CHARLES UNIVERSITY IN PRAGUE

FACULTY OF SCIENCE

Department of Analytical Chemistry

Contributions to Volatile Compound Generation of Arsenic, Silver and Gold by Tetrahydroborate Reaction for Atomic Absorption Spectrometry

Synopsis of the Ph.D. Thesis

Prague 2011 **Mgr. Stanislav Musil**

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The presented thesis is based on the following papers:

Paper I.

Musil S., Matoušek T.: **On-line pre-reduction of pentavalent arsenicals by thioglycolic acid for speciation analysis by selective hydride generation-cryotrapping-atomic absorption spectrometry.** *Spectrochim. Acta, Part B,* **63** (2008), 685–691.

Paper II.

Taurková P., Svoboda M., Musil S., Matoušek T.: **Loss of di- and trimethylarsine on Nafion membrane dryers following hydride generation.** *J. Anal. At. Spectrom.,* **26** (2011), 220–223.

Paper III.

Musil S., Kratzer J., Vobecký M., Hovorka J., Benada O., Matoušek T.: **Chemical vapor generation of silver for atomic absorption spectrometry with the multiatomizer: Radiotracer efficiency study and characterization of silver species.** *Spectrochim. Acta, Part B,* **64** (2009), 1240–1247.

Paper IV.

Musil S., Kratzer J., Vobecký M., Benada O., Matoušek T.: **Silver chemical vapor generation for atomic absorption spectrometry: minimization of transport losses, interferences and application to water analysis.** *J. Anal. At. Spectrom.,* **25** (2010), 1618–1626.

Paper V.

Arslan Y., Matoušek T., Kratzer J., Musil S., Benada O., Vobecký M., Ataman O. Y., Dědina J.: **Gold volatile compound generation: optimization, efficiency and characterization of the generated form.** *J. Anal. At. Spectrom.,* (2011), DOI:10.1039/C0JA00194E.

TABLE OF CONTENT

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry
CVG	Chemical vapor generation
DMAs(V)	Dimethylarsinate
FI	Flow injection mode
GF	Graphite furnace
HG	Hydride generation
iAs(III)	Arsenite
iAs(V)	Arsenate
L-cys	L-cysteine
LOD	Limit of detection
multiatomizer	Multiple microflame quartz tube atomizer
MAs(V)	Methylarsonate
σ_{blank}	Standard deviation of blank signal
QTA	Quartz tube atomizer
TEM	Transmission electron microscope(y)
TGA	Thioglycolic acid
TMAs(V)O	Trimethylarsine oxide
VC	Volatile compound
VCG	Volatile compound generation

1 OBJECTIVES OF THE THESIS

The presented dissertation thesis summarizes the results contained in five original research papers that were published in prestigious international scientific journals in the field of analytical chemistry and atomic spectrometry. It is devoted to the method of generation of volatile compounds using a tetrahydroborate reaction and detection in a quartz multiatomizer by atomic absorption spectrometry. The thesis can be divided into two thematic parts – speciation analysis of arsenic based on hydride generation technique with collection and separation in a cryogenic trap and generation of volatile species of transition metals.

The general objectives of this thesis have been as follows:

1) to develop a simple setup for on-line pre-reduction of pentavalent arsenicals coupled to a hydride generator and to apply it to oxidation state specific As speciation analysis (Paper I),
2) to test and compare Nafion membrane dryers and a sodium hydroxide dryer for their use in the same method with respect to losses of methylated arsines (Paper II),
3) to evaluate the relevance of individual experimental parameters of Ag and Au chemical vapor generation using atomization in a multiatomizer and atomic absorption spectrometry for sensitive detection (Papers III and V),
4) to characterize the nature of Ag and Au species in the gaseous phase (Papers III and V),
5) to track the analyte transfer in the course of chemical vapor generation of Ag and Au including the determination of efficiencies in each individual process of generation by means of radioactive indicators (Papers III–V),
6) to investigate and minimize transport losses of volatilized Ag species (Paper IV).

2 INTRODUCTION

Volatile compound generation (VCG) has been established as a powerful sample introduction technique in analytical atomic spectrometry [1]. It employs conversion of an analyte from a liquid sample to a volatile compound (VC) that is introduced to a detector in the gaseous phase. The generation step, performed in a generator, thus consists of these sequential processes: conversion of the analyte to the VC, release of the VC from the solution to the gaseous phase and transport of the released VC by a flow of a carrier gas to the detector [1]. In principle, VCG can serve as the sample introduction technique for various analytical methods, but it has attained the most extended use in atomic absorption spectrometry (AAS) due to its simplicity and cheap instrumentation.

The use of VCG offers much better detection power in comparison to nebulization techniques, which is given by following aspects. Firstly, the analyte is separated from the sample matrix. Secondly, much higher introduction and transport efficiency of the gaseous analyte to the detector can be achieved. Thirdly, the analyte collection and preconcentration from the gaseous phase is feasible. And finally, extremely mild atomization conditions can be used for the VCs [1]. Another great potential of VCG lies in the trace element speciation analysis.

At present the most popular VCs are hydrides of “classical“ hydride-forming elements, *i.e.* As, Bi, Ge, In, Pb, Sb, Se, Sn, Te and Tl. Hydride generation (HG) using tetrahydroborate in acid medium is considered to be the most widespread and successful technique of chemical vapor generation (CVG)[a]

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[a] The term of chemical vapor generation (CVG) specifies the general term of volatile compound generation (VCG) which does not take into consideration the means how the VCs are generated. Apart from CVG based on chemical reaction, there are two other approaches to VCG – electrochemical generation [2,3] and photochemical generation [4]. CVG or hydride generation (HG) are used in the thesis as terms for VCG of transition metals and of hydride forming elements, respectively, by the tetrahydroborate reaction.

for conversion of those elements to their corresponding volatile hydrides [5]. Mercury is usually included in this list even though it is generated as cold vapor of Hg^0. There are contradictory reports on the nature of the VCs of Cd [6].

Recently, the scope of VCG based on the tetrahydroborate reaction has been significantly expanded to the formation of volatile species of other transition elements: Ag, Au, Co, Cr, Fe, Ir, Mn, Mo, Ni, Os, Pd, Pt, Rh, Ru, Ti and Zn [7,8]. However, in spite of some analytical applications to real samples, the situation is not as simple as in the case of HG [7,8]. The mechanism of generation is unclear [9,10] and the identity of a final product is unknown. Many hypotheses regarding the nature of those generated VCs have been suggested, such as formation of hydrides [6,11–15], nanoparticles [16,17] or hydridometal complexes [10], but none of them has been proven by the real experimental evidence yet. The other drawback is relatively low CVG efficiency, *i.e.* the portion of the analyte introduced to the detector, in comparison to HG where HG efficiency is usually close to 100% [1,5]. It can be significantly enhanced when CVG is performed in the presence of various reaction modifiers [8].

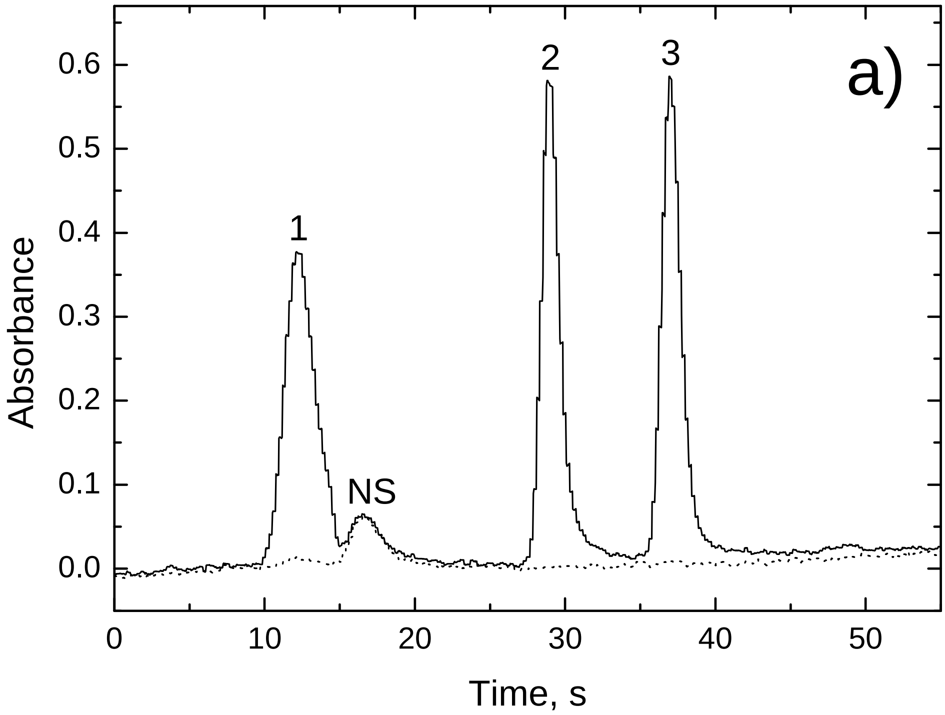
As for detection by AAS, atomization of the analyte in the form of the VC is a neccessary step. Atomization in the quartz tube atomizer (QTA) is the most common approach mainly due to its excellent sensitivity, easy operation and cheap equipment. It is also suitable for the use with separation techniques for speciation analysis because it operates continuously [1,5]. Recently a new advanced type of the QTA, a multiple microflame quartz tube atomizer (multiatomizer) [18,19], was developed and significantly improved the linearity of calibrations and resistance to interferences [19].

Arsenic is found in the environment in several chemical forms and its chronic exposure of humans from food and water is generally associated with cancer of skin and of other internal sites and with a further various adverse health effects. However, the toxicity of As species differs significantly and thus there is a worldwide interest in As speciation analysis. As mentioned above, there is a great potential of VCG in this field. There are three approaches to speciation analysis of As based on HG: selective HG, generation of substituted arsines with cryotrapping separation and post-separation HG [1,5]. The third possibility involves separation of individual analyte species, usually by high performance liquid chromatography, followed by HG and detection [20]. The method of selective HG based on pre-reduction employs the fact that only trivalent As species can be converted to their corresponding volatile arsines by the tetrahydroborate reaction in moderately acid medium. For complete conversion of pentavalent species from the same medium a pre-reduction step is neccessary. This behavior is commonly utilized in As speciation analysis when one aliquot is pre-reduced to determine the sum of trivalent and pentavalent arsenicals, another sample aliquot is not treated with pre-reductant and arsines solely from trivalent forms are generated. Concentration of pentavalent forms is thus calculated from the difference. Nowadays L-cysteine (L-cys) has become a popular pre-reductant owing to higher stability in comparison to originally used potassium iodide [21–26]. Generation of substituted arsines with cryotrapping separation can be used for As speciation analysis as well because the individual As species (inorganic or mono-, di- and trimethylated) can be converted to their corresponding volatile arsines [27]. In collection step they are retained in the cryogenic trap cooled by liquid nitrogen and then easily separated by heating the trap thanks to significant differences in their boiling points [27–29]. The corresponding boiling points are –55, 2, 35.6 and 70 °C in the sequence of arsine, methylarsine, dimethylarsine and trimethylarsine, respectively [27–29]. When combining both methods, selective HG and generation of substituted arsines, we can thus obtain the whole speciation information on all toxicologically important As species, *i.e.* trivalent and pentavalent inorganic, mono-, di- and trimethylated arsenicals.

3 ACHIEVED RESULTS

3.1 On-line Pre-reduction of Pentavalent Arsenicals by Thioglycolic Acid (Paper I)

Paper I demonstrates the feasibility of the pre-reducing agent, thioglycolic acid (TGA), for determination of pentavalent inorganic and mono-, di- and trimethylated arsenicals in comparison to currently used L-cys [21]. Since TGA has been supposed to react much faster with pentavalent arsenicals [30] at ambient temperature a new setup for on-line pre-reduction by TGA has been suggested. The application of segmented flow by air bubbles for suppression of axial dispersion and better mixing with the analyte solution in the pre-reduction coil has been considered as the most suitable way. Approximate reaction times of iAs(V), MAs(V) and DMAs(V) with TGA have been determined as less than 2 min.



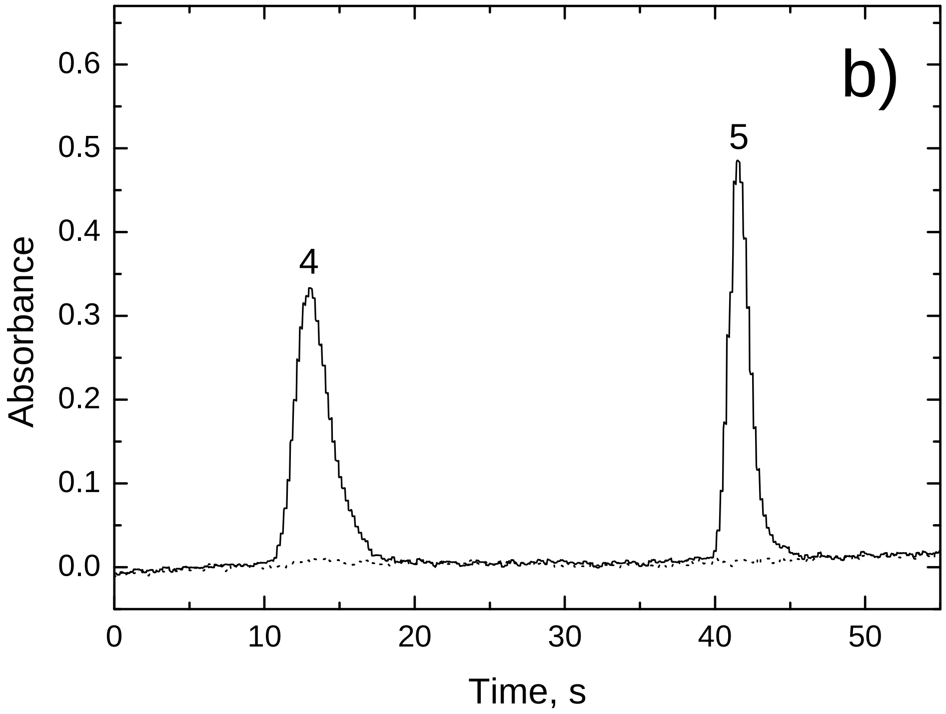


Fig. 1a,b Typical chromatograms of As species; a) measured with on-line pre-reduction, solid line – 2 ng ml^{-1} of iAs(V), MAs(V) and DMAs(V), dotted line – blank; b) measured without on-line pre-reduction, solid line – 2 ng ml^{-1} of iAs(III) and TMAs(V)O, dotted line – blank; 1 – iAs(V), 2 – MAs(V), 3 – DMAs(V), 4 – iAs(III), 5 – TMAs(V)O, NS – non-specific signal; sample loop volume 0.597 ml.

Typical chromatograms of pentavalent species measured with on-line pre-reduction and of iAs(III) and TMAs(V)O measured without pre-reduction are displayed in Fig. 1a,b. The LODs (based on $3\sigma_{\text{blank}}$ criterion, sample volume 0.597 ml) for all methylated arsenicals have ranged between 30 and 50 pg ml^{-1}. LODs for iAs(III) and iAs(V) have been worse, 100 and 135 pg ml^{-1}, respectively, mainly due to iAs(III, V) content in the blanks and non-specific absorption (Fig. 1a).

In order to demonstrate the method application to human urine samples a recovery study has been performed. The recoveries of all As species have been between 96 and 105%.

3.2 Losses of Methylated Arsines on the Nafion Membrane Dryer (Paper II)

The Nafion membrane dryer has been commonly used in analytical atomic spectrometry. It is an elegant way to remove water vapor and droplets from the gaseous stream and thus to avoid incidental blocking of the cryogenic trap by frozen water. The presence of water vapor can also cause fluctuations of signal baseline of atomic absorption or fluorescence spectrometer. No problems have been reported with the Nafion membrane dryers over the years [31,32] and it also became a standard part of a commercial atomic fluorescence spectrometer [33]. However, in this technical note (Paper II) we have reported on the serious losses of volatile dimethylarsine and trimethylarsine while passing this Nafion tube dryer. Impacts of such behavior on the accuracy of the speciation analysis based on the HG approach have been discussed in Paper II. The dryer with NaOH pellets as a water absorbent has been suggested as a safe alternative.

3.3 Chemical Vapor Generation of Ag and Au – Method Optimization (Papers III–V)

In the method of CVG of Ag the previously optimized generation conditions [16,34] have been adapted in Paper III for measurements with the quartz multiatomizer. The individual parameters of generation (*e.g.* optimum pH of the reaction mixture, the presence of reaction modifiers – Triton X-100 and Antifoam B) and the parameters of atomization (*e.g.* influence of the carrier gas flow rate, temperature and oxygen intake to the multiatomizer) have been optimized with regard to the best sensitivity obtained.

A special attention is paid in Paper IV to transport of the Ag species in the gaseous phase to the atomizer. The possible reasons of transport losses under various conditions have been analyzed. Subsequently, the new multiatomizer design has been produced (Fig. 2) in order to connect it directly to the generator and to keep the transport path as short as possible. The remarkable improvement and much better performance have been found when the multiatomizer inlet arm has been heated to 300 °C and when a small amount of O_2 to the carrier gas Ar has been added. As an illustration, the sensitivity has increased approximately 3 times in comparison to the previous setup with a spray chamber employed in Paper III.

The conditions found as optimal for generation of Ag has been taken as a base for generation of Au species in Paper V with some differences. It is worth noting that in accordance with earlier reports [13,14,35,36] sodium diethyldithiocarbamate has been found a further generation enhancer and that the optimum carrier Ar flow rate has been 240 ml min^{-1} which is about 5 times higher in comparison to Ag study.

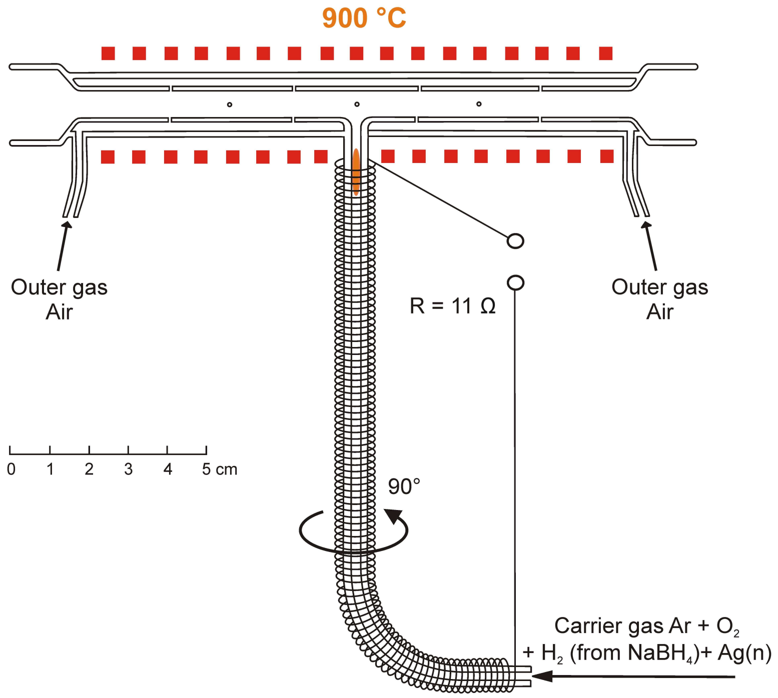


Fig. 2 Improved design of the multiatomizer for better transport of Ag volatile species. (Reproduced from Paper IV.)

3.4 Nature of Ag and Au Volatile Species (Papers III and V)

Investigations have been carried out in order to identify yet unknown nature of volatile Ag and Au species formed by the tetrahydroborate reaction. An aerosol study and observation of sampled gaseous phase in a transmission electron microscope (TEM) have proven that the analyte in the gaseous phase is apparently in the form of nanoparticles that are transported along with aerosol droplets by the carrier gas to the atomizer. As it is depicted in Fig. 3a,b the spherical particles of around 10 nm in size have been identified for CVG of both Ag and Au and these particles have been mainly associated in isolated clusters of a few to a few tens of particles. The Ag and Au atoms in those particles have been clearly identified with the help of energy dispersive X-ray spectroscopy microanalysis.

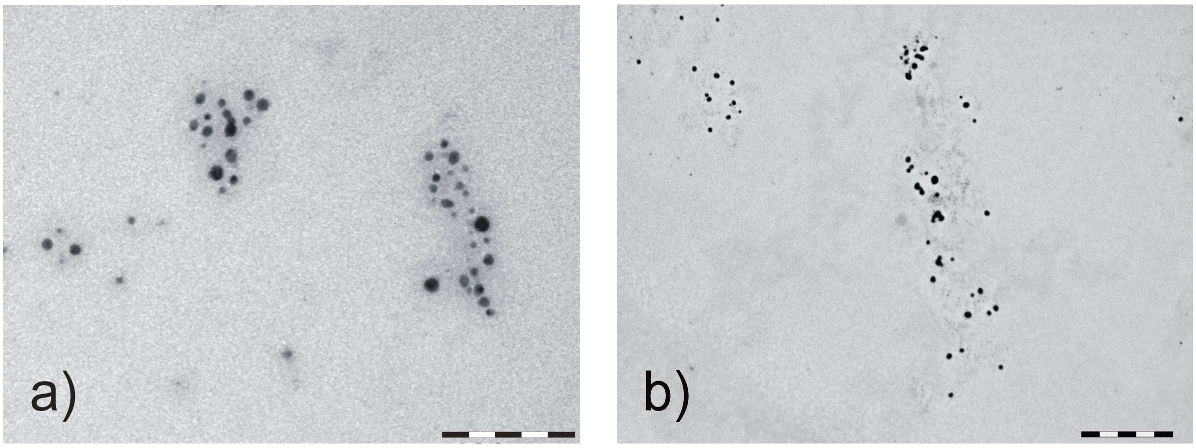


Fig. 3a,b TEM images of generated particles in the gaseous phase; a) Ag (scale bar = 100 nm), b) Au (scale bar = 200 nm).

3.5 Radiotracer Study of Generation Efficiency (Papers III–V)

CVG efficiency of Ag, transport efficiency and the distribution of the analyte within the system have been studied using ^{111}Ag indicator in Paper III. The fraction found in the trapping device situated in place of the multiatomizer, corresponding to overall CVG efficiency, has been determined as 8.1%. Another 15.3% has been found deposited in the conduits leading the gaseous phase.

In Paper IV, these data have resulted in modification of the multiatomizer design (Fig. 2) so that the gaseous phase with Ag species would be more effectively transfered to the optical tube. In the subsequent radiotracer study we have concentrated not only on the assessment of CVG efficiency but above all on transport at various temperatures of the inlet arm. The superiority of 300 °C over the other temperatures for efficient transport has been clearly demonstrated and CVG efficiency has been improved to 32.5%.

In the $^{198,(199)}$Au radiotracer experiments of Paper V, CVG efficiency of 11.9% has been assessed at the optimized carrier gas flow rate – 240 ml min^{-1}. Further results have also indicated that the release of Au to the gaseous phase can be even doubled when Ar purge flow rate is increased to 600 ml min^{-1}.

3.6 Analytical Performance and Application of Ag and Au Chemical Vapor Generation (Papers IV and V)

In general, applications of CVG of transition metals have been seldom reported in literature. Paper IV tries to present the improved method of Ag CVG with atomization in the modified quartz multiatomizer (Fig. 2) as quite suitable for water analysis. The LOD ($3\sigma_{\mathrm{blank}}$, sample volume 0.25 ml) has been assessed as 1.0 ng ml^{-1}. The developed method has also been evaluated by analyzing two proficiency-testing samples of drinking water with satisfactory conformity of results. The interference study has been performed in the presence of two typical hydride-forming elements (As and Se) and other transition metal ions (Cu, Co, Ni and Au). No significant suppression has been observed up to interferent concentration of 10 μg ml^{-1} with the exception of Au causing 18% signal depression already at 0.5 μg ml^{-1} level. In order to look into the mechanism of such interference, TEM has been employed for the mapping of supposed changes in the structure of the generated Ag particles.

The analytical performance for Au determination has been rather poor in Paper V because the reached LOD ($3\sigma_{\mathrm{blank}}$, sample volume 0.5 ml) for atomization in the multiatomizer has been 28 ng ml^{-1} under optimized conditions. This inferior analytical performance has been given most likely by the high Ar carrier flow rate that has not been compatible with the best multiatomizer performance due to serious dilution inside the atomizer. In-situ trapping of the generated Au species in the GF has also been widely investigated in Paper V, unfortunately, poor efficiency of the trapping step was responsible for analytical performance inferior to conventional liquid sample introduction.

4 CONCLUDING REMARKS

The entire thesis is devoted to the method of VCG using the tetrahydroborate reaction. It represents significant and previously unpublished contributions to understand the processes in VCG for analytical atomic spectrometry. All five papers included in this thesis have been published in the prestigious international scientific journals and the results have been also presented at both national and international conferences in the form of poster contributions or lectures. All the objectives have been successfully fulfilled and the main outputs are summarized below.

The setup for on-line pre-reduction of pentavalent inorganic, mono- and dimethylated As species using TGA as the fast pre-reductant has been developed. This unique way of pre-reduction is to our best knowledge the first method to perform on-line pre-reduction without the need of impractical heating of the reactor. It is better suited for the analysis of various samples that would require under normal circumstances time-consuming and laborsome pretreatment of each individual sample. Another prospective application of presented on-line pre-reduction could be in As speciation analysis methods employing post-separation HG approach where high and uniform generation efficiency for all forms would be highly desirable.

In the same method the pronounced losses of methylated arsines have been discovered on the Nafion tube dryer currently used in analytical atomic spectrometry. Impacts of such behavior to accuracy of speciation analysis by the methods where HG step is involved have been pointed out. The dryer with sodium hydroxide has been suggested as a possible and safe alternative.

In the method of CVG of Ag and Au the generation process has been thoroughly studied by various analytical methods and two main outputs have been reached. Firstly, the nanoparticles transported along with aerosol droplets have been experimentally identified as a final analyte product in the gaseous phase. This result of the thesis is believed to be the most important because the character of those (volatile) species has been only hypothesized in literature but never experimentally proven so far. These findings can help to explain yet unclear mechanism of generation of transition metals. Secondly, investigations of the transfer of Ag and Au within the generator using radionuclides of those elements have revealed efficiencies of the generation process and above all its weak points. These radiotracer studies have been thus found extremely important regarding the potential improvement in the generator or atomizer design.

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2002–2007	studies of analytical chemistry at the Charles University in Prague, Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Prague 2
1998–2002	Gymnasium Budějovická, Budějovická 680, 140 00 Prague 4
1989–1998	Elementary school of T.G. Masaryk, Modřanská 1375, 143 00 Prague 4

Language skills:

English	First Certificate in English, 2008

Honours and awards:

2010	1st Poster Prize at the 14th Czech-Slovak Spectroscopic Conference, sponsored by Thermo Fisher Scientific, Litomyšl, 31.5.–3.6.2010
2009	Analyst Poster Prize at the Colloquium Spectroscopicum Internationale XXXVI, Budapest, Hungary, 30.8.–3.9.2009
2009	JAAS Poster Prize at the Colloquium Spectroscopicum Internationale XXXVI, Budapest, Hungary, 30.8.–3.9.2009 (co-author)
2007	Spectroscopic Society of Ioannes Marcus Marci, Prague: The best Master thesis in the field of spectroscopy competition – 2nd prize

Other Activities:

2008	certified in handling of sources of ionization radiation

LIST OF PUBLICATIONS

Papers in impacted journals:

1. Musil S., Matoušek T.: On-line pre-reduction of pentavalent arsenicals by thioglycolic acid for speciation analysis by selective hydride generation-cryotrapping-atomic absorption spectrometry. *Spectrochim. Acta, Part B,* **63** (2008), 685–691.
2. Musil S., Kratzer J., Vobecký M., Hovorka J., Benada O., Matoušek T.: Chemical vapor generation of silver for atomic absorption spectrometry with the multiatomizer: Radiotracer efficiency study and characterization of silver species. *Spectrochim. Acta, Part B,* **64** (2009), 1240–1247.
3. Musil S., Kratzer J., Vobecký M., Benada O., Matoušek T.: Silver chemical vapor generation for atomic absorption spectrometry: minimization of transport losses, interferences and application to water analysis. *J. Anal. At. Spectrom.,* **25** (2010), 1618–1626.
4. Taurková P., Svoboda M., Musil S., Matoušek T.: Loss of di- and trimethylarsine on Nafion membrane dryers following hydride generation. *J. Anal. At. Spectrom.,* **26** (2011), 220–223.
5. Arslan Y., Matoušek T., Kratzer J., Musil S., Benada O., Vobecký M., Ataman O. Y., Dědina J.: Gold volatile compound generation: optimization, efficiency and characterization of the generated form. *J. Anal. At. Spectrom.,* (2011), DOI:10.1039/C0JA00194E

List of oral conference contributions:

1. 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, p. 113–117.

2. Musil S., Matoušek T., Rychlovský P.: Thioglycolic acid as on-line pre-reductant for speciation analysis of arsenic by selective hydride generation-cryotrapping-AAS. In: 4th International Student Conference: "Modern Analytical Chemistry", Book of proceedings, Prague, 28.–29.1.2008, p. 123–129.
3. Musil S., Matoušek T., Rychlovský P.: On-line pre-reduction of pentavalent arsenicals by thioglycolic acid for speciation analysis by HG-CT-AAS. In: Workshop of Speciation Analysis, Nová Olešná, Book of Abstracts, 22.–25.6.2009, p. 18–19.
4. Matoušek T., Musil S., Kratzer J., Arslan Y., Hovorka J., Benada O., Vobecký M.: Generation of volatile species of transition and noble metals by aqueous tetrahydroborate. In: CSI XXXVI - Colloquium Spectroscopicum Internationale, Book of Abstracts, Budapest, Hungary, 30.8.–3.9.2009, p. 108.
5. Musil S., Kratzer J., Vobecký M., Matoušek T.: Chemical Vapour Generation of Silver for Atomic Absorption Spectrometry: ^{111}Ag Radiotracer Study of Transport Efficiency and In-Situ Trapping on Quartz Surface. In: 5th International Students Conference “Modern Analytical Chemistry”, Book of proceedings, Prague, 21.–22.9.2009, p. 51–57.
6. Musil S., Arslan Y., Kratzer J., Vobecký M., Benada O., Matoušek T., Rychlovský P., Ataman O.Y., Dědina J.: Gold Chemical Vapor Generation by Tetrahydroborate Reduction for AAS: Radiotracer Efficiency Study and Characterization of Gold Species. In: 6th International Students Conference “Modern Analytical Chemistry”, Book of proceedings, Prague, 23.–24.9.2010, p. 11–14.
7. Svoboda M., Musil S., Matoušek T., Rychlovský P., Dědina J.: Arsenic Speciation Analysis by Hydride Generation-Cryotrapping-Atomic

Fluorescence Spectrometry with Flame-in-Gas-shield Atomizer. In: 6th International Students Conference "Modern Analytical Chemistry", Book of proceedings, Prague, 23.–24.9.2010, p. 19–22.

List of poster contributions:

1. Musil S., Matoušek T., Rychlovský P.: On-line pre-reduction of pentavalent arsenicals by thioglycolic acid for speciation analysis by selective hydride generation-cryotrapping-AAS. In: XIII. Spectroscopic conference. Lednice, 18.–21.6.2007, p. 77.
2. Musil S., Matoušek T., Rychlovský P.: On-line Pre-reduction of Pentavalent Arsenicals by Thioglycolic Acid for Speciation Analysis by Selective Hydride Generation-Cryotrapping-AAS. In: Colloquium Spectroscopicum Internationale XXXV. Xiamen, China, 21.–27.9.2007, p. 403.
3. Musil S., Kratzer J., Vobecký M., Matoušek T.: Chemical vapour generation of silver for AAS: assessement of introduction efficiency by ^{111}Ag radiotracer experiments. In: Tenth Rio Symposium on Atomic Spectrometry. Salvador - Bahia, Brazil, 7.–12.9.2008, p. 142.
4. Matoušek T., Musil S., Hovorka J.: Chemical vapour generation of silver for AAS: tracking silver nanoparticles in the gaseous phase. *In:* Tenth Rio Symposium on Atomic Spectrometry. Salvador - Bahia, Brazil, 7.–12.9.2008, p. 143.
5. Arslan Y., Matoušek T., Kratzer J., Musil S., Ataman O.Y., Dědina J.: Determination of Gold by Chemical Hydride Generation Atomic Absorption Spectrometry. In: CSI XXXVI - Colloquium Spectroscopicum Internationale, Book of Abstracts, Budapest, Hungary, 30.8.–3.9.2009, p. 165.

6. Musil S., Kratzer J., Vobecký M., Matoušek T.: Chemical vapour generation of silver for AAS: A radiotracer study of generation, transport and trapping efficiency in quartz multiatomizer. In: CSI XXXVI - Colloquium Spectroscopicum Internationale, Book of Abstracts, Budapest, Hungary, 30.8.–3.9.2009, p. 247.
7. Musil S., Kratzer J., Vobecký M., Benada O., Matoušek T.: Silver chemical vapor generation for atomic absorption spectrometry: method application, interference study and progress in analyte trapping on quartz surface. In: XIV. Czech-Slovak spectroscopic conference, Litomyšl, 31.5.–3.6.2010, p. Po-6.
8. Svoboda M., Taurková P., Musil S., Matoušek T., Rychlovský P., Dědina J.: Investigation of Cryogenic Trapping for Arsenic Speciation Analysis by Hydride Generation – AAS and AFS. In: European Symposium on Atomic Spectrometry, Wroclaw, Poland, 5.–8.9.2010, p. 114.
9. Musil S., Kratzer J., Arslan Y., Vobecký M., Benada O., Matoušek T., Rychlovský P., Ataman O.Y., Dědina J.: Chemical Vapor Generation of Gold for AAS: ^{198,199}Au Radiotracer Efficiency Study and Characterization of Gold Species. In: European Symposium on Atomic Spectrometry, Wroclaw, Poland, 5.–8.9.2010, p. 115.