Free Analyte Atom Distribution, Reactions and Analyte Reatomization in Quartz Tube Hydride Atomizers for Atomic Absorption Spectrometry

Dissertation

by

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2000

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This Thesis is based on the following papers referred to by Roman numerals:

PAPER I.
Spatially resolved absorption measurement of antimony atom formation and dissipation in quartz tube atomizers following hydride generation.
T. Matoušek, M. Johansson, J. Dědina and W. Frech
Spectrochim. Acta Part B ***54*** *(1999) 631-643.*

PAPER II.
Gas flow patterns and longitudinal se free atom distribution in quartz tube hydride atomizers for atomic absorption spectrometry.
T. Matoušek, J. Dědina, M. Johansson and W. Frech
Spectrochim. Acta Part B, ***55*** *(2000) 151-163.*

PAPER III.
Fate of free selenium atoms in externally heated quartz tube atomizers for hydride generation atomic absorption spectrometry and their reatomization at tube ends studied by means of the determination of longitudinal free atom distribution
T. Matoušek and J. Dědina
Spectrochim. Acta Part B, ***55*** *(2000) 545-557.*

PAPER IV
Multiple microflame - a new approach to hydride atomization for atomic absorption spectrometry.
J. Dědina and T. Matoušek
J. Anal. Atom. Spectrom., ***15*** *(2000) 301-304.*

The following papers have not been included in this Thesis:

PAPER A
On-line atomization of selenium hydride in graphite furnaces: estimate of atomic absorption coefficient and spectroscopic temperature.
J. Dědina, T. Matoušek and W. Frech
Spectrochim. Acta Part B, ***51*** *(1996) 1107-1119.*

PAPER B
Selenium hydride atomization, fate of free atoms and spectroscopic temperature in miniature diffusion flame atomizer.
J. Dědina, A. D' Ulivo, L. Lampugnani, T. Matoušek and R. Zamboni
Spectrochim. Acta Part B, ***53*** *(1998) 1777-1790.*

PAPER C
Způsob atomizace těkavých hydridů pro atomovou absorpční spektrometrii.
J. Dědina and T. Matoušek
Cz. patent PV 1926-99, (1999).

The Author solemnly declares that this Thesis has been based on his original research data and all other sources have been appropriately referenced. The extent of Author's participation on the Papers presented in this Thesis has been stated below.

Tomáš Matoušek

TABLE OF CONTENT

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry
CF	Continuous flow
EHQT	Externally heated quartz tube
FI	Flow injection
FIT	Flame-in-tube
GF	Graphite furnace
ICP	Inductively coupled plasma
MS	Mass Spectrometry
OES	Optical Emission Spectrometry
QTA	Quartz tube atomizer

1. INTRODUCTION

Generation of volatile hydrides has more than a century long history in methods such as the Marsh reaction and the Gutzeit test for arsenic determination. However, Holak's paper from 1969 [1] is usually considered as its introduction to the modern atomic spectroscopy.

At present, generation of volatile compounds (hydrides are the most important among them) is a well established and fully mature technique, as demonstrated by several monographs and reviews [2-5] and over 3000 publications [6]. Beside analyses of the elements traditionally determined by cold vapour (mercury) or hydride generation methods (antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin), generation of volatile species (either as monoatomic vapours or hydrides) of other elements has also been described: thallium and indium [2,7], cadmium [8,9], copper [10-12], nickel [12,13], zinc [12], rhodium, palladium, silver and gold [11]. Generation of other volatile compounds such as chelates, alkylderivatives, carbonyls, oxides and halides of up to 30 elements can be analytically utilized, too. [2,4,14].

Volatile compound generation can serve as sample introduction technique for various analytical methods [2]. It has attained most extended use in atomic absorption spectrometry (AAS) for the sensitivity given by separation of the analyte from the sample matrix and its preconcentration, a high efficiency of the sample transport to the atomization environment and the simple and cheap equipment. The holds for atomic fluorescence spectrometry (AFS) [2,15]. High efficiency of the analyte introduction to the plasma is also a reason for the popularity of hyphenation of hydride generation to the inductively coupled plasma- optical emission spectrometry (ICP OES) or inductively coupled plasma- mass spectrometry (ICP MS) instruments [2,16]. So far, about one third of the publications on volatile compounds are non-AAS [6].

Another potential of volatile compound generation methods lies in the trace element speciation analysis [4,14,17]. Generation of substituted hydrides followed by their separation is one possible way. However, most complete and accurate information on the distribution of the analyte forms is obtained by their separation followed by generation of volatile compounds and analyte detection. In principle, any separation method can be used for this task. As outlined above, the volatile compound generation methods do have a long history, a well established present status and promising future. However, still there are basic processes to be understood and equipment to be improved even for the fundamental and most widespread applications. The papers presented in this Thesis attempt to add to the present knowledge: attention is given to the understanding and overcoming of the phenomena impairing the performance of the quartz tube atomizers for AAS.

2. HYDRIDE GENERATION AND ATOMIZATION METHODS FOR AAS- STATE OF THE ART

2.1. HYDRIDE GENERATION METHODS

Hydrides were generated by the metal/acid reaction in the early days of this technique, however, sodium or potassium boronhydride ($NaBH_4$ or KBH_4) are now almost exclusively used as the reduction agents. Typically, 0.1 to 3% $NaBH_4$ solutions are used. This reaction has several advantages- it is very fast and exhibits good yields for most elements within a broad range of reaction conditions. The hydrogen originating from the boronhydride decomposition also enhances the analyte hydride release from the solution.

A considerable disadvantage of the boronhydride reaction is contamination of the blank, especially when using hydride collection techniques. To overcome this, the electrochemical hydride generation has been introduced [18-22]. Acids which are available at very high purity are then the only reagents added to the sample.

Common hydride generation systems employing the boronhydride reaction can be divided into three groups: Batch, continuous flow and flow injection generators.

Batch generators are usually closed vessels with inlets for a purge gas and a reductant and a gas outlet to the atomizer. They serve as reactors as well as gas- liquid separators. The most important advantages of generators of this type is a good sensitivity, as the analyte is generated from the whole sample within short time after addition of the reductant, and the simplicity of the design. On the other hand, they are susceptible towards liquid-phase interferences, and their use is labourious and difficult to automate.

Continuous flow (CF) hydride generators are much more suitable for the most popular detection methods, *i.e.* quartz tubes for AAS, diffusion flame for AFS and also for plasma sources, as they produce a stable flow of gas with a constant composition. A typical CF hydride generator employs constant flow of acidified sample (typically 1-10 ml min^{-1}, driven by a peristaltic pump) mixed with the flow of reductant in a T- piece. In another T-piece, a flow of a carrier gas can be introduced which helps to release the hydride formed into the gaseous phase. After passing through a reaction coil, the phases of the reaction mixture are separated in a gas liquid separator (either hydrostatic, with forced liquid outlet, or a membrane one [2,23,24]). A nebulizer of an ICP source is also occasionally adopted as a generation/phase separation unit [11,25]. The sample/blank introduction can easily be automated. CF hydride generators are sensitive, efficient and easy to operate. The resistance towards liquid phase interferences is improved, compared to batch generators. CF hydride generation is the method of choice if a constant hydride supply is desirable.

To increase the sample throughput and decrease the necessary sample volume, flow injection (FI) methods have been introduced to hydride generation [24,26]. In principle, FI hydride generators only differ from CF ones by a valve added, injecting a small sample volume to the continuous flow of the carrier acid. Most features of CF generators are maintained, but transient hydride supply is obtained. However, for large sample loop volumes the FI and CF system characteristics are getting closer.

A generated hydride can either be atomized immediately (the direct transfer methods), or further preconcentrated by collection and then atomized after the generation is completed (the collection methods). There are several methods of hydride collection, of which only cryotrapping and *in-situ* trapping in a graphite furnace are still employed to a greater extent. Cryotrapping has gained its popularity due to the fact that the hydride can be generated from very high sample volumes. This method has recently been successfully employed for speciation analysis [14,17]. The most popular hydride collection method is *in-situ* trapping in GF, which will be treated below, in the section devoted to hydride atomizers.

2.2. HYDRIDE ATOMIZATION FOR AAS

Three groups of hydride atomizers for AAS are basically used: Flame ones, quartz tube atomizers (QTA) and graphite furnaces (GF), of which the QTA are by far most common. Atomization in GF following in situ trapping has also gained importance in recent years. Reports on diffusion flame and on-line atomization in GF remain rather scarce, even though these techniques offer some undisputable advantages. The important properties of individual atomizer types are briefly compared in Table 1 and discussed below; the quartz tube atomizers, as the very subject of the papers presented in this Thesis, are treated separately in a subsequent section, in much more detail.

2.2.1. Flames

In the early years after the introduction of hydride generation, the nitrogen (argon)-hydrogen- entrained air flame (diffusion flame) supported on a conventional slot burner was a hydride atomizer that was used almost exclusively [2]. This flame has a lower background absorption than the standard premixed air-acetylene flame, however, it is still noisy and less sensitive compared to the QTA. An advantage is in an excellent resistance towards atomization interferences. This type of flame supported on a narrow quartz tube is the most common hydride atomizer for AFS [Paper B] [15].

Table 1: A comparison of individual hydride atomization methods for AAS.

	Diffusion flame	GF on line atomization	GF with *in-situ* trapping	QTA
Sensitivity	-	0	++	++
Linear range	+	+	0	-
Interferences	++	++	0	--
Cost	++	-	-	++
Operation	++	0	-	++
Popularity	-	--	+	++

2.2.2. Graphite furnaces

Hydrides can be basically atomized in GF in two ways- either on-line or after *in-situ* trapping. With the on-line atomization mode, hydride is entering the furnace preheated to the atomization temperature (typically over 1800°C)[Paper A][27,28]. The greatest disadvantages of the method, besides the interface problems, are a low sensitivity due to small furnace dimensions and fast corrosion of the graphite parts. On the other hand, the resistance towards atomization interferences is very good.

In-situ trapping and atomization in GF is one of the most popular and prospective methods [4,29]. The generated hydride is introduced through a capillary into the furnace preheated to a trapping temperature which lies typically between an ambient temperature and 1000°C. The analyte from the decomposed hydride is sequestered inside the furnace and is atomized in a standard manner after the generation step is completed. Uncoated graphite tubes or pyrocoated tubes with modifiers such as Pd are used for trapping. Permanent modifiers (Pd/Ir, Zr or other refractory metals) are now most popular [30,31] as they reduce the analysis time and suppress contamination. Naturally, superior relative sensitivities can be obtained. The weakness of this technique is the possibility of interferences of other hydride forming elements in the trapping step (although not as pronounced as in QTA). Another expanding field of GF with hydride generation- *in-situ* trapping is their use as electrothermal vaporization units for plasma sources [29].

2.3. QUARTZ TUBE ATOMIZERS

QTA are by far the most common hydride atomizers for AAS, especially for their excellent sensitivity, easy operation and low-cost equipment (all the manufacturers of AAS instrumentation offer hydride generation systems equipped with QTA). In contrast to in-situ trapping in GF, QTA operate continuously so that they are also suitable for coupling with separation techniques for speciation analysis [17]. On the other hand, they suffer from poor linearity of calibration graphs and from atomization interferences.

QTA are typically quartz T-tubes with an inlet arm and an optical tube (3- 10 mm i.d., 100 - 150 mm length) placed in the radiation beam of the spectrometr. They are traditionally divided into two groups: i. Externally heated quartz tubes (EHQT), which have an optical bar heated to a temperature of 700 - 1000°C. Standard air-acetylene flame or electrical furnaces are used for this purpose. These are more popular and all the commercial systems are of this type; ii. Flame-in-tube (FIT) atomizers contain a capillary for the delivery of oxygen ending near the T- junction. At the end of this capillary burns a small, almost invisible flame. The optical bar of such an atomizer need not necessarily be heated.

Despite the widespread use of QTA in routine practice, not all the processes taking place in the atomizer are completely understood. The nature of the processes leading to the formation of free analyte atoms is known relatively well. However, only indirect evidence is available on the fate of free atoms, mostly based on classical atomic absorption measurements at various atomization conditions.

The widely accepted mechanism of free analyte atom formation in QTA was originally suggested by Dědina and Rubeška [32] for the FIT atomizer, and later extended by Welz and Melcher [33] to EHQT. This mechanism has been confirmed in a number of studies (see the monograph [2] and the references therein). The presence of hydrogen radicals have been also proven directly [5,34,35] and even the spatial distribution of H- radicals was studied by Stauss [5,34]. Hydride is atomized via consecutive reactions with hydride radicals, such as, *e.g.*, for selenium:

$$SeH_2 + H \rightarrow SeH + H_2 \qquad (1a)$$

$$SeH + H \rightarrow Se + H_2 \qquad (1b)$$

The hydrides of other elements are atomized via analogous reactions. (With the exception of lead [36].Thermal decomposition rather than H-radical mechanism plays a role in this case.) Hydrogen radicals are formed by reactions of oxygen in excess hydrogen in the miniature flame (FIT) or at the beginning of the hot zone (EHQT)- the threshold temperature is reported to be 450-550°C [37,38]. The following reactions occur [32]:

$$H + O_2 \leftrightharpoons OH + O \qquad (2a)$$

$$O + H_2 \leftrightharpoons OH + H \qquad (2b)$$

$$OH + H_2 \leftrightharpoons H_2O + H \qquad (2c)$$

The presence of both hydrogen and oxygen is necessary for the atomization. In EHQT, a steep rise of the signal is observed with increasing O_2 supply followed by a plateau. On the exceeding of the stoichiometric H_2/O_2 ratio, the signal rapidly decreases again. The oxygen demand is determined by the atomization temperature (the lower the temperature, the higher the O_2 demand) [38,39]. Hydrogen is almost always present as it comes from the $NaBH_4$ decomposition. Oxygen is either added or is present in a sufficient amount, as a contaminant in the gases or is stripped from the solutions [38,39]. An addition of oxygen is reported to improve the atomizer characteristics, especially the sensitivity, the linearity of the calibration graphs and the resistance against atomization interferences [38,39], which is ascribed to an increased production of H-radicals.

There are two processes removing free atoms from the observation volume: forced convection (free atoms are driven out of the atomizer by the flow of gas) and chemical reactions, the latter being usually underestimated in the literature. The free analyte atoms start to react chemically immediately after they leave the atomizing H-radical cloud, which fills only small part of the atomizer volume. It should be noted that both the H-radicals and the free analyte atoms are thermodynamically unstable species under the QTA conditions. An equilibrium is not attained within the tube, so that the reaction rates of formation and decay control their concentration and consequently the atomic absorption signal.

The decay of the free atoms is supposed to be surface assisted, although the exact mechanism is unclear. It may look as follows [2,40]: i. the free atoms lose part of their energy through an interaction with the surface; ii: the surface bound analyte atoms form compounds (dimers, n-mers or hydride); iii. depending on the analyte and the temperature, the compounds may leave the surface. The quality of the atomizer inner surface plays a crucial role- the decay is strikingly enhanced in a contaminated atomizer [38,41]. Moreover, the surface alterations may cause day-to-day sensitivity changes, which is one of serious disadvantages of QTA.

Molecular oxygen is known to cause fast disappearance of free selenium atoms [42]. It has also been shown to be responsible for decay of free lead atoms in a QTA AAS detector for gas chromatography [36]. However, the role of molecular oxygen which possibly diffuses from the open tube ends in the processes leading to decay of free atoms in the QTA has not been evaluated for other hydride forming elements.

Poor linearity of the calibration graphs is another serious drawback of the QTA and even such phenomena as the rollover of calibration graphs have been observed for Se [42-44], Sb [45] and As [39,45]. This was formerly explained by the formation of analyte dimers [43] or an insufficient amount of H-radicals for efficient hydride atomization at higher concentrations [39,45]. A hypothesis was recently suggested by D'Ulivo and Dědina [42] which assumes that after leaving the H-radical cloud, the free atoms react with formation of dimers and polyatomic particles. These particles increase the surface available for the free atom decay reactions. In other words, the reacted analyte particles provide surface available for reactions not only on the tube walls but also in the atomizer free volume. The more analyte present, the more particles and the more surface is available. This may lead even to the calibration roll-over. Although this hypothesis can be extrapolated to the QTA, it has so far been developed and tested only on AFS atomizing units

The presence of other hydride forming elements in the sample also causes interferences within the atomizer [41,44,46-50]. These can be caused by either the competition for H-radicals between the analyte and an interferent (radical interferences) or an enhanced reaction rate of the free analyte atoms caused by the interferent (decay interferences) [41]. Although similar processes as those responsible for the calibration graph curvature are suspected [42] (the interferent would form the particles-see above), the exact mechanism of the atomization interferences of other hydride forming elements in QTA is still not understood.

The species originating from the reacted free analyte atoms can be reatomized but only upon another contact with hydrogen radicals [37,38]. This cannot be obtained without another introduction of oxygen into the tube. Despite an apparent potential of this phenomenon, no atomizer design has so far been described which would deliberately and successfully employ this effect to improve the analytical performance.

3. AIMS OF THE THESIS

Although the QTA were introduced in 1972 [51] and by now they are by far the most common hydride atomizers, the phenomena taking place inside are still not fully understood, and there is apparently a potential for further improvement of the QTA construction. After years of use, the possibility that classical AAS observations would bring a fundamental progress in our knowledge is rather small. Therefore, we intended to introduce spatially resolved measurements as a new valuable tool to study the processes leading to the decay of free atoms. Both the cross-sectional and longitudinal distribution of free atoms were to be studied, the former yielding information about the localization of the processes within the tube, the latter providing a picture of their fate on the way through the tube. Special attention was to be paid to the nature of the processes leading to a limited linearity of the calibration graphs. The results of these studies should serve as a base for the construction of a novel design of the QTA. Such design should improve the linearity of the calibration graphs and a tolerance to the atomization interferences, while the good sensitivity and the simplicity of the QTA should be maintained.

Selenium was chosen as a model element, as its behaviour is relatively well known, both in the hydride generation and the atomization step. It is known from the literature that the studied processes are fairly similar for selenium, arsenic, antimony and the other elements. In fact antimony had to be used as the model element in Paper I, because of the inconvenient spectral features of selenium.

4. EXPERIMENTAL

4.1. INSTRUMENTATION

The measurements of the atomic absorption signal were performed in all the papers included in this Thesis. However, only Paper IV is based solely on the measurements performed in the standard way, employing a commercial AAS instrument (Varian SpectrAA30, Mulgrave, Australia) without any modifications.

The measurements through the tube wall (see Section 5.1.2.) described in Papers II and III required precise positioning of the atomizer in the range corresponding to the length of its optical tube. For Paper II, an optical system was built based on an old-fashioned Varian AA6 AAS instrument (consisting of individual segments mounted on an optical bench) with a secondary optical bench for the positioning of the atomizer allowing scanning the signal over the whole length of the optical tube. A commercial AAS instrument (Varian SpectrAA 30) with a custom-made wide-range positioning device was employed for the same purpose in the experiments of Paper III.

A special optical system was constructed for the spatially resolved atomic absorption measurements in Paper I, similar to that of Johansson *et al.* [36]. A CCD camera was used as the spatially resolved detector: the spatially resolved intensity image was taken under the conditions of hydride generation from a blank solution followed by the image of generation from an analyte standard solution. The stored intensity images were subsequently combined to obtain spatially resolved absorbance images.

A selenium hollow cathode lamp was used as the radiation source in Papers III- IV, whereas electrodeless discharge lamps (for antimony and selenium) providing higher radiation intensity were employed in the systems described in Papers I and II.

4.2. HYDRIDE GENERATION

A continuous flow hydride generation system was used in all the papers presented in this Thesis to avoid the difficulties arising from transient signals produced by batch and flow-injection mode systems. Full control of the atomization atmosphere could thus be obtained. Steady- state signals were always recorded.

The compact CF hydride generator was designed in our laboratory and tailored for mechanistic studies. Its scheme and a detailed description can be found in Paper I. A maximum flexibility and easy operation was kept in mind during its construction. It consists of T-pieces interconnected by PTFE tubing; Rheodyne 1/16" flangeless fitting was used throughout. A gas-liquid separator with forced outlet was chosen to avoid problems caused by a possible overpressure at higher gas flow rates (hydrostatic phase separators are vulnerable to overpressure). It has an inner volume of only about 3 ml (it can be easily changed if necessary). The quartz glass material of the separator ensures a maximum inertness.

The purge gas flow rate through the hydride generator was always kept constant (50 ml min $^{-1}$), so that the observed signal could not be influenced by differences in the generator performance. To obtain a wide range of atomization conditions, an additional stream of gas was added downstream to the hydride generator.

For the measurements of atomization interferences in Paper IV, this system was modified similarly as suggested by Hulanicki *et al.* [49,50]. The generation of the analyte and interferent hydrides was separated in a semi-twin-channel system, *i.e.* using separate mixing of the analyte and interferent solutions with $NaBH_4$, but with a reaction coil and a gas-liquid separator common for both analyte and interferent. The risk of liquid-phase interferences affecting the evaluation of the atomizer performance is thus greatly reduced.

4.3. ATOMIZERS

Four different quartz-tube hydride atomizers were used throughout this Thesis:

In Papers I-II, a "dual mode" atomizer was employed (see Paper I). It allows measurements in both the FIT (heated or unheated) and the EHQT modes. This flexibility permits a direct comparison of the atomization processes in the individual modes without an uncertainty introduced by different tube dimensions and material or even different tube specimen [52].

In Papers I, III and IV, a commercial EHQT (Perkin- Elmer FIAS 200 system, Überlingen, Germany) was used. This is a representative of state-of-the-art routine use atomizers. Moreover, this type of atomizer was often used for studies of atomization processes [34,39,44,45,52], so that literature data for comparison could usually be found.

As the "FIAS" atomizer has rather thick walls, another one denoted "thin wall" atomizer was designed in Paper III. This EHQT atomizer has similar inside dimensions as the "FIAS" atomizer, but its optical tube is made of an optical grade quartz glass (Suprasil) only 0.5 mm thick. It should be noted that quartz absorbs light at the wavelength of Se analytical line (196 nm), and that the tube walls act as two divergent lenses, the magnitude of these effects increasing with increasing thickness of the tube wall and with decreasing tube radius. The "thin wall" tube design allows convenient measurements of the longitudinal distribution through the walls even at a temperature of 900°C (see Paper III for details).

Based on the new findings presented in Papers I-III, a brand new atomizer has been introduced in Paper IV (see Fig. 1 on page 16). The whole Paper IV. is devoted to the description of its features and performance, comparing its characteristics to those of the "FIAS" atomizer.

The atomizers needed to be heated in most experiments. A commercially available electrical furnace (Perkin-Elmer FIAS 200) and its in-house made replacement were used in experiments for Paper I and IV, respectively, as there were no special requirements on the heating device. In contrast, the instrument radiation beam could not be blocked by the heating device over most of the optical tube length for measurements through the tube wall performed in Papers II-III. This was solved by using an air-acetylene flame for atomizer heating in Paper II, whereas a custom-made electrical furnace was designed for Paper III, consisting of two halves separated by a 5 mm wide slit permitting the passage of radiation.

5. RESULTS AND DISCUSSION

5.1. SPATIALLY RESOLVED MEASUREMENTS (PAPERS I- III)

As mentioned in Sec. 2.3., different processes take place in different parts of the QTA. To obtain a deeper insight into the nature of the individual processes, it is necessary to have a possibility of spatially resolved observations both in radial and longitudinal direction. Although the measurements resolved radially were introduced to AAS (the approaches are summarized in the Introduction part of Paper I), few attempts were made to employ such approach in the QTA. Our preliminary results on selenium [2,53], followed later by Johansson *et al.* [36] who studied processes involved in the formation of free lead atoms in the QTA coupled to a gas chromatograph, are the only published data on spatially resolved measurements in the QTA except Papers I-III.

5.1.1. Cross-sectional free atom distribution (Paper I)

Paper I maps the free antimony atom cross-sectional distribution in both the FIT and the EHQT atomizers. The greatest difficulty encountered with this approach was the obtaining of a reasonable quality of the image over the whole tube length together with a reasonable spectral resolution and radiation intensity. A spatial resolution of 0.2 mm was achieved over the whole tube length. The spectral resolution of this system was assessed to be 9 nm. Antimony was used as the model element (in contrast to other papers in this Thesis which employ selenium), as it has a suitable absorbing line at 231.1 nm without any spectral interference (in contrast to Se 196.1 nm line). Antimony is known to behave similarly to arsenic and selenium [38,39,45,52] and also the results correspond well with our preliminary results on selenium [53]. The detector sensitivity was also much better at 231.1 nm compared to 196.1 nm, which improved the signal-to-background ratio.

A pronounced inhomogeneity of the free atom distribution was observed in the unheated FIT mode. The concentration of free atoms near the walls is much lower than in the tube centre. This is a direct experimental evidence of the role of the tube surface in the free atom decay, which has so far been proved only indirectly. Pronounced inhomogeneities dependent on the actual position of the capillary tip within the cross-section indicated a minimum gas mixing within the tube.

Much smaller free atom density gradients were observed in the heated atomizers, both “dual mode” (in heated FIT as well as in EHQT mode) and the “FIAS” ones, obviously due to a faster diffusion. Pronounced free atom density gradients were only observed at high analyte concentrations (300 ng ml^{-1} Sb), *i.e.* in the region of the calibration rollover (see below). A higher free atom concentration was found close to the wall, which is explained in terms of the decay on the surface of the supposed polyatomic particles formed by the decayed analyte (there are fewer particles near the wall, as they stick to the surface).

From the practical point of view, the free atom density gradients are negligible in the most common routine analysis hydride atomizers- EHQT. Moreover, the regions near the tube walls where the minute free atom density gradients appear are usually avoided by the radiation beam in standard instruments and thus no effect arising from a cross-sectional inhomogeneity [54] is to be expected.

5.1.2. Longitudinal free atom distribution (Paper II- III)

Papers II and III study the changes in the free selenium atom concentration along the length of the atomizer optical tube. It is an ideal tool to study fate of the free analyte atoms, as their distribution reflects the reactions of their formation and decay. A very simple method was employed- the atomic absorption measurements in various parts of the optical tube through the quartz tube walls, with the tube placed perpendicularly to the radiation beam. Paper II. maps the distribution in a broad range of atomization conditions (unheated/ heated FIT and EHQT), Paper III. is closely focussed to the most common analytical conditions (EHQT at a low purge gas flow rate).

Despite the fact that radiation is absorbed by quartz at a wavelength of 196 nm and the radiation path through the atomization environment is rather short, no problem was encountered during the measurements in the unheated atomizer. Continuous scanning over the tube length could be performed and the scans obtained while generating hydride from blank and standard solutions could be compared producing the final free atom distribution. However, the high attenuation of the radiation beam in the heated atomizer together with relatively fast changes of the tube absorption (caused probably by the quartz corrosion [55]) presented a serious problem. Although the use of the thin wall atomizer in Paper III improved the situation, the measurements in various parts of the tube had to be performed point by point, alternating blank and standard solution at a given position.

The H-radical mechanism of hydride atomization was proved. Under all the atomization conditions used, the highest density of free atoms was observed at the tube centre which confirms that the atomization step is very fast and that it proceeds mostly within the inlet arm. After entering the optical tube, the density of free atoms decreases as they start to react (decay). All the free atoms decay before reaching the tube ends. There is no difference between the FIT and EHQT mode with regard to the free atom distribution. It was directly proved that ambient oxygen penetrating from the tube ends play no role in the process of free analyte atom decay- no change in the free atom decay rate was observed when the O_2 diffusion was prevented by flames or windows placed on the tube ends.

The most important observation is that the free atom decay rate depends on the analyte supply to the atomizer- the higher the analyte supply, the faster the decay of free atoms. This confirms the hypothesis that the reacted analyte free atoms form particles with a reactive surface which further enhances the free atoms decay rate [42] . This will further be discussed in the following section devoted to the calibration graph curvature.

From the practical point of view, recommendations concerning the quartz tube dimensions are given in Paper III. Increasing optical tube length increases the sensitivity, however, the sensitivity contributing regions are just only those where free atom reactions occur. An increased sensitivity can thus be expected but at the price of problems with calibration graph curvature and probably also atomization interferences [42]. Over a certain limit, lengthening of the tube has no sense at all, as all the free atoms are already reacted and cannot be reatomized without another contact with H- radicals.

5.2. CALIBRATION GRAPH CURVATURE IN QTA (PAPERS I- IV)

A special attention is paid in Papers I-IV to the curvature of the calibration graphs, as their poor linearity is one of the serious disadvantages of the QTA.

In Paper I, all the possible calibration graph curvature sources inherent to the detector system [54] at the 231,1 nm Sb line were either eliminated or their extent could be assessed: the way of absorbance calculation from spatially resolved data excludes the influence of an inhomogeneous free atom distribution [56]. Also the spectral features of the Sb 231.1 nm line [54] should not cause any deviation from linearity. The non-absorbable radiation from adjacent week lines was assessed as 7% or less of the overall intensity of the analytical line, whereas as much as about 20% would be necessary to explain the observed deviation from linearity. The residual curvature originated within the QTA and was ascribed to chemical reactions occurring within the tube.

The nature of these reactions was further investigated in Papers II- III. It was found that the reason is not an incomplete atomization at high analyte concentrations as concluded in Refs. [39,45], as the density of free atoms in the tube centre where atomization proceeds increases linearly. An enhanced analyte free atom decay rate was observed- the density of free atoms along the optical tube decreased much faster at higher analyte concentrations. This is in line with the hypothesis of formation of tiny polyatomic particles formed by the reacted analyte (see Sec. 2.3.).

A new type of quartz tube hydride atomizer (Multiple Microflame QTA) was introduced in Paper IV, which had the whole inner volume filled with H- radicals maintaining the analyte in the state of free atoms by recurrent atomization (see below). This is not allowing the formation of free atom decay products, which means that calibration graph curvature due to the reactions described above is suppressed. In other words, any observed deviations from calibration linearity are inherent to the detection system and do not originate in the atomizer, as proved directly by linear calibration on the less sensitive Se 204.0 nm line [Paper IV].

5.3. ANALYTE REATOMIZATION (PAPER II-IV)

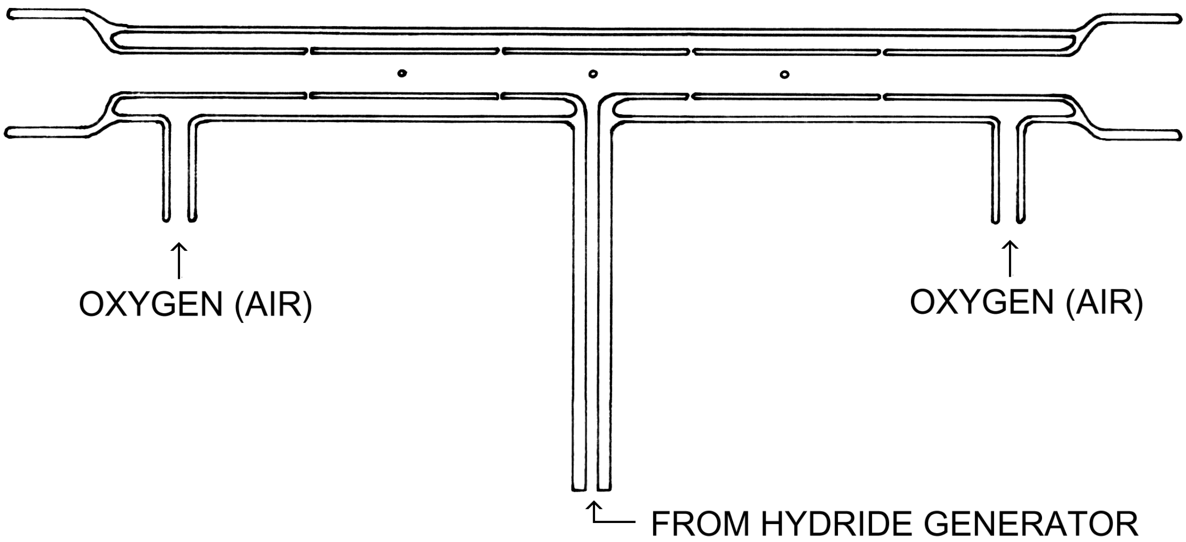
As described in the previous sections, the analyte hydride is atomized immediately after entering the atomizer. After that, free atoms start to react and decay. The reacted free atoms can only be reatomized upon another contact with H-radicals, which are however unavailable unless oxygen is introduced again into the atomizer [2,38,39]. No design of the QTA for routine use successfully employing deliberate analyte reatomization within the tube was reported until now. The holed QTA by Grinberg *et al.* [57] is believed to perform in a different way [Paper IV].

We discovered in Paper II and elaborated in Paper III that free atoms are re-appearing near the tube ends in a conventional heated QTA with proper tube end design. This remained unnoticed in the literature until now (a thorough discussion of the tube end design is presented in Paper III), although Stauss [5,34] observed a relative increase in the H- radicals population near the ends of the EHQT. It was explained by the diffusion of ambient oxygen from the ends towards the hot part of the atomizer, where H-radicals can be formed. After their formation in these H-radical rich end reatomization regions, the free analyte atoms leave the observation volume without the possibility of any unwanted subsequent reactions (see Sec. 5.2). The overall impact of the “reaction” regions relative to the H- radical rich regions is thus decreased. It has been shown that calibration graph characteristics are significantly improved compared to the situation when end reatomization is prevented in the same atomizer: the sensitivity increased by 21% and the linear range was about doubled [Paper III]. The atomizer noise level was not influenced. Not only the indirect evidences are presented in Papers II-III, but also a direct observation of the free atoms re-appearing close to the tube ends.

The knowledge detailed above was used to design a revolutionary hydride atomizer for AAS- the Multiple Microflame QTA. Paper IV describes its function and performance together with the comparison with the conventional QTA. This atomizer design also became a subject of a patent [Paper C].

The optical tube of this atomizer consists of two concentric tubes (see Fig. 1). The inner tube, which corresponds to an optical tube of a conventional QTA, has many tiny orifices along its length. An argon/ oxygen mixture or air is led between the two tubes and enters the inner tube through these orifices. At the entrance, microflames are formed producing H-radicals by reactions with the hydrogen present inside the tube. The whole observation volume is thus filled with H-radicals. If the free analyte atoms decay, the products are immediately reatomized by H-radicals. In other words, recurrent analyte atomization proceeds over the whole optical tube length. The analyte can be present in the form of free atoms only. Except the aforementioned improvement in the linearity of calibration graphs, the sensitivity for selenium was improved by 10 % and mainly the tolerance limit (the interferent concentration causing a 10% signal suppression) towards the atomization interference of arsenic was improved by one order of magnitude-from 0.04-0.05 to 0.5-0.55 µg ml^{-1} compared to the conventional QTA (the “FIAS” atomizer).

Fig. 1. Multiple microflame quartz tube atomizer



6. CONCLUDING REMARKS

Spatially resolved measurements of free atoms of hydride forming elements within the quartz tube hydride atomizers for AAS have been introduced. Both the cross-sectional and the longitudinal free atom distribution has been thoroughly investigated, bringing valuable information concerning the nature of the processes taking place within QTA. From the practical point of view, no effects arising from an inhomogeneous free atom distribution are to be expected in the most common EHQT atomizer.

The role of the tube surface in the decay of the free analyte atoms has been demonstrated. Strong evidence has been obtained on analyte reactions within the QTA, leading to the formation of polyatomic analyte particles enhancing the free atom decay. These reactions are responsible for calibration graph curvature or even roll-over. It should be noted that the existence of such particles was not directly proven here, e.g., by using non-specific absorption or light scattering and more effort is needed in this direction. On the other hand, absolutely no indication was found for the earlier hypothesis that a lack of hydrogen radicals at higher analyte concentrations is responsible for these effects.

It was recently suggested that atomization interferences are proceeding via an accelerated decay of the free analyte atoms rather than via a decreased efficiency of the analyte atomization. This was however never proved experimentally, which is another possible field for the use of the longitudinal free atom distribution measurements: the decreased atomization efficiency due to the decreased population of hydrogen radicals would result in the uniformly decreased absorption profile, whereas the accelerated decay of the free analyte atoms would manifest itself in a steeper decrease in the free atom population along the tube length.

The processes leading to the analyte reatomization at the ends of the heated QTA have been discovered. This phenomenon improves the analytical characteristics of the atomizer. Recommendations are given concerning the QTA dimensions and design, so that full advantage can be taken of the end-section reatomization and the problems arising from free analyte atom decay reactions can be minimized.

Based on the knowledge of the processes occurring in quartz tube atomizers, a novel type of hydride atomizer was proposed, named Multiple Microflame QTA. This patented atomizer design employs recurrent analyte atomization and yields substantially better linearity of the calibration graphs and an order of magnitude better tolerance towards atomization interferences compared to the conventional QTA, while maintaining its excellent sensitivity, simplicity, easy operation and a low cost. However, its development is still in the beginning and only the future will show whether this is another important step on the way towards an ultimate hydride atomizer for atomic absorption spectrometry.

ACKNOWLEDGEMENTS

Chtěl bych poděkovat všem kolegům a přátelům, kteří, tak či onak, přispěli ke zdárnému dokončení této práce.

Zvláště pak bych chtěl vyjádřit svůj vděk

Dr. Jiřímu Dědinovi za skvělé, trpělivé a neustávající vedení a to nejen po stránce odborné

Prof. Karlu Štulíkovi za všestrannou pomoc v průběhu celého studia a jazykovou korekci této práce

Vlastě Korunové, Aničce Selecké a ing. Vobeckému za veškerou pomoc, spolupráci a vytváření příjemného pracovního prostředí.

My gratitude to Wolfgang Frech, who allowed me to spend incredible and invaluable time in Umeå. Thanks to Magnus Johansson for fruitful collaboration and to Karin, Håkan, Douglas, Negassi and others in the department for a friendly environment full of inspiration. Special thanks to Douglas and Wolfgang for their excellent single malt introductory course.

Stodovi, za neustálé udržování mé mysli v bdělém stavu

Největší dík patří mé rodině a zejména mé ženě Janě za důvěru, nekonečnou trpělivost a podporu.

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