



Akademie věd České republiky

Teze disertace  
k získání vědeckého titulu "doktor věd"  
ve skupině věd chemických

## **On the way towards the ideal hydride atomizer for atomic absorption and atomic fluorescence spectrometry**

Komise pro obhajoby doktorských disertací v oboru: analytická chemie

Jméno uchazeče: **RNDr. Jiří Dědina, CSc.**

Pracoviště uchazeče: Ústav analytické chemie AV ČR, v.v.i.

Místo a datum: Praha, červen 2007

## Contents

Summary	2
1. Introduction	3
2. Aim of the dissertation	5
3. On-line atomization for AAS	6
3.1. <i>Conventional quartz tube atomizers</i>	7
3.1.1. <i>Influence of atomization parameters on sensitivity</i>	8
3.1.2. <i>Interferences</i>	10
3.1.3. <i>Assessment</i>	11
3.2. <i>Miniature diffusion flames</i>	11
3.2.1. <i>Interferences</i>	13
3.2.2. <i>Assessment</i>	13
3.3. <i>Flame-in-gas-shield atomizer</i>	14
3.3.1. <i>Interferences</i>	15
3.3.2. <i>Comparison of performance with MDF</i>	15
3.4. <i>Flame-in-flame atomizer</i>	15
3.5. <i>Multiatomizer</i>	16
3.6. <i>Graphite furnaces</i>	17
4. In-atomizer trapping AAS	19
4.1. <i>In-situ trapping in graphite furnaces</i>	19
4.2. <i>Trapping in a quartz tube - atomization in QTA</i>	20
5. Atomic fluorescence spectrometry	24
6. Conclusions	25
List of papers of the dissertation	26
List of other references quoted in the thesis	29
List of other publicatins of the author	32

## Summary

The submitted dissertation treats all existing approaches to on-line hydride atomization for atomic absorption (AAS) and atomic fluorescence spectrometry (AFS) as well as to in-atomizer trapping for AAS.

Regarding on-line atomization for AAS, conventional quartz tubes are currently the most commonly used devices. They provide high sensitivity and low baseline noise. Running and investment costs are low. The most serious disadvantage is the poor resistance against atomization interferences and often unsatisfactory linearity of calibration curves. Miniature diffusion flame (MDF) is extremely resistant to interferences, simple, cheap and user-friendly. Its essential disadvantage is low sensitivity. Mechanism of processes taking place in the atomizers (atomization, fate of free analyte atoms, interferences) was elucidated. This allowed to design a novel device, known as a multiatomizer, to overcome disadvantages of previous atomizers. The multiatomizer matches performance of conventional quartz tubes in terms of sensitivity and baseline noise as well as in running and investment costs. The multiatomizer, however, provides much better (i) resistance against atomization interferences and (ii) linearity of calibration curves.

Regarding in-atomizer trapping, it enhances the sensitivity of the determination and eliminates the effect of the generation kinetics and of surges in gas flow on the signal shape. This is beneficial for the accuracy of the determination. It could also be an effective tool for reducing some interferences in the liquid phase. In-situ trapping in graphite furnaces (GF) is presently by far the most popular approach to the in-atomizer trapping. A radiotracer study provided a convincing proof that the in-situ trapping of selenium hydride, arsine and stibine in graphite furnaces can be complete when performed under optimized conditions. A recently suggested approach to in-atomizer trapping, trapping on quartz surfaces in an excess of oxygen with subsequent atomization in multiatomizer or in conventional quartz tubes, is very promising. It requires only simple and cheap equipment. The potential to reach very low detection limits is even better than for in-situ trapping in GF. However, it is a novel method which will have to be tested more extensively before it can be considered to be a tool for routine analysis.

Almost all the applications of AFS employ a miniature diffusion flame for the atomization. The alternative, the flame-in-gas-shield atomizer, is more complicated but it offers a substantially better signal to noise ratio.

The current state-of-the-art of all individual atomizers, including advantages, drawbacks and perspectives, is recapitulated in detail.

## 1. Introduction

In principle, a sample can be introduced to an atomic spectrometer either in the liquid, solid or gaseous phase. Gaseous phase sample introduction techniques are usually based on volatile compound generation. A selective conversion of the analyte from the liquid sample to the gaseous phase is carried out via an appropriate chemical reaction resulting in a volatile compound of the analyte. The popularity of volatile compound generation arises for several reasons, e.g. the relative simplicity of the procedure and low cost of the apparatus. However, the main reason lies in the principle of the method. It involves separation from the sample matrix offering considerable suppression of matrix effects. Further, high efficiency of transport of gaseous analyte to the detector and simple analyte preconcentration provides exceptional detection power.

By far the most popular volatile compounds generated are covalent binary hydrides, namely of arsenic, antimony, bismuth, germanium, lead, selenium, tellurium and tin. Following the first report on the hydride generation (HG) atomic absorption spectrometry (AAS) by Holak [36], the unquestionable advantages of the method led to its application to virtually all elements capable of forming volatile hydrides. Theory, instrumentation, methodology and analytical applications of HG for atomic spectroscopy methods are exhaustively and critically covered until 1992 - 1993 in our monograph specifically devoted to HG [28]. See Refs. [37] [38] [39] [29] [30] [40] [41] for more recent reviews of HG. Besides hydrides and "cold" mercury vapor [39], the other analytically useful volatile compounds are alkyl derivatives, chelates, halides and oxides [28]. Volatile forms of cadmium [42] can also be successfully generated. Unexpectedly, in the last decade a novel application of volatile compound generation has been introduced - the use of the acid-tetrahydroborate reaction to form novel volatile species of metals [43] [44] [45] [46] [47].

In addition to volatile compound generation, gaseous phase sampling occurs when atomic spectroscopy detectors are hyphenated to a separation unit for speciation analysis of volatile metal compounds [48] [49].

The covalent binary hydrides can be taken as the model for all volatile compounds. The reason is that hydrides still form by far the most important group of analytically useful volatile compounds. Also, all new developments in atomization approaches were developed and tested with hydrides. Applications for atomization of other volatile compounds followed.

The final step of the process of element determination or of speciation analysis employing HG is atomization and detection. Since the atomization step is independent

of the generation step it is meaningful to treat it separately. The general target of our research is

**to optimize the atomization step for AAS and atomic fluorescence spectrometry (AFS) detection with respect mainly to accuracy and signal to-noise-ratio in order to fully utilize the potential of HG.**

The optimization of the atomization step should result in an atomizer fulfilling the following criteria:

(i) Complete conversion of analyte to free atoms.

(ii) No reactions of free atoms in the observed volume.

These two criteria imply that the only form of analyte present in the observation volume of the atomizer is free atoms. This means no decay of free atoms in the observation volume even in the presence of potential interferents, i.e. no atomization interferences.

(iii) Long residence time of free atoms in the observation volume.

This is required to reach high sensitivity. This criterium is in certain contradiction to criterium (ii), since the risk of free atom reactions clearly increases with the residence time.

(iv) Minimum contribution to measurement noise.

This is required to achieve a low detection limit (LOD).

(v) Analyte preconcentration in the atomizer.

Preconcentration is a clear benefit but it can be provided only by in-atomizer trapping approaches to atomization. It can improve the LOD, however, it is not useful for applications, e.g. "hyphenated" speciation analysis, requiring on-line signal detection.

(vi) User friendliness including a robustness of atomizer function.

(vii) Low running and investment cost.

Such an atomizer, meeting all the above criteria, could be considered to be an ideal atomizer. The real-world atomizers can only approximate individual criteria to certain extent.

## 2. Aim of the dissertation

The general target of the dissertation was:  
**to investigate ways how to approach ideal hydride atomizers for AAS and for AFS.**

To reach this target, the following explicit aims of the dissertation were specified:

- ▶ **to gain the knowledge of the processes taking place in hydride atomizers for AAS and AFS,**
- ▶ **to find the mechanism of atomization interferences in these atomizers**
- ▶ **to design and test new generation of hydride atomizers.**

In principle, atomization methods can be either on-line or they can incorporate in-atomizer trapping to enhance the sensitivity of the determination. In reality, only the on-line approach to atomization is used for AFS. Besides, the scope of atomizers utilized for AFS is much narrower than in the case of AAS and AFS atomizers can also be employed for AAS. Therefore, on-line atomization for AAS is addressed first followed by in-atomizer trapping approaches to atomization for AAS. Finally, the specificities of atomizers for AFS are treated.

Individual papers of the submitted dissertation are quoted by their respective numbers ([P01] to [P26]) - see the Section "List of papers of the dissertation". The other literature sources quoted in the thesis are numbered consecutively: [27] to [54] - see the Section "List of other references quoted in the thesis".

### 3. On-line atomization for AAS

On-line atomization means that hydride from the hydride generator is immediately introduced to the observation volume of the spectrometer and atomized there. The AAS (or AFS) signal observed is generally time dependent. The temporary value of the signal is proportional to the atomizer sensitivity. The influence of individual atomizer and spectrometer factors on atomizer sensitivity can be illustrated for the case of tubular atomizers in AAS: besides numerical constants, it depends on (i) the atomic absorption coefficient, (ii) atomizer temperature, (iii) atomization efficiency, (iv) total gas flow rate, (v) atomizer dimensions, and (vi) extent of decay of free analyte atoms within the atomizer [P4] [P5]. The dimension of atomizer sensitivity in AAS is (time mass<sup>-1</sup>). Alternatively, it can be expressed as peak area characteristic mass,  $m_0$ , defined as analyte mass (delivered to the atomizer) corresponding to integrated absorbance 0.0044 s.

The atomizer sensitivity expresses the atomizer performance. However, the performance of the whole analytical procedure is best expressed by the sensitivity defined by relating peak height to analyte concentration in the sample. This will be further termed "procedure sensitivity". It is controlled by the ability of the hydride generator to completely convert analyte to hydride and to supply generated hydride to the atomizer as fast as possible. It should be underlined that the ability of generator to supply hydride fast is, with the exception of hydride collection methods (cryogenic trapping) [P4], essentially limited: in flow methods of HG [P4] by the maximum feasible sample flow rate and in batch methods by the maximum feasible sample volume and/or tetrahydroborate flow rate.

In any case, the relevant parameter for practical analysis is not sensitivity but LOD. LOD is usually controlled, besides by the procedure sensitivity, by contamination arising in the sample preparation step but also in the process of HG. Disregarding contaminations, which are typically not controlled by the method of hydride generation or atomization actually chosen, LOD is controlled by the ratio of the procedure sensitivity to the measurement noise. The contribution of operating atomizer to the measurement noise will be further termed "atomizer noise".

It can be concluded that any atomizer is characterized by the two essential parameters: atomizer sensitivity and atomizer noise.

In the following, our investigation of individual approaches to on-line atomization will be treated, starting with the most popular conventional quartz tube atomizers. Then miniature flame atomizers will be addressed followed by the multiatomizer which is

actually a hybrid of previous atomizer types. Atomization in a graphite furnace (GF) will be described in the end of this Section.

### 3.1. Conventional quartz tube atomizers

Quartz tube atomizers (QTA) are usually T-tubes with the horizontal arm (optical tube) aligned in the optical path of the AAS spectrometer. The central arm of the T-tube serves for delivery of hydrides carried by a flow of gas from a hydride generator. All these QTA will be further termed in this review "conventional QTA" in order to distinguish them from the multiatomizer which is treated in Section 3.5. According to how the oxygen required for optimum atomizer performance (see below) is introduced, conventional QTA can be classified into two basic types: flame-in-tube atomizer (FIT) and conventional externally heated QTA (conventional EHQTA).

Various designs of FIT atomizers have been used [28]. We introduced a convenient design [P1] [P2] [P3] [P5] [P9] [P10] employing a capillary centered in the inlet arm of the T to introduce a small flow of oxygen to the atomizer to support a highly fuel-rich, hydrogen-oxygen diffusion microflame.

According to our theory [P1] [P2] [P3] [27] [P7] [P8], hydrides are atomized via interaction with hydrogen radicals (H radicals). In the microflame, H radicals are formed by "radical generating" reactions between oxygen and hydrogen.

Outside the hot microflame, H radicals tend to vanish by "terminating" chemical reactions. H radicals therefore form an inhomogeneous cloud with density decreasing with the distance from the hot zone. The cloud size is controlled, under the actual oxygen supply to the microflame, by the rate of H radical terminating reactions. Significant terminating reaction is that with molecular oxygen [P1]. As a result, a cloud of H radicals which is confined to a small volume is fixed at the end of the capillary.

Conventional EHQTAs employ either an electrical resistance device or the acetylene-air flame to heat the optical tube of the atomizer to a temperature between 700 °C and 1100 °C [P3]. At least a small fraction of hydrogen in the atomizer atmosphere is required for hydride atomization. Otherwise no free atoms are observed. Hydrogen is usually present since it is formed by decomposition of tetrahydroborate used for HG. Conventional EHQTAs do not employ a special tube to introduce oxygen but a certain oxygen content in the gas mixture is necessary for achieving optimum sensitivity [P3]. The oxygen demand is usually covered by traces of oxygen always present in sample, reagent solutions and gases [P23]. At the beginning of the hot zone of the atomizer a cloud of H radicals, analogous to that in FITs, is formed by reactions



between oxygen and hydrogen. The cloud fills only a small portion of the volume of the atomizer [P8].

In both types of conventional QTA, hydride is, under optimum conditions, fully atomized in the cloud by reactions with extremely energetic H radicals. At the optimum oxygen flow rate, the hydride is completely atomized within the H radical cloud [P1]. Free analyte atoms are stable within the H radical cloud, i.e. in the presence of a sufficient excess of H radicals. The same mechanism of hydride atomization in a conventional EHQTA as in a FIT indicates that these two types of conventional QTA are, in principle, identical [P3] [P8].

The analyte free atoms formed in a H radical cloud in a conventional QTA are then transported further into the optical tube of the atomizer. There are two processes removing free analyte atoms from the atomizer optical tube. The first one is mechanical - the forced convection which drives them out by the gas flow. The second removal process is due to chemical reactions of free atoms which are unstable outside the H radical cloud. Therefore the "unprotected" free atoms immediately start to react after leaving the cloud. Under typical analytical conditions, all free atoms disappear before they reach the optical tube ends [P16]. The mechanism of the decay of the free atom population is unclear. At least in the case of Se and As, it has been proven that it was critically influenced by the state of inner atomizer surface [P7] [P10] and that the decay products were removed from the optical tube by the flow of carrier gas [P1] [P2] [P7] [P9]. At high analyte concentrations the decay is dominated by reactions in the free space. Free analyte atom recombination is only the first step of a sequence of reactions leading to a formation of polyatomic species and even particles. The polyatomic species and/or particles might accelerate the decay of the remaining free atoms, perhaps through reactions on the large reaction surface of the particles [P10] [P16] [P18].

The species formed by the decay of free analyte atoms can be reatomized but only by an interaction with H radicals which, in turn, can be formed only in an additional flame or upon introduction of oxygen to the hot atomizer section. Reatomization of once decayed analyte atoms is impossible in the central section of the optical tube of a conventional QTA. It can proceed only when oxygen from the ambient atmosphere can diffuse to the section of the optical tube which is heated to a temperature sufficient to start H-radical generating reactions between hydrogen and oxygen.

### *3.1.1. Influence of atomization parameters on sensitivity*

The sensitivity of conventional QTA is markedly influenced by several parameters such as oxygen supply, gas flow rate and identity, temperature, optical tube design and state of the inner surface of the optical tube.

Oxygen supply. A certain oxygen supply - oxygen demand - is required for every atomizer. It depends mainly on atomizer temperature and its inner diameter. The demand is extremely low under typical atomization conditions in conventional EHQTAs so that it is usually covered by the oxygen present as contaminant in the system.

Gas flow rate. Generally, sensitivity increases with decreasing the total gas flow rate [P1] [P4] [P5] [P6] [P7] [P9]. However, it is usually not feasible to employ gas flow rates below 50 to 100 ml min<sup>-1</sup>.

Carrier gas identity. Selenium sensitivity in argon or nitrogen was reported higher than in hydrogen [P7]. This can be partially explained by the expected effect of various carrier gases on the atomic absorption coefficient [P6].

Temperature. The optimum atomization temperature does not depend on analyte identity but on the oxygen supply and on atomizer design [P8] [P7].

Optical tube design. Typically, sensitivity increases with increased length and decreased diameter of the atomizer optical tube [P1] [P8]. The sensitivity might be improved by careful optimization of the optical tube dimensions and the tube end design, so that analyte reatomization near the ends could take place: The tube length outside the furnace should be kept as short as possible [P16]. An elongation over 160 mm would not make sense, as no sensitivity increase can be expected [P16]. The narrowest optical tubes tested had 3.5 mm i.d. [P1] [P8]. At any rate, flames burning at the ends of the optical tube should be avoided because they deteriorate LOD, mainly because of a dramatic increase in the atomizer noise level.

Quality of the inner quartz surface. The influence of the surface quality most often manifests itself as a significant difference (in tens %) among the sensitivities observed in individual atomizers of the same design [P9]. A random incidence of "reactive areas" on the inner atomizer surface was suggested [P9] as the explanation of the observed differences in sensitivity. Since sensitivity is controlled by decay of free analyte atoms on the atomizer surface, it could be substantially enhanced by making the surface passive towards free analyte atoms and/or by minimizing access of free atoms to the surface. Passivation of the surface seems to be an extremely difficult task, in particular since various sample components which enter the atomizer may continuously modify the surface [P1].

It should be emphasized that the influence of the individual parameters is not independent of settings of other parameters. Consequently, there is no scientific basis in attempting to pick up optimum values for one of the parameters, e.g. atomization temperature, from the literature and then try to associate it with the given hydride forming element. The most marked illustration is the influence of atomization temperature and oxygen supply in the conventional EHQTA [P8] [P7], discussed above.

A correlation of an optimum value of a parameter with the identity of the given hydride forming element is meaningful only in the case that all the other experimental parameters, except that one which is correlated, are the same for all measurements. This can be realized, in practice, only when performing all the measurements in the same laboratory.

### 3.1.2. Interferences

Species transported together with the analyte hydride to any hydride atomizer may be a source of interferences [P2]. Atomization interferences are intimately coupled to the mechanism of hydride atomization and of the fate of free atoms in the observation volume of the atomizer. Considering the mechanism of hydride atomization, two mechanisms of atomization interference could be expected:

- (i) A "radical population" interference occurs when an interferent reduces the H radical population in the radical cloud [P2].
- (ii) An analyte decay interference occurs when an interferent accelerates the decay of free analyte atoms in the atomizer [P2]. Interferent atom recombination leads to the formation of polyatomic species and even particles. They accelerate the decay of the free atoms through reactions on the reactive particle surface. The species formed can be reatomized but only by an interaction with H radicals [P10]. The magnitude of the interference depends on the probability of contact of free analyte atoms with the interferent in the volume of the atomizer.

We studied atomization interferences in conventional QTA extensively [P2] [P10] [P19] [P22] [P23]. The most often reported interferences are those among volatile hydride forming elements [P2] [P10] [P19].

As a model for the interferences in FIT atomizer, interferences in the determination of selenium from As(III), Bi(III), Pb(II), Sb(III), Sn(IV), Te(IV) and also Hg(II) were studied; <sup>75</sup>Se radiotracer was employed to distinguish atomization interferences from other effects [P2]. Two FIT atomizers, large and small, differing only in horizontal bar dimensions, were employed. The effects due to tin and antimony, which are almost of the same magnitude in both atomizers, were interpreted as radical population interference and the effects due to other elements, which are much more pronounced in the large atomizer, were accounted to analyte decay interference [P2]. A more recent, detailed study of As interference in Se atomization revealed that only the analyte decay interference was significant in FIT [P10].

The resistance of conventional QTA towards atomization interferences is generally poor [P2] [P10] [P19]. In conventional EHQTA, the radical population interference might be more pronounced compared to FIT atomizers. The typical value

of the tolerance limit [P2] of the interferent concentration is 10 to 40 ng ml<sup>-1</sup> [P19]. The reason is that the oxygen supply, which controls H radical production [P1], can be rather low in conventional EHQTA.

The extent of atomization interferences in conventional QTA can be reduced substantially by optimization of relevant parameters, e.g. by increasing temperature, increasing oxygen supply or total gas flow rate to the atomizer and by making atomizer optical tube shorter and narrower [P1]. The control of these parameters is more feasible with FITs than with conventional EHQTAs. Nevertheless, even in the fully optimized FIT the magnitude of interference is still substantially higher than in other hydride atomizers (see below).

### 3.1.3. Assessment

Conventional EHQTAs have always been by far more popular than FITs since all commercial QTA are of this type. Until the mid nineties, conventional QTAs were the most commonly used hydride atomizers for AAS. Since then AAS partially lost its position in favor of other atomic spectrometry methods. At the same time, in-situ trapping in GF became the established atomization approach for AAS so that the number of applications of atomization in conventional QTA decreased significantly. However, conventional QTAs are still frequently employed in laboratories all over the world.

As far as the supply of oxygen is sufficient, hydride is completely atomized in the H radical cloud formed in conventional QTAs. However, the serious disadvantage of the atomizer is the poor resistance to atomization interferences and often unsatisfactory linearity (or even a rollover) of calibration curves [P8] [P16]. This is due to the fact that free atoms can react with other species in the optical tube after leaving the H radical cloud. On the other hand, conventional QTAs provide long residence time of free atoms in the optical path and subsequently very high atomizer sensitivity: we found  $m_0$  between 8 and 18 pg for As, Se and Sb [P21] [P15] [P19]. Additionally, the atomizer noise is low - it can even be negligible compared to the spectrometer noise. High atomizer sensitivity and low atomizer noise are promising to minimize the LOD as illustrated by the LOD as low as 20 pg ml<sup>-1</sup> we estimated for Se determination [P15]. The further advantage of conventional QTA is its low running and investment cost.

### 3.2. Miniature diffusion flames

Miniature diffusion flame (MDF) is a standard hydride atomizer for AFS in both commercial and laboratory assembled apparatus. The typical MDF design [P14] [P18]

[P22] [P23] is very simple - just a vertical quartz tube (support tube) with i.d. typically between 3 and 8 mm as the burner of the argon/hydrogen mixture introduced to the atomizer together with the analyte hydride.

The spatial temperature distribution in the MDF is highly inhomogeneous with temperatures ranging from 150 °C to 1300 °C. The minimum temperature is "inside" the flame, i.e. in the support tube axis close to the top of the tube. The maximum temperature is observed in the outer zones of the flame where the reactions between hydrogen fuel and ambient oxygen actually take place [P14].

H radicals are formed in the outer zone of the flame by the same "radical generating" reactions between oxygen and hydrogen as in the above treated case of conventional QTA. H radicals can thus diffuse to the cooler inner sections of the flame. They can even diffuse as deep as at least 3 mm inside the support tube [P14]. Outside the hot zone of the flame, H radicals tend to vanish by terminating chemical reactions. The main terminating reaction is that with molecular oxygen. In MDF, however, molecular oxygen access to the flame volume is prevented by the hot outer flame shell where oxygen is consumed. This is an efficient shield preventing loss of H radicals inside the flame. Consequently, the whole flame volume contains a high concentration of H radicals [P14].

The distribution of free atoms created in MDF is controlled by the atomization of the analyte hydride, by physical processes and by chemical reactions of the free atoms. Even the maximum temperature in MDF is too low to expect a measurable fraction of free atoms in a thermodynamic equilibrium [P20]. The mechanism of hydride atomization is analogous to that in conventional QTA: by analyte interaction with H radicals. Because of the high H radical population within the flame volume of the MDF atomizer, hydride is already fully atomized when passing the atomizer top. The "chemical" removal of free atoms proceeds analogously as the above treated removal of H radicals: via an interaction with molecular oxygen [P12]. Consequently, the outer flame shell where molecular oxygen is consumed prevents also loss of free atoms by chemical reactions with molecular oxygen within the flame. Even if free analyte atoms reacted by another mechanism the formed molecular species should be expected to be reatomized by the interaction with the vast excess of H radicals.

In summary, analyte is present exclusively in the free atom form within the whole flame volume. The free atom distribution is controlled rather by the physical processes than by the loss of free atoms by chemical reactions. Free atoms are isolated from oxygen by the hot outer shell of the flame.

Sensitivity in MDF is influenced mainly by total flow rate of the argon/hydrogen mixture [P12] and by the hydrogen fraction in the mixture. The mixture flow rate has two

contradictory effects: the beneficial influence is that it provides better shielding and therefore better protects free atoms from loss due to chemical reactions. The detrimental influence of increasing the flow rate is the dilution of free atoms which inevitably reduces sensitivity. Consequently, the optimum gas flow rate is a compromise between shielding and dilution [P14]. Typical sensitivity ( $m_0$ ) for selenium is around 0.5 ng [P10] [50]. Arsenic yields a similar sensitivity as selenium [P22].

### 3.2.1. Interferences

In general, the resistance of MDF towards atomization interferences is excellent. For example, the tolerance limit for As interference to Se determination is 70  $\mu\text{g ml}^{-1}$  - three orders of magnitude better than compared with the conventional QTA [P10]. The high population of H radicals within the whole flame, i.e. within the whole observation volume accounts for the extremely high resistance of MDF against atomization interferences [P10].

Another species besides hydrides which can be expected to be present in analyzed samples and which is a potential source of interferences is molecular oxygen [P22] [P23]. The magnitude of oxygen interference is dramatically dependent on the analyte element; the tolerance limit of oxygen concentration in antimony determination is as low as 20  $\mu\text{l l}^{-1}$  in the gas mixture reaching the atomizer [P23]. The oxygen interference, however, is rather a potential nuisance than a real problem - in fact it has not been reported in routine analysis. The reason could be that the influence of oxygen contamination on the signal does not manifest itself as interference when the oxygen concentration in samples and in standards is equal. Anyway, the influence of oxygen contamination of the gas mixture reaching the atomizer should be completely prevented by removing it by reaction with hydrogen in externally heated support atomizer tube.

### 3.2.2. Assessment

MDF provides very efficient analyte atomization and, in contrast to conventional QTA, there are virtually no reactions of free atoms in the observed volume. Atomization interferences are negligible. The atomizer sensitivity corresponds to the short optical path within the observation volume and to the relatively high gas flow rate. The atomizer noise is insignificant compared to the spectrometer noise of AAS instruments. MDF is particularly user-friendly since it provides excellent long-term signal stability and it is extremely cheap both in investment and in running costs. In summary, the only reason why MDF cannot be considered to be an ideal hydride atomizer is the relatively low atomizer sensitivity and, subsequently, high LOD - both are about 30 to 60 times worse than in conventional QTA.

In spite of that, MDF is currently only rarely employed to atomize hydrides for AAS but it is almost exclusively used for AFS detection. This will be discussed below.

### 3.3. *Flame-in-gas-shield atomizer*

We developed this atomizer (FIGS) [P12] for AFS but it can be used for AAS as well. It makes use of an argon shielded, highly fuel-rich hydrogen oxygen microflame, which is identical to that employed in the FIT atomizer, but burns in a gas shield instead of inside a quartz tube. The core of the atomizer is identical to the MDF: it is the same quartz support tube with the inlet of the mixture of hydrogen and argon containing the hydride. Also the same mixture flow rate as for MDF is typically employed. In contrast to the MDF, there is a capillary, i.d. 0.5 to 0.8 mm, centered inside the quartz support tube. It serves to introduce a very small flow of oxygen. At the end of the capillary oxygen burns in the excess of hydrogen to form the microflame. The observation volume above the top of the support tube must be protected from the ambient atmosphere by a laminar flow of argon provided by a simple shielding unit [P12] [P17] [P22] [P23] [P18].

The relevant oxygen supply rates yielding analytically useful signals are between 1.8 and 10 ml min<sup>-1</sup>. The size of the flame is controlled by the oxygen supply. Because the microflame is identical to that employed in the FIT atomizer the temperature distributions in the FIGS and FIT atomizers are similar [P17]. The formation of a small cloud of H radicals fixed at the end of the capillary as well as hydride atomization in the cloud proceeds exactly as in the case of the FIT described above. The H radical cloud extends to the radial coordinate close to the edge of the atomizer tube [P17].

The distribution of free atoms created in FIGS is, in principle, controlled by the same processes as for MDF: by atomization of the analyte hydride, by physical processes and by chemical reactions of the free atoms. In the case of FIGS, the relevant chemical reaction of free atoms is with molecular oxygen transported from the ambient atmosphere by local turbulences to the column of free atoms through the protective argon flow produced by the shielding unit. Even small amounts of oxygen penetrating through the shield flow can be responsible for the observed disappearance of free selenium atoms [P17]. Consequently, free analyte atoms form a cone narrowing with increasing observation height. This is reflected in a decrease of the AAS signals with the observation height [P22].

The main parameter controlling sensitivity is the total flow rate of the argon/hydrogen mixture. In contrast to MDF, the isolation of free atoms from ambient oxygen molecules is not by the hot outer shell of the flame but by the independently

controlled shield gas flow which does not dilute free atoms. In principle, this makes it possible to achieve substantially higher atomizer sensitivity than with MDF since the FIGS sensitivity steadily increases with decreasing argon/hydrogen mixture flow rate [P12].

### 3.3.1. Interferences

The magnitude of interferences in FIGS is controlled by the distance between the atomization and detection zones. The best tolerance to interferences, comparable with that in the miniature diffusion flame, was obtained for the minimum distance of the zones [P10]. The extent of interference is also lower for higher flow rates of oxygen to the capillary.

Regarding the oxygen interference, it can be observed when the gas introduced to the atomizer contains even less than  $15 \mu\text{l l}^{-1}$  oxygen [P23]. Analogous to the case of MDF, the magnitude of oxygen interference is controlled by the identity of the analyte element [P22] [P23].

### 3.3.2. Comparison of performance with miniature diffusion flames

There are three fundamental functions controlling performance of both atomizers: (i) production of H radicals, (ii) isolation of free atoms from ambient oxygen molecules and (iii) dilution of analyte in the observation volume. In MDF, all these three functions are controlled by a single parameter: by the flow rate of the argon/hydrogen mixture [P14]. In contrast, all the three functions are controlled independently in FIGS [P12] [P17]: production of H radicals by the flow rate of oxygen to the microflame, isolation of free atoms is controlled by the flow rate of shielding argon and dilution of analyte is controlled by the flow rate of the carrier gas.

In summary, the shield unit makes the experimental arrangement of the FIGS atomizer more complex. Also the operation of FIGS is more complicated since the flow rates of oxygen to the microflame and of the protective argon must be optimized. On the other hand, FIGS is much more flexible because of the independent control of population of H radicals, shielding and analyte dilution. A further advantage of FIGS is that better sensitivity can be achieved. Additionally, FIGS offers a much higher potential in terms of miniaturization.

### 3.4. Flame-in-flame atomizer

The flame-in-flame atomizer (FIF) is actually a modification of FIGS in which the protecting shielding flow of Ar is replaced by the diffusion flame.



There is the same hot zone in the FIF atomizer as in the case of FIGS under the same oxygen supply rate combined with the hot zone of the diffusion flame. At high oxygen supply rate both hot zones or, at least, both their respective H radical clouds can merge. The population of free analyte atoms formed in the H radical cloud of FIGS can decay outside the cloud to form non-atomic analyte species. These species can be reatomized in the H radical cloud of the diffusion flame [P22]. The higher concentration of H radicals than either in FIGS or in MDF brings further improvement in the resistance of FIF towards all kinds of atomization interferences [P23].

### 3.5. *Multiatomizer*

The only disadvantage of MDF is short residence time of free atoms in the optical path resulting in low sensitivity. Otherwise its performance is excellent due to the fact that analyte is in permanent interaction with H radicals. In contrast, conventional QTA provide a long residence time of free atoms in the optical path and subsequently very high sensitivity but otherwise its performance is poor because free atoms can react with other species in the optical tube after leaving the H radical cloud which fills only a small portion of the atomizer observation volume. Hence, a combination of MDF and conventional QTA made in such a way as to retain the advantages and remove the disadvantages of both these atomizers should result in an ideal hydride atomizer. The solution seems to be straightforward: to fill the whole volume of a QTA optical tube with H radicals. In this manner, the analyte would be maintained in the free atomic state by a permanent interaction with H radicals (as in MDF) along the whole length of the optical tube.

This is the idea behind the multiple microflame QTA (multiatomizer), which we designed to overcome disadvantages of conventional QTA. The multiatomizer is similar to the conventional QTA. The only difference is that the heated horizontal arm of the multiatomizer has double walls so that it is formed by two concentric tubes: inner (optical) and outer tube. The wall between both tubes of the horizontal arm is punctured over its length by multiple tiny orifices. The purpose of the cavity between the two tubes is to dose air, typically at the flow rate of around 25 to 35 ml min<sup>-1</sup>, through the orifices to the inside of the optical tube [P15] [P19]. A much higher fraction of the optical inner volume in multiatomizer is filled by H radicals than in conventional QTA. This is reflected in the elimination of curvature of the calibration curves and one to two orders of magnitude better resistance against interferences than the conventional QTA [P15] [P19].

In principle, the sensitivity of a multiatomizer should be influenced by the relevant experimental parameters such as total gas flow rate and identity, temperature, optical tube size and state of the inner surface of the optical tube in the same way as was discussed above for conventional QTA. However, the experimental evidence is lacking because of the limited number of reports published so far on applications of the multiatomizer [P15] [P21] [P24] [P25] [P26] [P19] [34] [35] [31] [32]. The sensitivity estimated under identical experimental parameters in multiatomizer is within 10 % of that in conventional QTA with virtually the same optical tube size. Also LOD does not change appreciably after replacement of a conventional QTA by a multiatomizer of similar optical tube size [P15] [P19].

To summarize, the multiatomizer provides a substantially better performance than conventional QTA - it retains the most important advantage of conventional QTA (without having any additional requirements with respect to either the heating device or to the hydride generator): the high sensitivity, and substantially ameliorates its fundamental disadvantages - the poor resistance to atomization interferences and unsatisfactory linearity of calibration curves [P15] [P19].

### 3.6. Graphite furnaces

On-line atomization in a GF employs the direct introduction of generated hydride to the furnace preheated to the atomization temperature. The proper choice of the interface between the hydride generator and the injection hole of the GF is of critical importance since it must withstand the atomization temperature and hydride losses must be avoided. In the course of our investigation of on-line atomization of hydrides in GF [P5] [P11] [P20], we tested several materials for the interface. Boronitride appeared to be a very convenient material. Also hydride losses were avoided when using boronitride tubing for the interface [P11] [P20].

According to our more recent study of atomization of arsine and selenium hydride in a transversely heated GF [P20], the mechanism of hydride atomization at temperatures between 600 °C and 1100 °C is analogous to that in conventional QTA. Se sensitivity expressed as  $m_0$  for atomization at temperature 900 °C under carrier Ar flow rate of 90 ml min<sup>-1</sup> was 49 pg [P20]. The lower sensitivity than in conventional QTA is due to the short length of GF. At higher temperatures, the thermal atomization also plays a role and the analytes studied approach complete atomization at temperatures around 2000 °C. The sensitivity is thus independent of oxygen and hydrogen supply to the atomizer. The observed Se sensitivity (1800 °C, Ar flow rate 90 ml min<sup>-1</sup>) was ( $m_0$ )

55 pg [P20]. The lower sensitivity compared to that yielded by liquid sample injection is due to the Ar flow accelerating removal of free atoms out of the furnace.

The extent of interference was approximately ten times lower than in conventional QTA under exactly the same gas flow rates and temperature. However, when increasing atomization temperature from 900 °C to 1800 °C magnitude of the arsine interference on selenium determination decreases by one order of magnitude [P20].

In conclusion, on-line atomization in GF provides lower sensitivity but better tolerance to atomization interferences, especially at high atomization temperatures, than conventional QTA. This approach to hydride atomization could be convenient for laboratories not equipped for atomization in quartz tubes.

#### 4. In-atomizer trapping AAS

One of the inherent advantages of generation of volatile forms of analyte for analytical atomic spectrometry is that the analyte can be easily preconcentrated either in a special collection device or directly in the atomizer. In-atomizer trapping is the most convenient way of analyte collection. Until recently, the only widely used approach to in-atomizer trapping was in-situ trapping in GF but then procedures based on trapping on quartz surfaces emerged. Both these approaches to in-atomizer trapping will be treated in the respective Sections below.

The procedure of in-atomizer trapping consists of two steps: (i) trapping and (ii) volatilization/atomization. In the first step, the volatile analyte compound carried from a generator is trapped in the atomizer until its evolution is completed. For the optimum performance of the method it is highly desirable to trap the generated hydride completely. In the second step, the trapped analyte is volatilized and atomized within typically less than 1 s.

There is a substantial difference compared to on-line atomization: the procedure sensitivity is no longer limited by the performance of the hydride generator. It is controlled by the atomizer performance (i.e. by the atomizer sensitivity, by the trapping efficiency and by the ability of the atomizer to volatilize and atomize the analyte efficiently and as fast as possible) and, mainly, it is directly proportional to the sample volume. Since the sample volume can be, in principle, very large, in-atomizer trapping significantly enhances the procedure sensitivity. In addition, in-atomizer trapping eliminates the effect of the generation kinetics and of surges in gas flow on the signal shape. In-atomizer trapping could also be an effective tool for reducing interferences in the liquid phase by sample dilution or by slower addition of the reducing agent [28]. The reason is that the collection allows the dilution or the slower addition without reducing the procedure sensitivity.

##### 4.1. *In-situ trapping in graphite furnaces*

In-situ trapping in GF is the most popular approach to the in-atomizer trapping. Since the mid nineties it has become, together with conventional QTA, the most commonly used hydride atomizers for AAS. In recent years, it seems to be partially losing its position in favor of other atomic spectrometry methods, however, in-situ trapping in GF is still one of the most popular atomization methods for all analytically important hydrides. Metal treated surfaces of the GF have been almost exclusively employed in the last decade.

In the first step of the procedure of in-situ trapping in GF, the atomizer is usually heated to ca. 200 - 600 °C to trap the analyte hydride carried from a generator. In the second step, the trapped analyte is volatilized and atomized at temperatures generally >2000 °C. Obviously, hydride should be introduced to the furnace in a manner ensuring minimum losses and permitting convenient operation. Geometry and quality of inner graphite surface, trapping temperature and flow rate of the carrier gas are the critical experimental parameters. It should be emphasized that they are interrelated which cause confusion when evaluating a single parameter, for example the trapping temperature, without taking into account all the other parameters [P13].

The most convenient and presently almost exclusively used interface between the hydride generator and graphite furnace is a capillary, most often of quartz, inserted through the sampling port of the furnace [28]. After hydride evolution from the generator is complete, the capillary is removed and the volatilization/atomization may be launched.

The trapping efficiency is a critical parameter for the performance of the method. The trapping efficiency for a given analyte obviously depends on furnace design, modification of the surface where trapping takes place (graphite tube wall or platform), trapping temperature and the carrier gas flow rate [P13]. The most accurate estimate of the trapping efficiency can be achieved by the application of radiotracers. We performed a radiotracer study of selenium hydride, arsine and stibine trapping in the transversely heated GF with a palladium modified surface. It provided convincing proof that the trapping is complete when performed under optimized conditions. The optimum conditions for selenium hydride are reached for a broad range of Pd modifier mass, trapping temperature, carrier gas flow rate and the injection capillary distance from the platform surface [P13].

Because in-situ trapping in GF involves analyte collection it significantly enhances the procedure sensitivity. The atomizer noise is low. Consequently, very low LODs can be achieved. The resistance of in-situ trapping in GF towards interferences is reasonably good. In-situ trapping in GF is a mature method well established in various applications. It is important that it can be easily automated. These are the reasons to rank in-situ trapping in GF as the currently most convenient approach to hydride atomization for AAS.

#### *4.2. Trapping in a quartz tube - atomization in quartz tube atomizers*

Another promising approach to in-atomizer trapping is to collect hydride in a quartz tube which can be, in principle, integrated with a quartz tube atomizer.

A successful trapping of  $\text{PbH}_4$  in a bare quartz tube trap with subsequent volatilization and atomization in the conventional EHQTA was announced in 2002 [51]. However, this approach does not necessarily have to work for the most important hydrides. The reason is that the traces of molecular oxygen, required for atomization of analytes such as As, Sb, Se, etc. in the optical tube (see the discussion of the atomization mechanism in quartz tube atomizers above), are consumed in the heated trap by reactions with hydrogen. Therefore the analyte forms volatilized in the second step of the procedure from the trap are not atomized in the optical tube of the conventional EHQTA. The signal observed is thus only due to free atoms formed in the trap which can partially or even completely decay before reaching the optical tube.

To enable the atomization of antimony species volatilized from the quartz trap, we replaced the conventional EHQTA by a multiatomizer [P21]. Even though the interfacing of the quartz trap with the multiatomizer [P21] resulted in a LOD of  $3.9 \text{ pg ml}^{-1}$  antimony, the performance of the method was not optimal - the efficiency of trapping and volatilization was only 65 %.

Our subsequent experiments [P26] indicated that the most serious reason for the incomplete trapping/volatilization were analyte losses in the trapping step which were unavoidable in the presence of hydrogen developed in hydride generator. The simplest way to remove hydrogen was to burn it out in a stoichiometric excess of oxygen. The other imperative for the trap and atomizer experimental setup is to minimize temperature gradients between the heated trap and atomizer. To conform to these requirements a trap-and-atomizer device was designed, which is actually the multiatomizer described above with its inlet arm modified to serve as the trap and to accommodate the oxygen delivery capillary employed for burning out hydrogen [P26]. The capillary setup of the device makes it possible to fix the  $\text{H}_2/\text{O}_2$  flame at the end of the oxygen delivery capillary during the trapping step. Consequently, there is certain length of the inlet arm between the flame and the optical tube providing the "hydrogen free" atmosphere. This inlet arm section thus serves as an efficient trap since under oxygen excess the analyte hydrides are converted to oxides which are retained at the trap due to interaction with the quartz surface. To volatilize and atomize trapped analyte species, the inlet arm heating is changed to the actual volatilization temperature and the oxygen flow is replaced by a flow of hydrogen. At the elevated quartz surface temperature and under the hydrogen excess the trapped analyte species are volatilized and transported to the optical arm of the multiatomizer to be atomized there [P26].

The efficiency of trapping and volatilization found with this trap-and-atomizer device for As, Bi, Sb and Se, respectively, was 50 % [P26], 100 % [33], 100 % [33] and 70 % [P26]. The procedures are fairly robust even for As and Se [P26] indicating the

potential of this approach to preconcentration of arsine and selenium hydride for analytical practice in spite of the unsatisfactory performance of the present apparatus which cannot provide complete trapping and volatilization.

The influence of trap temperature in the trapping as well as in the volatilization step on the efficiency of trapping and volatilization was studied for all the four analytes [P26] [33]. It appeared that antimony and bismuth species could be efficiently collected in the quartz tube trap even at temperatures typical for hydride atomization (800 - 1000 °C) [33]. Such a temperature is sufficient to release the collected species in the volatilization step. This suggested that conventional EHQTA, without any trap, could be used for in-situ stibine and bismuthine collection and subsequent analyte atomization. Subsequently, it was confirmed experimentally that the commercially available conventional EHQTA without any interfaced trapping device can be employed for the in-situ trapping of stibine under a stoichiometric excess of oxygen over hydrogen and the volatilization and atomization of trapped analyte can be performed just by switching off the oxygen inlet. The efficiency of trapping and volatilization was  $100 \pm 2 \%$  and LOD was  $2.8 \text{ pg ml}^{-1}$  [P24]. A slight modification of the atomizer consisting in introduction of all gases flowing from the hydride generator through a capillary axially centered in the inlet arm made possible the lossless trapping and subsequent analyte atomization (efficiency of trapping and volatilization  $100 \pm 2.5 \%$ ) also for Bi. This was reflected in LOD of  $3.9 \text{ pg ml}^{-1}$  [P25]. It should be highlighted that LOD was controlled for Sb as well as for Bi by the analyte content in blanks so that even lower LOD could be reached if the contamination were reduced.

However, neither the unmodified nor the slightly modified conventional EHQTA can be employed for the in-situ trapping of hydrides of As or Se [P24] [P25]. In the case of Se, this is compatible with the observation that the trapping efficiency of selenium species in the trap-and-atomizer device decreases sharply with trapping temperature to fall below 10 % at the trap temperature above 500 °C [P26]. In contrast, the trapping efficiency of arsenic species in the trap-and-atomizer device decreases only slightly at the trap temperature of 900 °C [P26]. Arsenic cannot be preconcentrated in the conventional EHQTA probably because the trapped As species require more H radicals to be atomized than other species of the other studied analytes [33].

The atomizer sensitivity of trapping in a quartz tube with subsequent atomization in QTA is very good [P26] [P24] [P25] - in principle the same as for on-line atomization. Only for analytes requiring higher hydrogen flow rate in the volatilization/atomization step for efficient volatilization, the resulting sensitivity is lower - by 60 % in the worst case [P26]. Consequently, the atomizer sensitivity is still substantially better than for GF. The resulting procedure sensitivity is excellent since the efficiency of trapping and

volatilization is close to unity and the peaks observed in the volatilization/atomization step are narrow. Because of the low atomizer noise, the LOD lower than for in-situ trapping in GF should be expected in general.

There is not enough data on interferences. They were studied only for stibine trapping under a stoichiometric excess of oxygen in the commercially available conventional EHQTA. The extent of interference of Bi, Sn and As was in the same range as for in-situ trapping in GF. On the other hand the extent of interference elements like Ge, Se, Te and Pb is one order of magnitude lower [P24].

In summary, trapping on quartz surfaces in an excess of oxygen with subsequent atomization in multiatomizer or in conventional EHQTA is very promising approach to in-atomizer trapping. It requires only simple and cheap equipment. The potential to reach very low LOD is even better than for in-situ trapping in GF. However, it is a novel method which will have to be tested extensively before it can be considered to be a tool for routine analysis.



## 5. Atomic fluorescence spectrometry

AFS coupled to HG has the potential to reach a very low LOD and because of its low purchase and operating costs, it can be an attractive alternative to mass spectrometric techniques. Even though the simple and sensitive non-dispersive apparatus can be easily assembled using commercially available components, HG AFS became a widely used analytical tool for determination of volatile compound forming elements after the availability of the first commercial AFS instrument [52]. Commercially available detection systems consist of a boosted-output hollow cathode lamp as the radiation source and MDF as the atomizer [52]. With the new millennium, the use of AFS interfaced to generation of volatile compounds became a well-established technique and a serious competitor to AAS.

The aim of this dissertation is to treat hydride atomizers. This is a simple task in the case of AFS since almost all the applications employ MDF. Only a few reports, all published by us [P12] [P17] [P22] [P23] [P18], deal with the FIGS atomizer. Other atomizers are rather exceptions, e.g. in-situ trapping in GF [53] [54] for laser excited AFS.

Design, atomization mechanism, interferences as well as the influence of individual experimental parameters on sensitivity in MDF and FIGS is treated in detail above in Sections devoted to AAS. All the discussion is valid also for the use of these atomizers for AFS.

In contrast to AAS where the noise produced in MDF is negligible compared to the spectrometer noise of AAS instruments, in AFS the MDF noise can control the observed LOD [P12]. The straightforward way to reduce atomizer noise is to use a FIGS atomizer which can improve the AFS LODs substantially in comparison with MDF. For example, the AFS sensitivity provided by FIGS is at least two-fold higher and its inherent noise is substantially lower than to MDF. This offers the possibility to improve LOD by more than one order of magnitude [P12].

## 6. Conclusions

According to definition, ideal is "being entirely without fault or flaw". In this sense, the way towards the ideal atomizer can never be crowned with complete success. However, I believe that the dissertation illustrates convincingly our progress in approaching ideal hydride atomizers for AAS and for AFS. We gained considerable knowledge of the processes taking place in all hydride atomizers. We found the mechanism of atomization interferences in these atomizers. We also succeeded in designing new generation of hydride atomizers: multiatomizer for AAS and FIGS for AFS. The multiatomizer matches performance of conventional QTA in terms of sensitivity and baseline noise as well as in running and investment costs, however, it provides much better (i) resistance against atomization interferences and (ii) linearity of calibration curves. FIGS offers a substantially better signal to noise ratio than the almost exclusively used MDF, it is more flexible and it offers a much higher potential in terms of miniaturization. Finally, we developed a novel concept of in-atomizer trapping: trapping on quartz surfaces in an excess of oxygen with subsequent atomization in multiatomizer or in conventional QTA. It requires only simple and cheap equipment. The potential to reach very low detection limits is even better than for in-situ trapping in GF.

## List of papers of the dissertation

- [P1] J. Dědina, I. Rubeška, Hydride atomization in a cool hydrogen-oxygen flame burning in a quartz tube atomizer, *Spectrochim. Acta Part B* 35 (1980) 119-128.
- [P2] J. Dědina, Interference of volatile hydride forming elements in selenium determination by atomic absorption spectrometry with hydride generation, *Anal. Chem.* 54 (1982) 2097-2102.
- [P3] J. Dědina, Flame-in-tube atomization in hydride AA technique. Mechanism of atomization, interferences and comparison with atomization in heated flameless quartz tube atomizers, in: B. Welz (Ed.), *Fortschritte in der atomspektrometrischen Spurenanalytik*, Vol. 1, Verlag Chemie, Weinheim, 1984, pp. 29 - 47.
- [P4] J. Dědina, Optimization of hydride generation methods for AAS, *Fresenius Z. Anal. Chem.* 323 (1986) 771-782.
- [P5] J. Dědina, W. Frech, E. Lundberg, A. Cedergren, Atomisation of selenium hydride in the graphite furnace, *J. Anal. At. Spectrom.* 4 (1989) 143-148.
- [P6] J. Dědina, Atomic absorption coefficient of the selenium 196 nm line - theoretical computation and experimental evaluation, *Spectrochim. Acta Part B* 46 (1991) 379-391.
- [P7] J. Dědina, Quartz tube atomizers for hydride generation atomic absorption spectrometry : mechanism of selenium hydride atomization and fate of free atoms, *Spectrochim. Acta Part B* 47 (1992) 689-700.
- [P8] J. Dědina, B. Welz, Quartz tube atomizers for hydride generation atomic absorption spectrometry - mechanism for atomization of arsine - invited lecture, *J. Anal. At. Spectrom.* 7 (1992) 307-314.
- [P9] J. Dědina, B. Welz, Quartz tube atomizers for hydride generation atomic absorption spectrometry: fate of free arsenic atoms, *Spectrochim. Acta Part B* 48 (1993) 301-314.
- [P10] A. D' Ulivo, J. Dědina, Interferences in hydride atomization studied by atomic absorption and atomic fluorescence spectrometry, *Spectrochim. Acta Part B* 51 (1996) 481-498.
- [P11] J. Dědina, T. Matoušek, W. Frech, On-line atomization of selenium hydride in graphite furnaces: estimate of atomic absorption coefficient and spectroscopic temperature, *Spectrochim. Acta Part B* 51 (1996) 1107-1119.
- [P12] J. Dědina, A. D' Ulivo, Argon shielded, highly fuel-rich, hydrogen-oxygen diffusion micro flame - a new hydride atomizer, *Spectrochim. Acta Part B* 52 (1997) 1737-1746.

- [P13] B. Dočekal, J. Dědina, V. Krivan, Radiotracer investigation of hydride trapping efficiency within a graphite furnace, *Spectrochim. Acta Part B* 52 (1997) 787-795.
- [P14] J. Dědina, A. D' Ulivo, L. Lampugnani, T. Matoušek, R. Zamboni, Selenium hydride atomization, fate of free atoms and spectroscopic temperature in miniature diffusion flame atomizer, *Spectrochim. Acta Part B* 53 (1998) 1777-1790.
- [P15] J. Dědina, T. Matoušek, Multiple microflame - a new approach to hydride atomization for atomic absorption spectrometry, *J. Anal. At. Spectrom.* 15 (2000) 301-304.
- [P16] T. Matoušek, J. Dědina, 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, *Spectrochim. Acta Part B* 55 (2000) 545-557.
- [P17] A. D' Ulivo, J. Dědina, L. Lampugnani, T. Matoušek, Mechanism of selenium hydride atomization, fate of free atoms and temperature in argon shielded, highly fuel-rich, hydrogen-oxygen diffusion micro flame studied by atomic absorption spectrometry, *J. Anal. At. Spectrom.* 17 (2002) 253-257.
- [P18] A. D' Ulivo, J. Dědina, The relation of double peaks, observed in quartz hydride atomizers, to the fate of free atoms in the determination of arsenic and selenium by atomic absorption spectrometry, *Spectrochim. Acta Part B* 57 (2002) 2069-2079.
- [P19] T. Matoušek, J. Dědina, A. Selecká, Multiple microflame quartz tube atomizer - further development towards the ideal hydride atomizer for atomic absorption spectrometry, *Spectrochim. Acta Part B* 57 (2002) 451-462.
- [P20] T. Matoušek, J. Dědina, W. Frech, On-line atomization of selenium hydride in graphite furnaces: mechanism and interferences, *J. Anal. At. Spectrom.* 17 (2002) 1323-1329.
- [P21] D.K. Korkmaz, J. Dědina, O.Y. Ataman, Stibine preconcentration in a quartz trap with subsequent atomization in the quartz multiatomizer for atomic absorption spectrometry, *J. Anal. At. Spectrom.* 19 (2004) 255-259.
- [P22] A. D' Ulivo, J. Dědina, L. Lampugnani, A. Selecká, Mechanism of atomization interference by oxygen at trace level in miniature flame hydride atomizers, *Spectrochim. Acta Part B* 60 (2005) 1270-1279.
- [P23] A. D' Ulivo, J. Dědina, L. Lampugnani, Effect of contamination by oxygen at trace level in miniature flame hydride atomizers, *J. Anal. At. Spectrom.* 20 (2005) 40-45.

- [P24] J. Kratzer, J. Dědina, In-situ trapping of stibine in externally heated quartz tube atomizers for atomic absorption spectrometry, *Spectrochim. Acta Part B* 60 (2005) 859-864.
- [P25] J. Kratzer, J. Dědina, In situ trapping of bismuthine in externally heated quartz tube atomizers for atomic absorption spectrometry, *J. Anal. At. Spectrom.* 21 (2006) 208-210.
- [P26] J. Kratzer, J. Dědina, Arsine and selenium hydride trapping in a novel quartz device for atomic-absorption spectrometry, *Anal. Bioanal. Chem.* 388 (2007) 793-800.

## List of other references quoted in the thesis

- [27] J. Dědina, Evaluation of hydride generation and hydride atomization for AAS, *Prog. Analyt. Spectrosc.* 11 (1988) 251-360.
- [28] J. Dědina, D.L. Tsalev, *Hydride Generation Atomic Absorption Spectrometry*, Wiley & Sons, Inc., Chichester, 1995.
- [29] J. Dědina, *Atomic Absorption Spectrometry, Hydride Generation*, in: R. A. Meyers (Ed.), *Encyclopedia of Environmental Analysis and Remediation*, John Wiley & Sons, Inc., New York, 1998, pp. 524 - 542.
- [30] J. Dědina, *Flow Methods in Gas-liquid Separations*, in: A. Sanz-Medel (Ed.), *Flow Analysis Atomic Spectrometric Detection*, Elsevier, Amsterdam, 1999, pp. 237 - 273.
- [31] T. Matoušek, J. Dědina, M. Vobecký, Continuous flow chemical vapour generation of silver for atomic absorption spectroscopy using tetrahydroborate (III) reduction - system performance and assessment of the efficiency using instrumental neutron activation analysis, *J. Anal. At. Spectrom.* 17 (2002) 52-56.
- [32] A. Hernandez-Zavala, T. Matoušek, Z. Drobná, D.S. Paul, F. Walton, B.M. Adair, J. Dědina, D.J. Thomas, M. Stýblo, *Speciation Analysis of Arsenic in Biological Matrices by Automated Hydride Generation-Cryotrapping-Atomic Absorption Spectrometry with Multiple Microflame Quartz Tube Atomizer (Multiatomizer)*, *J. Anal. At. Spectrom.* (2007) submitted.
- [33] J. Kratzer, J. Dědina, to be submitted.
- [34] T. Matoušek, A. Hernandez-Zavala, M. Svoboda, L. Langrova, B.M. Adair, Z. Drobná, D.J. Thomas, M. Stýblo, J. Dědina, *Oxidation state specific speciation analysis of methylated arsenicals by hydride generation - automated cryotrapping - gas chromatography-atomic absorption spectrometry with the multiatomizer: the method development*, *J. Anal. At. Spectrom.* (2007) submitted.
- [35] D.S. Paul, A. Hernandez-Zavala, F.S. Walton, B.M. Adair, J. Dědina, T. Matoušek, M. Stýblo, *Examination of the effects of arsenic on glucose homeostasis in cell culture and animal studies: development of a mouse model for arsenic-induced diabetes, toxicology and applied pharmacology*, *Toxicology and Applied Pharmacology* (2007) in print.
- [36] W. Holak, *Gas-sampling technique for arsenic determination by atomic absorption spectrophotometry*, *Anal. Chem.* 41 (1969) 1712-1713.
- [37] H. Matusiewicz, R.E. Sturgeon, *Atomic spectrometric detection of hydride forming elements following in situ trapping within a graphite furnace*, *Spectrochim. Acta Part B* 51 (1996) 377-397.

- [38] A.G. Howard, (Boro)hydride techniques in trace element speciation, *J. Anal. At. Spectrom.* 12 (1997) 267-272.
- [39] B. Welz, M. Sperling, *Atomic Absorption Spectrometry*, Wiley-VCH, Weinheim, 1999.
- [40] A.R. Kumar, P. Riyazuddin, Mechanism of volatile hydride formation and their atomization in hydride generation atomic absorption spectrometry, *Anal. Sci.* 21 (2005) 1401-1410.
- [41] D.L. Tsalev, Vapour generation or electrothermal atomic absorption spectrometry? - Both!, *Spectrochim. Acta Part B* 55 (2000) 917-933.
- [42] P. Bermejo-Barrera, J. Moreda-Pineiro, A. Moreda-Pineiro, A. Bermejo-Barrera, Use of flow injection cold vapour generation and preconcentration on coated graphite tubes for the determination of cadmium in sea-water by electrothermal atomic absorption spectrometry, *J. Anal. At. Spectrom.* 11 (1996) 1081-1086.
- [43] R.E. Sturgeon, Z. Mester, Analytical applications of volatile metal derivatives, *Appl. Spectrosc.* 56 (2002) 202A-213A.
- [44] P. Pohl, Recent advances in chemical vapour generation via reaction with sodium tetrahydroborate, *TrAC, Trends Anal. Chem.* 23 (2004) 21-27.
- [45] R.E. Sturgeon, X. Guo, Z. Mester, Chemical vapor generation: are further advances yet possible?, *Anal. Bioanal. Chem.* 382 (2005) 881-883.
- [46] P. Pohl, B. Prusisz, Chemical vapor generation of noble metals for analytical spectrometry, *Anal. Bioanal. Chem.* (2007) in print.
- [47] T. Matoušek, The efficiency of chemical vapour generation of transition and noble metals, *Anal. Bioanal. Chem.* 388 (2007) 763-767.
- [48] R. Cornelis, J. Caruso, H. Crews, K. Heumann (Eds.), *Handbook of Elemental Speciation, Techniques and Methodology*, Wiley, NY, 2003.
- [49] J. Szpunar, R. Lobinski, *Hyphenated Techniques in Speciation Analysis*, RSC, Cambridge, 2003.
- [50] A. D'Ulivo, L. Gianfranceschi, L. Lampugnani, R. Zamboni, Masking agents in the determination of selenium by hydride generation technique, *Spectrochim. Acta Part B* 57 (2002) 2081-2094.
- [51] D.K. Korkmaz, N. Ertas, O.Y. Ataman, A novel silica trap for lead determination by hydride generation atomic absorption spectrometry, *Spectrochim. Acta Part B* 57 (2002) 571-580.
- [52] W.T. Corns, P.B. Stockwell, L. Ebdon, S.J. Hill, Development of an atomic fluorescence spectrometer for the hydride-forming elements, *J. Anal. At. Spectrom.* 8 (1993) 71-77.

[53] H.L. Pacquette, S.A. Elwood, M. Ezer, D.J. Swart, J.B. Simeonsson, Hydride generation laser induced fluorescence of arsenic and selenium in the inductively coupled plasma and electrothermal atomizer, *Appl. Spectrosc.* 54 (2000) 89-93.

[54] H.L. Pacquette, S.A. Elwood, M. Ezer, J.B. Simeonsson, A comparison of continuous flow hydride generation laser- induced fluorescence and laser-enhanced ionization spectrometry approaches for parts per trillion level measurements of arsenic, selenium and antimony, *J. Anal. At. Spectrom.* 16 (2001) 152-158.



## List of other publications of the author

(The papers forming the dissertation are not listed here.)

### *Papers published in Journals having impact factor*

1. J. Dědina, J. Schraml, V. Chvalovský, PMR study of association of trimethylsilyl substituted alcohols and their carbon and germanium analogues, *Collect. Czech. Chem. Commun.* 37 (1972) 3762-3770.
2. V. Skála, J. Kuthan, J. Dědina, J. Schraml, Reaction of some dicyanopyridines with methylmagnesium iodide. Observation of the nuclear Overhauser effect in the presence of NMR shift reagent, *Collect. Czech. Chem. Commun.* 39 (1974) 834-841.
3. J. Dědina, J. Schraml, Nuclear Overhauser effect and <sup>1</sup>H-NMR of 1,2-dimethoxy-4-hydroxy-5-nitrobenzene, *Collect. Czech. Chem. Commun.* 40 (1975) 1538-1541.
4. J. Dědina, J. Kuthan, J. Paleček, J. Schraml, <sup>1</sup>H-NMR spectra and nuclear Overhauser effect in E and Z isomers of 3-substituted 3-aminoacrylonitrile, *Collect. Czech. Chem. Commun.* 40 (1975) 3476-3490.
5. J. Dědina, J. Schraml, Application of homonuclear Overhauser effect to molecules with internal motion, *Collect. Czech. Chem. Commun.* 42 (1977) 3239-3264.
6. J. Dědina, J. Schraml, Z. Arnold, J. Šauliová, Homonuclear Overhauser effect study of trimethinium salts, *Collect. Czech. Chem. Commun.* 43 (1978) 3356-3364.
7. M. Vobecký, J. Dědina, L. Pavlík, M. Valášek, Gamma-ray interferences in the determination of selenium by the INAA method, *Radiochem. Radioanal. Lett.* 38 (1979) 197-201.
8. V. Korunová, J. Dědina, Determination of trace concentrations of mercury in biological materials after digestion under pressure in nitric acid catalyzed by vanadium pentoxide, *Analyst* 105 (1980) 48-51.
9. J. Kopecký, J. Dědina, J. Votruba, P. Svoboda, J. Houštěk, S. Babitch, Z. Drahota, Stoichiometry of dicyclohexylcarbodiimide-ATPase interaction in mitochondria, *Biochem. Biophys. Acta* 680 (1982) 80-87.
10. J. Kopecký, S. Pavelka, J. Dědina, V. Siglerová, K. Vereš, Stability of dicyclohexylcarbodiimide in an aqueous medium. The effect of mitochondrial phospholipids, *Collect. Czech. Chem. Commun.* 48 (1983) 662-667.
11. J. Dědina, W. Frech, A. Cedergren, I. Lindberg, E. Lundberg, Determination of Se by GF AAS. Part 2. Role of Ni for analyte stability, *J. Anal. At. Spectrom.* 2 (1987) 435-439.

12. J. Dědina, W. Frech, I. Lindberg, E. Lundberg, A. Cedergren, Determination of Se by GF AAS. Part 1. Interaction between Se and carbon, *J. Anal. At. Spectrom.* 2 (1987) 287- 291.
13. J. Dědina, Evaluation of hydride generation and hydride atomization for AAS, *Prog. Analyt. Spectrosc.* 11 (1988) 251-360.
14. V. Korunová, Z. Škodová, J. Dědina, Z. Valenta, J. Pařízek, Z. Píša, M. Stýblo, Serum selenium in adult Czechoslovak (central Bohemia) population, *Biol. Trace Elem. Res.* 37 (1993) 91-99.
15. T. Matoušek, M. Johansson, J. Dědina, W. Frech, Spatially resolved absorption measurement of antimony atom formation and dissipation in quartz tube atomizers following hydride generation, *Spectrochim. Acta Part B* 54 (1999) 631-643.
16. T. Matoušek, J. Dědina, M. Johansson, W. Frech, Gas flow patterns and longitudinal distribution of free selenium atoms in quartz tube atomizers for hydride generation atomic absorption spectrometry, *Spectrochim. Acta Part B* 55 (2000) 151-163.
17. T. Matoušek, J. Dědina, M. Vobecký, Continuous flow chemical vapour generation of silver for atomic absorption spectroscopy using tetrahydroborate (III) reduction - system performance and assessment of the efficiency using instrumental neutron activation analysis, *J. Anal. At. Spectrom.* 17 (2002) 52-56.
18. Y.M. Sadagoff, J. Dědina, Atom diffusion in furnaces—models and measurements, *Spectrochim. Acta Part B* 57 (2002) 535-549.
19. J. Šíma, P. Rychlovský, J. Dědina, The efficiency of the electrochemical generation of volatile hydrides studied by radiometry and atomic absorption spectrometry, *Spectrochim. Acta Part B* 59 (2004) 125-133.
20. I. Karadjova, L. Lampugnani, J. Dědina, A. D' Ulivo, M. Onor, D.L. Tsalev, Organic solvents as interferents in arsenic determination by hydride generation atomic absorption spectrometry with flame atomization, *Spectrochim. Acta Part B* 61 (2006) 525-531.
21. J. Dědina, Atomization of volatile compounds for atomic absorption and atomic fluorescence spectrometry: On the way towards the ideal atomizer, *Spectrochim. Acta Part B* (2007) in print.
22. E.C. Figueiredo, J. Dědina, M.A.Z. Arruda, Metal furnace heated by flame as a hydride atomizer for atomic absorption spectrometry: Sb determination in environmental and pharmaceutical samples, *Talanta* (2007) in print.
23. D.S. Paul, A. Hernandez-Zavala, F.S. Walton, B.M. Adair, J. Dědina, T. Matoušek, M. Stýblo, Examination of the effects of arsenic on glucose homeostasis in cell culture and animal studies: development of a mouse model for arsenic-induced

diabetes, toxicology and applied pharmacology, *Toxicology and Applied Pharmacology* (2007) in print.

#### *Books and chapters in books*

24. J. Dědina, D.L. Tsalev, *Hydride Generation Atomic Absorption Spectrometry*, Wiley & Sons, Inc., Chichester, 1995.
25. J. Dědina, *Atomic Absorption Spectrometry, Hydride Generation*, in: R. A. Meyers (Ed.), *Encyclopedia of Environmental Analysis and Remediation*, John Wiley & Sons, Inc., New York, 1998, pp. 524 - 542.
26. J. Dědina, *Flow Methods in Gas-liquid Separations*, in: A. Sanz-Medel (Ed.), *Flow Analysis Atomic Spectrometric Detection*, Elsevier, Amsterdam, 1999, pp. 237 - 273.

#### *Patents*

27. J. Dědina, *Zařízení pro kontinuální přípravu hydridů*, (1984) AO 233157.
28. J. Dědina, *Atomizátor pro stanovení hydridotvorných prvků metodou atomové absorpční spektrometrie*, (1984) AO 216063.
29. J. Dědina, T. Matoušek, *Způsob atomizace těkavých sloučenin, zejména hydridů, stanovovaných prvků pro atomovou absorpční spektrometrii a zařízení k provádění tohoto způsobu*, (1999) AO 287635.
30. J. Dědina, J. Kratzer, *Způsob prekoncentrace antimonu pro jeho stanovení metodami atomové spektrometrie*, (2004) PV-2004 - 854, 2-8-2004.
31. J. Dědina, J. Kratzer, *Způsob prekoncentrace bismutu pro jeho stanovení metodou atomové absorpční spektrometrie*, (2005) PV 2005 - 761, 8-12-2005.
32. J. Dědina, O. Grossová, *Modulární konstrukce atomizátoru hydridů pro atomovou absorpční spektrometrii*, (2005) PV 2005-306, 13-5-2005.
33. J. Dědina, J. Kratzer, *Způsob prekoncentrace těkavých hydridů pro ultrastopovou analýzu s detekcí atomovou absorpční spektrometrií a zařízení k provádění tohoto způsobu*, (2007) PV 2007-112, 13-2-2007.