechanistic study with bismuth as a model analyte proved that efficient volatilization requires both hydrogen presence (100 ml min^{-1} H_2 corresponding to its 57% fraction in the carrier gas) and increased temperature of the quartz surface (870 °C). The analyte is volatilized probably due to the H radical mechanism. Simultaneous presence of oxygen and hydrogen in the volatilization step results in production of a large amount of H radicals. Under these conditions, in the presence of the H radicals, analyte can be efficiently volatilized employing significantly lower volatilization temperature compared to experiments where only hydrogen in absence of oxygen was used.

Volatilized forms of antimony and bismuth can be detected after preconcentration in the conventional quartz tube atomizer heated to 900 °C. Thus, the volatile forms are either free atoms or they can be atomized by the same mechanism as hydrides during on-line atomization in the conventional quartz tube atomizer. In contrast, arsenic can be detected after the preconcentration only in a multiatomizer supplied with air as outer gas. No signal is recorded when the multiatomizer is replaced by the conventional quartz tube atomizer heated to 900 °C. This observation indicates that arsenic might be volatilized in a hydrogen-rich atmosphere as clusters of As atoms that can be converted to free atoms only in the presence of a high concentration of H radicals, which is realized in the multiatomizer optical arm. Although the volatilized forms of all the analytes might be atomized by the same mechanism, As requires much higher H-radical concentration than Sb or Bi.

4.5 Comparison of the studied analytes

Since all the four analytes tested were studied in the same apparatus setup one can compare the results and draw the conclusions. The elements studied may be divided into two groups according to similarities in their behavior during trapping, volatilization and atomization. As and Se are the elements of the first group, whereas Sb and Bi belong to the second group. The boiling points[16] of the first group elements are between 600-700 °C, whereas their oxides (As_2O_3 and SeO_2) boil around 400 °C. The boiling points for both elemental and oxide forms of the second group analytes are significantly higher being well above 1500 °C. The experimental data are in a good agreement with these physico-chemical properties. Optimum trapping and volatilization temperatures found for As and Se are lower than those observed for Sb and Bi (see Tab. 4).

Low volatility of the trapped form may on the one hand cause difficulties in the second step of the collection procedure. On the other hand, volatile analytes may be lost in the trapping step. However, suitable collection conditions can be optimized for each individual analyte.

Naformátováno

Naformátováno

5 Conclusions

The main outputs of this thesis are:

1) a novel approach to the preconcentration procedure, which employs the oxygen excess over hydrogen in the trapping step

2) the design of the compact and all-purpose trap-and-atomizer device based on the quartz multiatomizer

3) optimized trapping, volatilization and atomization conditions for all four analytes studied – As, Sb, Bi a Se

4) development and validation of the in-situ trapping of Sb and Bi hydrides in the conventional quartz atomizer for their routine ultratrace determination - compared to the common approach (HG-AAS without preconcentration) our way of trapping decreases the detection limit of 1-2 orders of magnitude but does not require any extra equipment or analysis expenses and is not labor consuming

5) insights into the mechanisms of the processes during analyte trapping, volatilization and atomization obtained by radiotracer and atomic absorption measurements

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