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Miniature plasma DBD atomizer for AAS and AFS

Miniaturní plazmové DBD atomizátory pro AAS a AFS

Bachelor's thesis

Supervisor: RNDr. Jan Kratzer, Ph.D.

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#### Declaration

I declare that I carried out this bachelor thesis independently, and only with the cited sources, literature and other professional sources. I declare that this thesis has not been used to gain any other academic title.

In Prague on 10.1.2019

Marek Straka

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I am also grateful to my parents and family for continuous encouragement and support.

## **Abstract**

Five designs of dielectric barrier discharge (DBD) atomizers have been constructed and optimized employing arsane as a model analyte. The individual DBD designs differed from each other in the style of electrode attachment, electrode shape and area. An externally heated quartz tube atomizer and another DBD atomizer design that have been studied before were used as reference. All the atomizer designs studied including the reference atomizers were found compatible with detection by atomic absorption spectrometry (AAS) giving comparable sensitivity of  $0.44 \text{ s ng}^{-1} \text{ As}$  and detection limit around  $0.2 \text{ ng ml}^{-1} \text{ As}$  under optimum atomization conditions. However, significant differences in optimum operation conditions were found among the DBD designs in terms of the applied voltage depending strongly on the style of electrode attachment. The design with metal strip electrodes glued to a quartz body requires more than 14 kV to be operated. The design with sputtered electrodes of the same shape can reach the same sensitivity with 8.5 kV. Selected DBD designs have been proven to be compatible also with other spectrometric detectors such as atomic fluorescence spectrometry (AFS) reaching detection limit  $0.05 \text{ ng ml}^{-1} \text{ As}$  or atomic emission spectrometry (AES) with detection limit of  $30 \text{ ng ml}^{-1} \text{ As}$  showing the universality of the planar DBD designs.

## **Keywords**

Atomic spectrometry, dielectric barrier discharge atomizer, arsenic, hydride generation

## **Abstrakt**

Cílem práce bylo zkonstruovat pět nových uspořádání plazmových atomizátorů s dielektrickou bariérou (DBD) a optimalizovat je pro atomizaci hydridu arsenu jako analytu. Jednotlivé konstrukce se vzájemně lišily tvarem a plochou elektrod i způsobem jejich upevnění. Jako srovnávací atomizátory byly použity vyhřívaný křemenný atomizátor a jedna konstrukce DBD atomizátoru s lepenými elektrodami. Všechny testované atomizátory včetně srovnávacích jsou kompatibilní s atomovou absorpční spektrometrií (AAS) jako detektorem a jsou v nich za optimálních podmínek dosahovány shodné hodnoty citlivosti ( $0,44 \text{ s ng}^{-1} \text{ As}$ ) a detekčního limitu  $0,2 \text{ ng ml}^{-1} \text{ As}$ . Optimální podmínky atomizace se však mezi různými DBD konstrukcemi výrazně liší a závisí hlavně na způsobu uchycení elektrod. Konstrukce s lepenými elektrodami vyžaduje budicí napětí 14 kV pro dosažení maximální citlivosti pro arsen, zatímco pro konstrukci s naprašovanými elektrodami postačuje napětí 8,5 kV. Vybrané konstrukce DBD atomizátorů jsou kompatibilní s dalšími spektrometrickými detektory jako je atomová fluorescenční spektrometrie (AFS), kde je dosahováno detekčního limitu  $0,05 \text{ ng ml}^{-1} \text{ As}$  a atomová emisní spektrometrie (AES) s detekčním limitem  $30 \text{ ng ml}^{-1} \text{ As}$ . Tyto výsledky ukazují univerzálnost nových konstrukcí DBD atomizátorů.

## **Klíčová slova**

Atomová spektrometrie, plazmový atomizátor s dielektrickou bariérou, arsen, generování hydridů

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## **List of abbreviations**

AAS – atomic absorption spectrometry

AFS - atomic fluorescence spectrometry

AES – atomic emission spectrometry

DBD – dielectric barrier discharge

GLS – gas-liquid separator

HG – hydride generation or hydride generator

HV – high voltage

ICP - inductively coupled plasma

MS –mass spectrometry

i.d. – inner diameter

MMQTA – multiple microflame quartz tube atomizer

PVC – polyvinyl chloride

OES – optical emission spectrometry

QTA – quartz tube atomizer

## 1. Goals and objectives

- Test five new types of hydride atomizers based on a dielectric barrier discharge (DBD) plasma employing As as model analyte. Assess their compatibility with atomic spectrometric detectors including atomic absorption (AAS), atomic fluorescence (AFS) and atomic emission (AES) spectrometry.
- Optimize atomization conditions for arsenic hydride (arsane) in these five novel DBD designs with AAS detection. The experimental parameters to be optimized include high voltage settings and discharge gas (Ar) flow rate.
- Compare basic analytical figures of merit (sensitivity, detection limits) of all novel designs of DBD hydride atomizers to the externally heated quartz tube atomizer used conventionally and a reference DBD atomizer employing AAS as a detector.



## 2. Introduction

### 2.1 Arsenic

Arsenic is a semi-metal that forms covalent and ionic species. Typical oxidation states of As compounds are  $-III$ ,  $+III$  and  $+V$ . Allotropic forms of elemental As are grey, yellow and black, the first one being the most stable. As is used in microelectronics, semiconductor production, glass and ceramics fabrication, agriculture and forestry as insecticides, herbicides and wood preservatives. In the past As was also used in a medication for syphilis and is still used as antiparasitic agent in veterinary medicine. Sources of As in the environment are both natural and anthropogenic. Volcanic activity, leaching from ores and minerals are the most common natural sources. Anthropogenic sources are mining, smelting, coal combustion and agricultural activities. As in environment is very mobile as it is subjects to biotic and abiotic transformation processes like oxidation, reduction, adsorption, desorption, dissolution, precipitation and volatilization. These processes depend on pH and redox conditions.<sup>1</sup>

Different As species have different toxicity which directly depends on their mobility in water and body fluids. In general organic As compounds are less toxic than inorganic. Arsine is the most toxic compound, followed by inorganic arsenites and organic trivalent compounds. As has no essential function in human body. Chronic As poisoning is very common worldwide and can cause skin lesions, diabetes, hypertension and cancer.<sup>2</sup>

Monitoring As concentration in the environment, food and clinical samples at trace or ultratrace levels is very important. Speciation analysis, which is quantification of individual As species in the sample, is often more required rather than determination of total As content due to different toxicity, mobility and bioavailability of different species. Analytical methods used for routine total arsenic determination are usually spectrometric. High performance liquid chromatography (HPLC) is the most common and effective technique for As speciation analysis, usually combined with inductively coupled plasma mass spectrometry as a detector (HPLC-ICP-MS). Since speciation analysis of As is not further studied in this bachelor thesis approaches to speciation will not be discussed more in detail.

## **2.2. Atomic absorption spectrometry**

Spectrometric methods such as atomic absorption (AAS) or atomic fluorescence spectrometry (AFS), and inductively coupled plasma (ICP) either with optical emission (OES) or mass spectrometric (MS) detection belong to the most frequent and powerful detection techniques in the field of trace element and speciation analysis. Atomic absorption spectrometry (AAS) is widely used analytical technique employed for element determination (metal and metalloids) at trace and ultratrace levels.<sup>3</sup> It is based on the absorption of radiation by free analyte atoms in the ground state. An atomic absorption spectrometer consists of a radiation source, an atomizer associated with sample introduction system, a monochromator and a detector. The most typical radiation sources are hollow-cathode lamps or electrodeless discharge lamps. The radiation source always contains the element to be determined. Applying voltage and current to the radiation source the element of interest is sputtered to gaseous phase forming excited free atoms by collisions with inert gas inside the source. During de-excitation processes characteristic wavelengths are emitted that can be absorbed by free atoms of analyte in the atomizer.<sup>3</sup>

Atomizer converts the sample to free atoms mostly in ground state. Commonly used atomizers are flame (flame AAS – FAAS) and graphite tubes (electrothermal AAS – ETAAS).<sup>3</sup> Liquid sample is delivered to a flame realized most typically by a mixture of acetylene-air in FAAS. In ETA-AAS a small amount (10-50  $\mu\text{l}$ ) of the sample is dosed directly inside the graphite tube. Temperature programme is subsequently applied to a graphite tube consisting of drying and pyrolysis steps in which sample matrix is removed.<sup>3</sup> Atomization of analyte with signal reading is the last step followed by graphite tube cleaning. FAAS is the simplest approach with high sample throughput and low investment and operation costs. However, it reaches the highest detection limits due to analyte dilution in the flame. On the contrary, ETA-AAS is more expensive but reaching better detection limit in  $\text{ng ml}^{-1}$  range. The third technique in AAS is hydride generation (HG-AAS) discussed in detail in section 2.4.

## **2.3. Atomic emission spectrometry**

Atomic emission spectrometry (AES) is another atomic spectroscopy technique that has number of advantages against AAS, such as higher number of elements that can

be measured (75 elements vs. 62), no need for a radiation source (specific wavelength energy source). Moreover a number of elements can be measured simultaneously instead of one by one, as is the case with AAS. AES uses a typical spectral range of 165 to 750 nm.<sup>4</sup> The sample is atomized in a plasma, or flame where gaseous metal atoms are liberated and collisional excitation takes place. Excited metal atoms and ions then emit distinctive wavelengths of energy that are measured by a detector. Wavelength of emitted radiation is used for qualitative evaluation whereas its intensity serves for quantitative evaluation.

#### **2.4. Atomic fluorescence spectrometry**

Atomic fluorescence spectrometry (AFS) is based on excitation of free analyte atoms in ground state by high intensity monochromatic lamp.<sup>5</sup> Since the excited states of analyte atoms are unstable they drop back to original ground state. As a consequence, the excess of energy is emitted in the form of fluorescence radiation which is detected. Since atomic species do not have vibrational energy levels, the emitted photons are at the same wavelength as the incident radiation. This process of re-emitting the absorbed photon is termed as resonance fluorescence and is characteristic for atomic fluorescence.<sup>5</sup> The same radiation sources as in AAS can be employed in AFS, i.e. hollow cathode or electrodeless discharge lamps. Originally, also the same flame burners with acetylene-air as in AAS have been used as atomizers in AFS. However, they suffered from high levels of noise. Therefore, miniaturized diffusion flames (DF) employing a mixture of Ar with H<sub>2</sub> as fuel and ambient air as oxidant have been introduced. Later, advanced designs of DF, e.g. flame in gas shield (FIGS) atomizers have been introduced.<sup>6,7</sup> In FIGS, controlled flow rate of oxygen as oxidant is introduced into the mixture of Ar with H<sub>2</sub> as fuel whereas the flame is protected from ambient atmosphere by a laminar flow of Ar inert gas (Ar shield) to prevent ambient oxygen diffusion into the flame. DF and FIGS atomizers are limited only to volatile analytes being introduced into the flame in gaseous phase, liquid sample nebulization is not possible. As a consequence, AFS is exclusively combined with hydride generation (see section 2.5.) as a sample introduction technique.<sup>7</sup>

## **2.5. Hydride generation**

Hydride generation (HG) is a sample introduction technique. It is based on analyte reduction to a gaseous hydride.<sup>8</sup> This method can be used with elements such as As, Sb, Bi, Ge, Sn, Pb, Se and Te. HG using NaBH<sub>4</sub> as a reduction agent is the most common approach termed as chemical HG.<sup>8</sup> Alternatively, electrochemical or photochemical HG can be employed in which analyte reduction by electric current and UV radiation in presence of additives is used, respectively.<sup>9</sup> Chemical HG under optimum conditions reaches efficiency ~100% resulting in quantitative analyte introduction into the detector.<sup>8</sup> As a consequence, HG is capable to improve detection limit of given spectrometric detector by a factor of 20 compared to liquid sample nebulization considering the efficiency of conventional nebulizers to be around 5 %.<sup>9</sup> Other advantage of HG is analyte separation from liquid sample matrix which reduces the risk of interferences. HG is compatible with all spectrometric detectors such as AAS, AES, AFS as well as ICP with OES or MS detection.<sup>9</sup>

## **2.6. Quartz tube atomizer**

Quartz tube atomizer (QTA) is currently the most used hydride atomizer in AAS. The atomizer is T-shaped and has two sections: an inlet arm through which the gaseous phase is supplied, and an optical arm where the atomization occurs. The optical arm is heated by acetylene-air flame or more often by an electrical resistance oven to a range between 700-1100 °C.<sup>8</sup> Atomization of hydride is based on a radical mechanism. Close to the optical-inlet arm joint, oxygen reacting with hydrogen creates a cloud of hydrogen radicals which react with analyte hydride resulting in formation of free atoms. The position of the cloud varies, depending on different factors, such as temperature, design of the atomizer, composition and flow rate of carrier gas.<sup>6-9</sup> The advantages of QTA are low price, high sensitivity and low background noise. Disadvantages are low linear dynamic range and low resistance to interferences. Quality and condition of inner surface of the atomizer can impair the sensitivity and the shape of signal. The inner surface of the atomizer can be cleaned with a 7:3 solution of nitric acid and hydrofluoric acid for 10 minutes. Advanced designs of QTA exist, in which the production of hydrogen radicals is controlled by introduction of small amounts of oxygen/air into the

atomizer. These designs include flame in tube atomizers or multiple microflame quartz tube atomizers (MMQTA), the latter one being discussed more in detail in section 3.4.

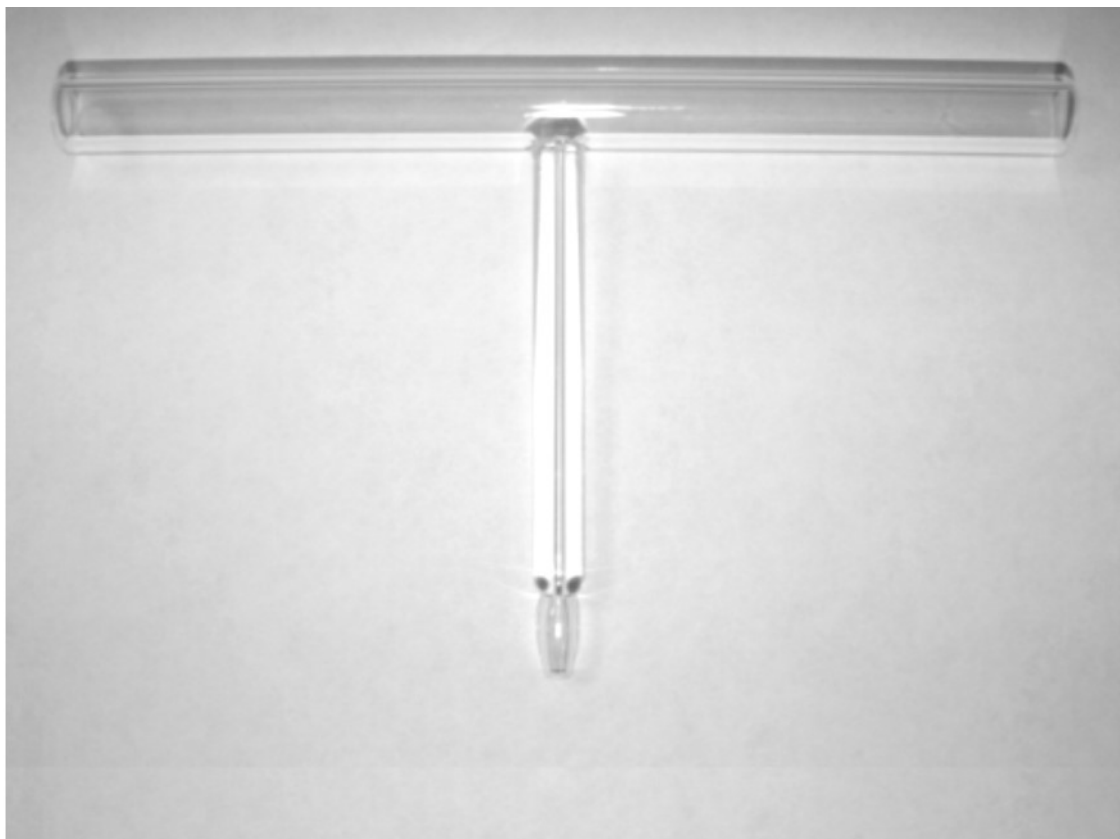


Figure 2.1. Photograph of a quartz tube atomizer (QTA).

### **2.7. Dielectric barrier discharge atomizer**

Dielectric barrier discharge (DBD) devices are low temperature plasma sources operating at atmospheric pressure.<sup>10</sup> The DBD configuration is characterized by the presence of at least one dielectric barrier providing a small gap between two powered electrodes. Apart from analytical spectroscopy, DBD is also a useful tool for industrial applications such as surface treatment, plasma coating, thin-film deposition, etc.<sup>11</sup>

High voltage is put on both electrodes which creates a discharge inside the optical arm. The charge on the dielectric creates a local electric field which effects against electric field on electrodes and stops further continuation of the discharge. For the further continuation of the discharge it is needed either to increase the voltage or to change its polarity, which is why an alternating current is used.<sup>10</sup> The discharge creates

electrons with high energy that collide with ambient gas molecules and atomize, excite or ionize them. In analytical chemistry and in connection with hydride generation the energy of DBD plasma can be used for formation of hydride (DBD plasma assisted HG) or DBD can be employed for hydride atomization with AAS or AFS detection. If hydride atomization is followed by free atoms excitation by DBD plasma also AES can be used as a detector. All the applications of DBD in HG are in detail described elsewhere.<sup>12,13</sup>

A DBD atomizer design with planar configuration of electrodes is used in AAS with the optical axis of the spectrometer being parallel with the electrodes. Thus, absorption of radiation by free analyte atoms is measured through the whole volume of the DBD plasma. On the contrary, a cylindrical (tubular) design of DBD atomizer is typical for AFS detection employing concentric arrangement of the electrodes.<sup>12</sup> Whereas all the main system components, i.e. radiation source-atomizer-detector, lie on a straight line in AAS (180° geometry), a 90° geometry is dictated by AFS principle. Since metal non-transparent electrodes are used in DBDs, the only way to record the signal in AFS is above the cylindrical DBD atomizer. However, this region accessible for signal detection lies completely outside the plasma area, where analyte atomization takes place. As a consequence, fast decay of free analyte atoms occurs in that region resulting in impaired sensitivity and necessity of shield gas unit usage to decrease the decay. The above mentioned limitations of the cylindrical DBD atomizer in AFS might be solved by planar design of the device, in which analyte fluorescence would be detected directly in the plasma region. The only challenge of the planar design is the fact that, in accord with the 90 ° geometry required in AFS, one of the electrodes has to be transparent for the fluorescence radiation measured.

Quality and condition of inner surface of the DBD atomizer can lower the sensitivity and the shape of signal. The inner surface of the atomizer can be cleaned with a 7:3 solution of nitric and hydrofluoric acid. The advantages of DBD are low instrumentation and maintenance cost, simplicity, capability to work with various gases and the ability to create and sustain the discharge at atmospheric pressure.

Five different designs of DBD atomizers were used and optimized in total in this thesis in order to assess their compatibility with AAS, AFS and AES detectors and feasibility for routine applications employing arsane as model analyte. The DBD

designs tested are based on a planar construction of the devices. Semi-transparent electrodes allow measurements of analyte emission or fluorescence in the plasma.

### 3. Experimental section

#### 3.1. Reagents

All reagents were of analytical reagent grade or higher purity. Deionized water ( $< 0.1 \mu\text{S cm}^{-1}$ , Ultrapure, Watrex, USA) was used to prepare solutions. Working As standards were prepared fresh daily from  $10 \text{ mg l}^{-1}$  As stock solution (prepared from  $\text{As}_2\text{O}_3$ , Lach-Ner, Czech Republic) by dilution in  $1 \text{ mol l}^{-1}$  HCl (Merck, Germany). A blank consisted of  $1 \text{ mol l}^{-1}$  HCl. The reductant was a 0.5% (m/v) solution of  $\text{NaBH}_4$  (Sigma Aldrich, Germany) in 0.4% (m/v) KOH (Lach-Ner, Czech Republic) filtered after preparation and stored frozen. The NaOH beads (NaOH, purum, beads diameter  $\geq 3$  mm, Lach-Ner, Czech Republic) were used as a filling of a dryer cartridge for water vapor and aerosol removal. Nitric acid (65%, p.a., Lach-Ner, Czech Republic) was used to clean the DBD atomizers if necessary. Compressed Ar (4.6) was produced by SIAD Czech, Ltd.

#### 3.2. Instrumentation

**Atomic absorption spectrometry.** A GBC model SavantAA atomic absorption spectrometer (GBC, Australia) was employed without background correction. A Photron As boosted hollow cathode lamp (superlamp) operated at 193.7 nm line with 2.0 nm spectral bandpass and a lamp current of 20 mA (boost current 7-15 mA).

**Atomic fluorescence spectrometry.** The in-house assembled research grade nondispersive AFS was employed, equipped with an As electrodeless discharge lamp (EDL system II, PerkinElmer, USA). The operating current for the lamp was 340 mA and the feeding power was square-wave modulated (40 Hz). An interference filter (193 nm, full width at half-maximum 18.7 nm, CVI Melles Griot, USA) was employed to isolate fluorescence radiation from the DBD atomizer, and a solar blind photomultiplier (165–320 nm, PerkinElmer Optoelectronics, USA) as the detector.

**Atomic emission spectrometry.** A miniature fiber optics UV-VIS spectrometer, model BLACK-Comet C (StellarNet Inc., USA) equipped with a concave grating



covering a range of 183-850 nm and armored solarization resistant 1000  $\mu\text{m}$  fibre optic cable (F1000-UVVIS-SR-1) was employed to acquire emission spectra.

### 3.3. Hydride generator and procedure

Hydride generator, depicted in Fig. 3.1. consisted of a multichannel peristaltic pump (Ismatec, Switzerland) with tubes made out of Tygon with i.d. of 0.51 mm for reduction agent, 1.02 mm for blank or standard solution and 1.85 mm for waste disposal. A three-way valve served to switch between standard and blank intake. Other tubings for gases and liquids were made out of teflon with i.d. of 1.0 mm connected with T-shaped connector made out of PEEK (polyether ether keton). A gas-liquid separator (GLS) with forced outlet had inner volume of about 3 ml and its function was to separate gaseous and liquid phase. Carrier gas (argon) was added at a flow rate of 50  $\text{ml min}^{-1}$  Ar upstream the GLS to support  $\text{AsH}_3$  separation and its transport to the atomizer. The dryer realized by a polypropylene cartridge 100 mm long with 15 mm inner diameter filled with NaOH beads (beads diameter  $\geq 3$  mm) was inserted downstream GLS to prevent aerosol from entering the atomizers. Optimum conditions for  $\text{AsH}_3$  generation were taken from previous studies<sup>14,15</sup> and are summarized in Table 3.1.

Measurements were performed in the on-line atomization mode with direct transfer of arsane generated from the GLS through the NaOH dryer into the respective atomizer. Sample introduction time of 30 s was employed followed by introduction of blank to flush the GLS resulting in transient signals with a peak width of ca 30 s. This was used for AAS and AFS measurements. Steady state signals were measured with AES detection. Therefore, sample introduction time was extended to 60 s with AES measurements performed between 30 s and 45 s after the standard introduction begun. Standard solution of 10  $\mu\text{g l}^{-1}$  As prepared in 1  $\text{mol l}^{-1}$  HCl was used if not stated otherwise. Switching between standard and blank was performed using a manual three-way valve. Argon at a flow rate of 50  $\text{ml min}^{-1}$ , if not stated otherwise, was employed as a carrier gas serving subsequently also as a discharge gas to sustain the DBD plasma. The flow rate of hydrogen evolved from decomposition of  $\text{NaBH}_4$  was experimentally found to be approximately 15  $\text{ml min}^{-1}$ . Experimental conditions are summarized in Table 3.1.

Table 3.1. Optimal hydride generation conditions.

HCl concentration (mol l <sup>-1</sup> )	blank/sample flow rate (ml min <sup>-1</sup> )	NaBH <sub>4</sub> /KOH concentration	reductant flow rate (ml min <sup>-1</sup> )
1.0	3.5	0.5%/0.4%	1.2

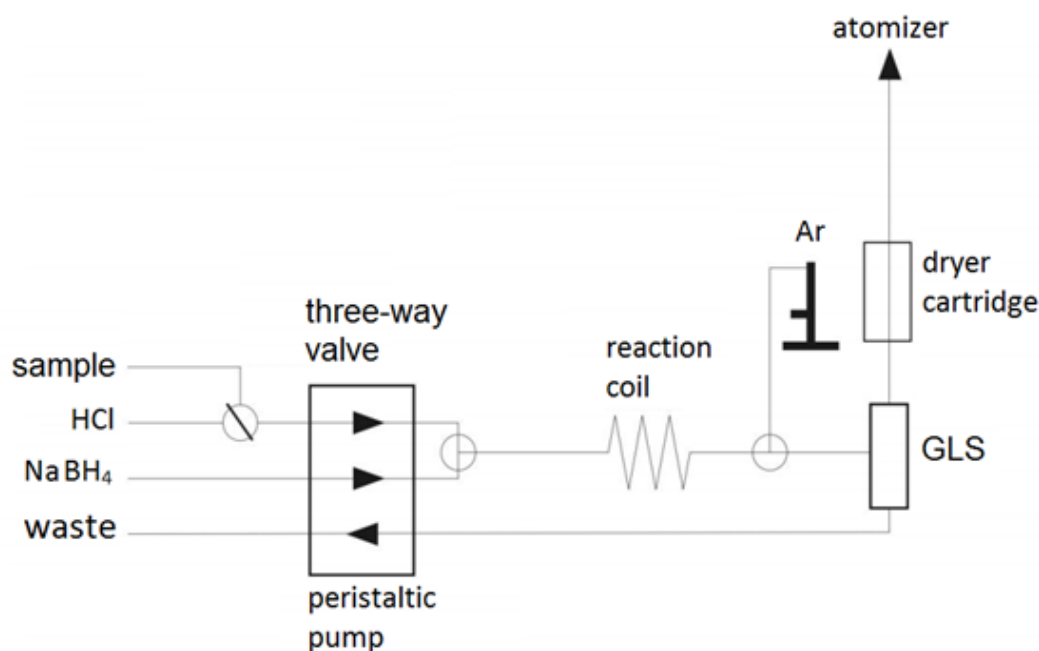


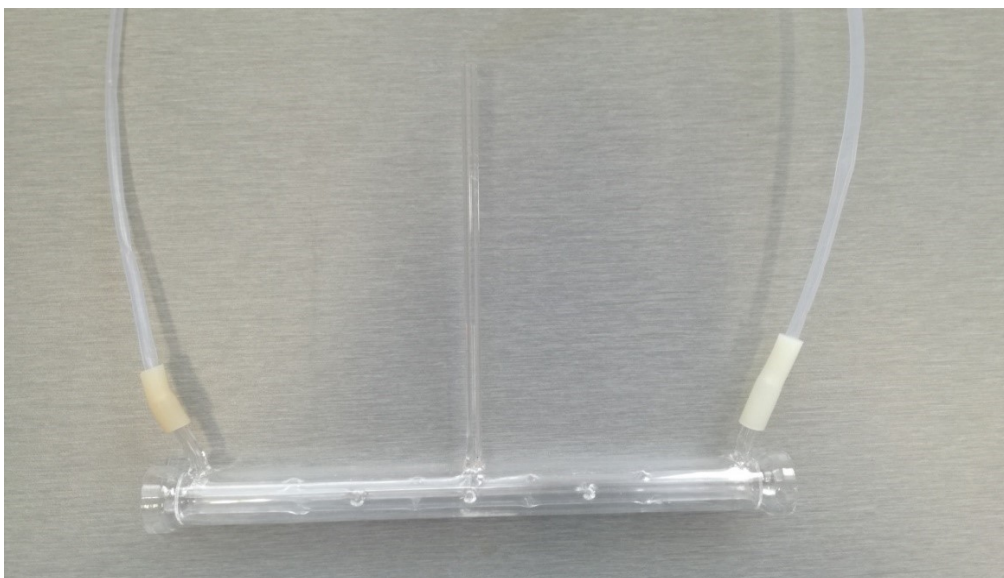
Figure 3.1. Scheme of the hydride generator with GLS and dryer cartridge.

#### 3.4. Multiple microflame quartz tube atomizer

A multiple microflame quartz tube atomizer (MMQTA) is advanced design of QTA. It has a T-shaped with a double walled optical arm, consisting of two concentric tubes. The inside one having holes to allow controlled oxygen/air supply. The air is introduced to the cavity between the two tubes from both ends of optical arm (see Fig.3.2.). The inner tube of the optical arm is 150 mm long with 6mm i.d. perforated by 14 holes, and is heated by an electrical resistance oven (AEHT-01 model produced by RMI, Czech Republic) to around 900 °C. The inlet arm is 100 mm long with 2mm i.d. and served for introduction of gases from GLS to the atomizer. The main difference from QTA is that there is not a single cloud of hydrogen radicals in the middle of the optical arm as

in the QTA (see section 2.6), but there are clouds of H radicals at each hole in the inner tube, where oxygen meets with hydrogen. As a consequence, the optical tube is filled more homogeneously with H radicals resulting in longer existence of free atoms or their reatomization.<sup>8,9</sup>

A)



B)

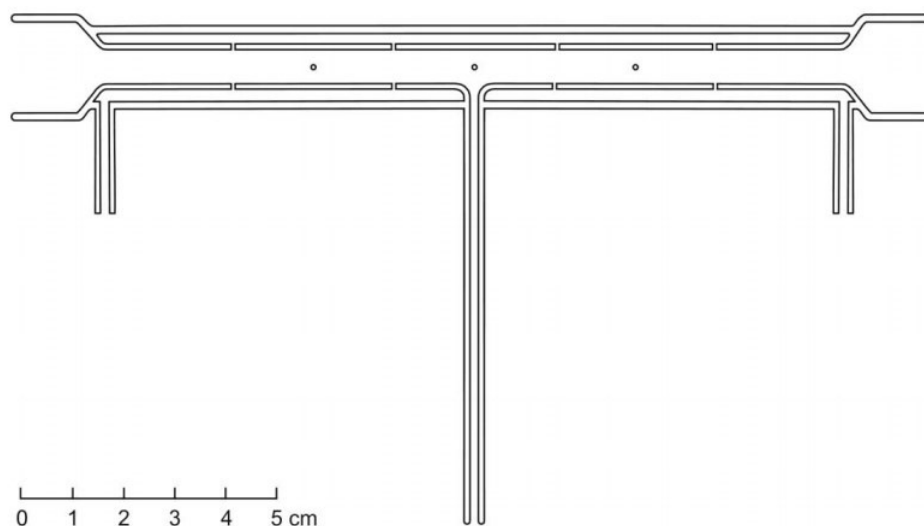


Figure 3.2. Photograph (A) and a scheme (B) of the multiple microflame quartz tube atomizer (MMQTA). The scheme is taken from reference<sup>14</sup>.

### 3.5. Reference dielectric barrier discharge atomizer

The reference dielectric barrier discharge atomizer (REF) was made by Lifetech company in Brno. Its T-shaped body is custom made (Brno University of Technology, Faculty of Chemistry) out of quartz with inner dimensions of the planar optical arm 7 mm x 3 mm and length of 75 mm, and inlet arm 20 mm long, 2 mm inner diameter and 4 mm outer diameter. Two compact electrodes made out of copper (50 mm long, 5 mm wide, 0.15 mm thick) are glued to the outer surface of the optical arm and covered from outside with a layer of epoxy resin to prevent contact with air and discharge formation outside of the chamber (parasitic discharge). The whole atomizer is placed in a high density polyvinyl chloride (PVC) frame with a computer fan at the bottom to cool the atomizer. The REF atomizer is depicted in Fig. 3.3. The reference DBD as well as all the DBD designs tested were coupled to the same power supply source consisting of a sinusoidal waveform frequency generator (excitation frequency 28.5 kHz) and a high voltage transformer both fabricated by Lifetech (Brno, Czech Republic) and described previously.<sup>15,16</sup>

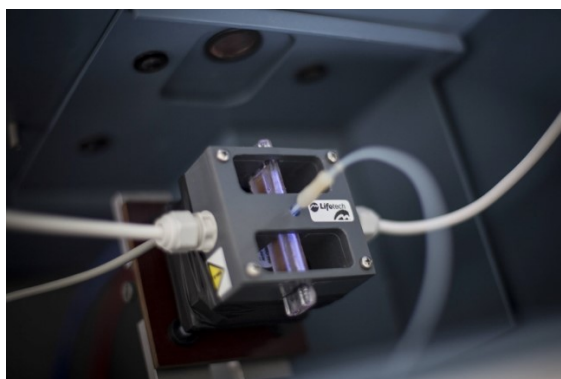


Figure 3.3. Photograph of a reference design (REF) of the DBD atomizer.

### 3.6. New designs of DBD atomizers

The new designs of DBD atomizers investigated in this thesis, all have the same quartz planar T-shaped body with the same dimensions as the REF atomizer had. However, the main difference is in the electrodes, which are not glued to the outer surface of DBD body, as is the case with REF atomizer, but sputtered on the center of the outer surface of the atomizer. The electrodes consist of 20 nm bottom layer of Cr

and 200 nm outer layer of Cu. The Cr layer is there to enable sputtering of a firm and permanent layer of Cu. The atomizers are not placed in a PVC supporting frame as REF atomizer and thus do not have a computer fan for cooling. The electrodes were sputtered at Leibniz Institut für Analytische Wissenschaften (ISAS) in Dortmund, Germany.

The compact-compact (CC) atomizer, depicted in Figure 3.4.A, has two rectangle shaped sputtered electrodes (5 x 50 mm). The next type of atomizer has also two rectangular shaped electrodes but they are shorter (5 x 20 mm) than the electrodes of CC atomizer. Therefore, it was named compact-compact-short (CCS) atomizer (see Fig. 3.4.B). Another design is compact-grid (CG) atomizer (not shown in Fig. 3.4.). It has one rectangle and one grid shaped electrode, both sputtered over an area of 5 x 50 mm. Grid-grid (GG) atomizer has two grid shaped electrodes, as depicted in Fig. 3.4.C. Grid-grid-wide (GGW) atomizer is a follow-up design with two grid shaped electrodes that have wider gaps than GG atomizer (see Fig. 3.4.D for illustration).

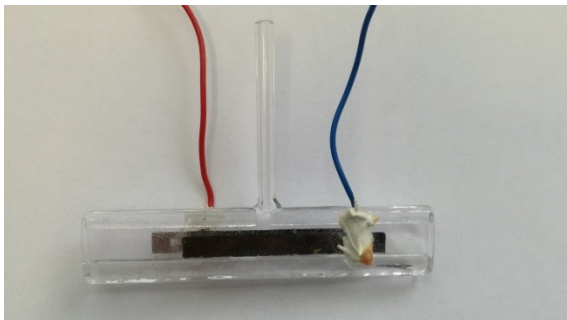
All the atomizers employed and compared in this thesis are briefly summarized in Table 3.2. for better clarity.

Table 3.2. List of all used atomizers, their names and abbreviations

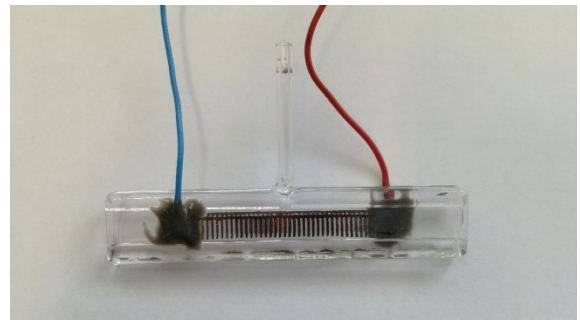
Acronym	Name	Electrodes	Electrodes shape	One electrode area (mm <sup>2</sup> )
MMQTA	Multiple microflame quartz tube atomizer	-	-	-
REF	Reference (Lifetech)	0.15 mm Cu metal strips, glue attached	rectangular, 5 x 50 mm	250
CC	Compact-Compact	sputtered electrodes	rectangular, 5 x 50 mm	250
CCS	Compact-Short	bottom layer	rectangular, 5 x 20 mm	100
CG	Compact-Grid	20 nm Cr	rectangular, 5 x 50 mm	250 <sup>C</sup> /125 <sup>G</sup>
GG	Grid-Grid	upper layer 200 nm Cu	grid, 5 x 50 mm	135
GGW	Grid-Grid-Wide		wide grid, 5 x 50 mm	104

C – compact electrode, G – grid electrode

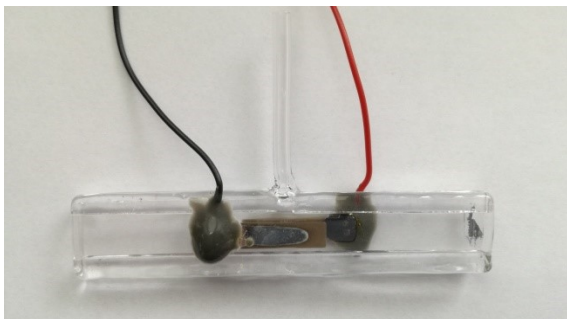
A)



C)



B)



D)

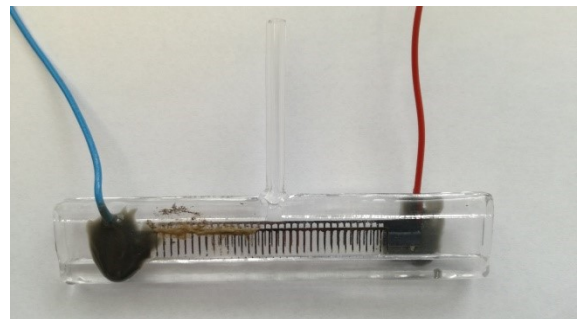


Figure 3.4. Photographs of various designs of new types of DBD atomizers: a compact-compact (A), compact-compact-short (B), grid-grid (C) and grid-grid-wide (D) design.

## 4. Results and discussion

### 4.1. MMQTA with AAS detection

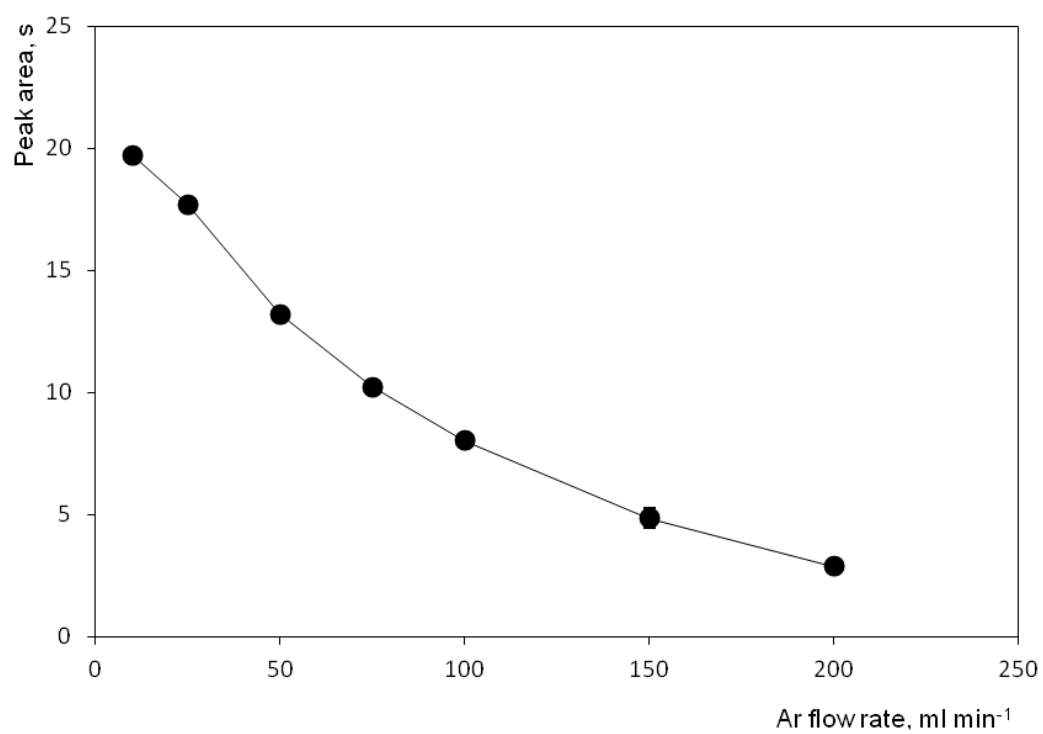
QTA design is the most common type of hydride atomizers as discussed in section 1.5. Multiatomizer (MMQTA) is an advanced design of QTA allowing to reach better sensitivity and resistance to interferences as shown in section 3.4. Ar flow rate, air flow rate and atomization temperature were all optimized for MMQTA atomizer since optimization of these parameters, especially outer air flow rate, is recommended for each individual piece because MMQTA designs are constructed manually by the glass blow maker. As a consequence, the diameter and distribution of diameters of the manually made holes in the inner tube of optical arm of MMQTA can differ significantly from piece to piece. As a result, each piece of MMQTA can have different optimum flow rate of outer air to reach the most efficient atomization of analyte.

Optimization of Ar flow rate depicted in Fig. 4.1.A shows steady decline of As signal with decreasing Ar flow rate. This is due to dilution of free arsenic atoms in the optical path with higher volume of Ar introduced. The optimal Ar flow rate was set to  $50 \text{ ml min}^{-1}$ . Although As signal was not the highest, it showed the best repeatability.

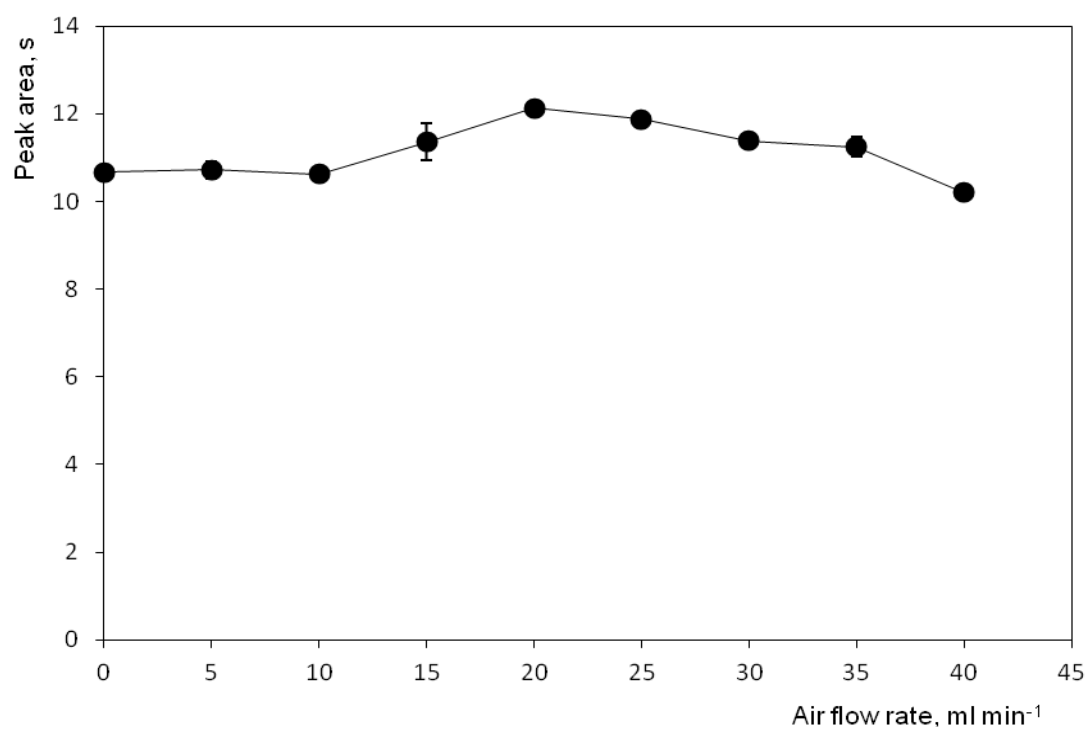
The effect of outer air on As signal is shown in Fig. 4.1.B. Air flow rates between 0 and  $40 \text{ ml min}^{-1}$  were tested with the optimum found at  $20 \text{ ml min}^{-1}$  where the highest As signal and the best repeatability were reached. Outer air at optimum flow rate improves As signal by 12% compared to no air supply.

Optimization of atomization temperature is shown in Fig. 4.1.C. Temperature settings between  $800 \text{ }^\circ\text{C}$  and  $1000 \text{ }^\circ\text{C}$  were investigated. The highest signal was observed at  $1000 \text{ }^\circ\text{C}$  with the signal at  $900 \text{ }^\circ\text{C}$  and  $800 \text{ }^\circ\text{C}$  to be lower by 3 % and 13 %, respectively. Optimum atomization temperature of  $900 \text{ }^\circ\text{C}$  was chosen despite reaching slightly lower As signal than with  $1000 \text{ }^\circ\text{C}$  but having better repeatability of the results.

A)



B)





C)

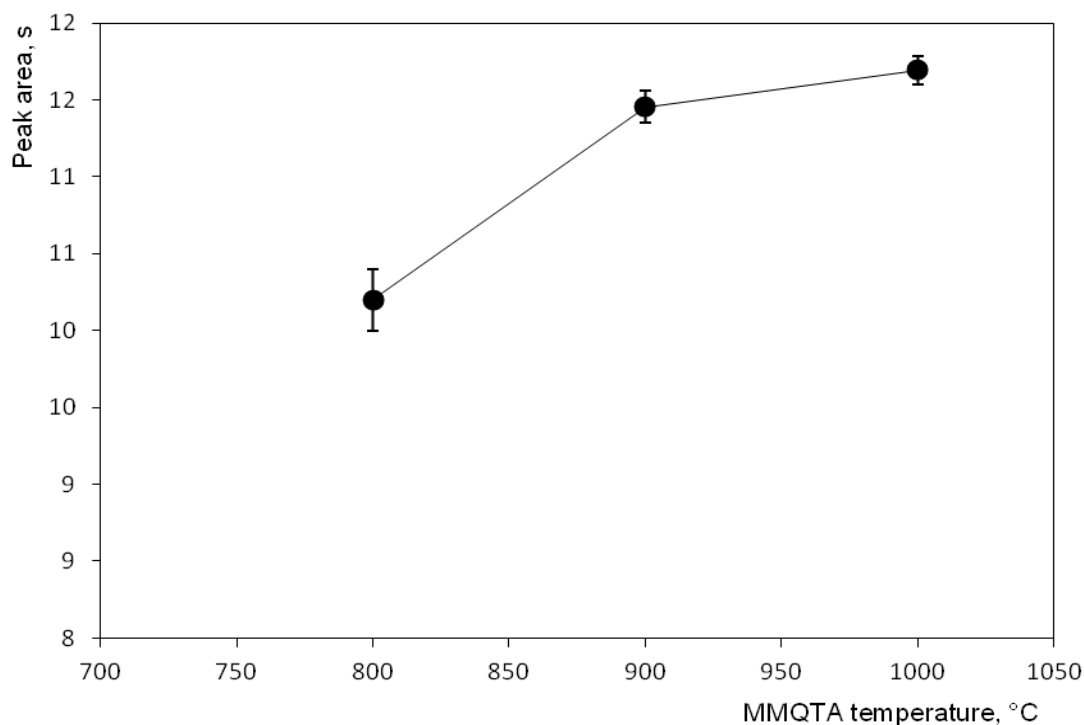


Figure 4.1. Effect of Ar flow rate (A), outer air flow rate (B) and the atomization temperature (C) on As signal intensity with AAS detection. Standard concentration  $10 \mu\text{g l}^{-1}$  As. If not being a parameter to be optimized, atomization temperature was kept at  $900^\circ\text{C}$ , Ar flow rate at  $50 \text{ ml min}^{-1}$  and outer air flow rate at  $20 \text{ ml min}^{-1}$ .

The dryer realized by a column packed with NaOH inserted downstream the GLS was used in all measurements as described in detail in section 3.3. The dryer prevents small liquid droplets, which have not been separated in the GLS, from getting into the atomizer. As can be seen from Table 4.1., the presence of the dryer has a significant effect on As signal intensity and repeatability of the results with the DBD type atomizer. The DBD design termed as REF was used but the behavior is valid for all designs tested in this work. In MMQTA atomizer the presence of dryer had almost no effect (Table 4.1.) on As signal. This observation is logical and has been reported previously by Novák et al.<sup>14,15</sup> The DBD atomizer operates at a temperature slightly higher than ambient and each droplet of liquid can cause plasma instabilities resulting in impaired atomizer performance. On the contrary, MMQTA heated to  $900^\circ\text{C}$  is very robust and can easily cope with small amount of droplets entering randomly its optical

arm. The droplets are evaporated without any effect on As signal. For the sake of simplicity and to easily compare the results the dryer was used in all further measurements.

Table 4.1. Comparison of the results with and without NaOH dryer. MMQTA and DBD design of REF atomizer tested. Standard concentration  $10 \mu\text{g l}^{-1}$  As,  $50 \text{ ml min}^{-1}$  Ar,  $900^\circ\text{C}$  atomization temperature in MMQTA,  $20 \text{ ml min}^{-1}$  outer air;  $9.0 \text{ kV}$  high voltage supply rate for DBD atomizer.

Atomizer design	MMQTA		REF	
	With dryer	Without dryer	With dryer	Without dryer
average peak area (s)	11.0	10.8	10.2	5.0
standard deviation (s)	0.2	0.1	0.2	1.4

Prereduction by addition of KI and ascorbic acid to reach their final concentration in the standard of 8% and 0.5%, respectively, was investigated as recommended in the literature<sup>8</sup>. The standard ( $10 \mu\text{g l}^{-1}$  As) was left for 30 minutes to react to be subsequently measured by HG-AAS with atomization in MMQTA. Signals of standard after prereduction and without treatment were compared. Using prereduction by KI/ascorbic acid, the average peak area was increased by 20 %. Standard deviation remained virtually the same. Due to increased labor needed for sample preparation and no practical significance of the increased signal in our measurements, prereduction was not further employed.

Under optimized generation and atomization conditions sensitivity of  $0.53 \text{ s ng}^{-1}$  As and a detection limit of  $0.15 \mu\text{g l}^{-1}$  As can be reached in MMQTA.

#### 4.2. Optimization of DBD designs with AAS detection

Ar flow rate and high voltage (HV) supply rate were optimized for all designs of DBD atomizers described in sections 3.5 and 3.6. The same power supply source was employed for all the DBD atomizers based on a sinusoidal waveform generator described in detail in section 3.5. The effects of different ways of electrode attachment

(glued versus sputtered electrodes) and different electrode shapes on As signal were studied. Subsequently sensitivity of different designs under optimal conditions was compared.

When optimizing HV supply rate a steep increase of As signal was always seen when increasing HV from minimum voltage requested for discharge ignition to higher values. After the steep increase of the signal, a broad plateau was reached that slightly decreased later with higher applied voltage. This phenomenon was seen with all DBD designs. The results are summarized in Fig. 4.2.A.

The REF and CC designs were suitable for studying the effect of a different method of electrode attachment since the electrodes of REF design atomizer were glued while the electrodes of CC design were sputtered on the outer surface of the atomizer body. Both designs differ significantly in minimum HV value requested to reach optimum signal. This reaches 14 kV for REF design while HV of only 8.5 kV is sufficient for CC design. The CC design reached temperatures of about 30 °C after few hours of testing. On the contrary the temperature of REF design reaches about 50 °C even with the small computer fan attached. This higher amount of heat in REF design is produced by parasitic discharges between atomizer body and electrode. The results show the advantage of sputtered electrodes, with lower voltage requirement and less heat produced, which eliminates the need for active cooling, as is the case of REF design.

Ar flow rate was optimized individually for each DBD design under optimum HV supply. The results are depicted in Fig. 4.2.B. The higher the Ar flow rate was, the lower the signal intensity was. This was due to the free atoms dilution in the carrier gas. With Ar flow rate of 25 ml min<sup>-1</sup> the discharge was unstable with very low repeatability of As signal. The optimal Ar flow rate was at 50 ml min<sup>-1</sup> for all DBD designs tested, with the best peak area, peak shape and repeatability.

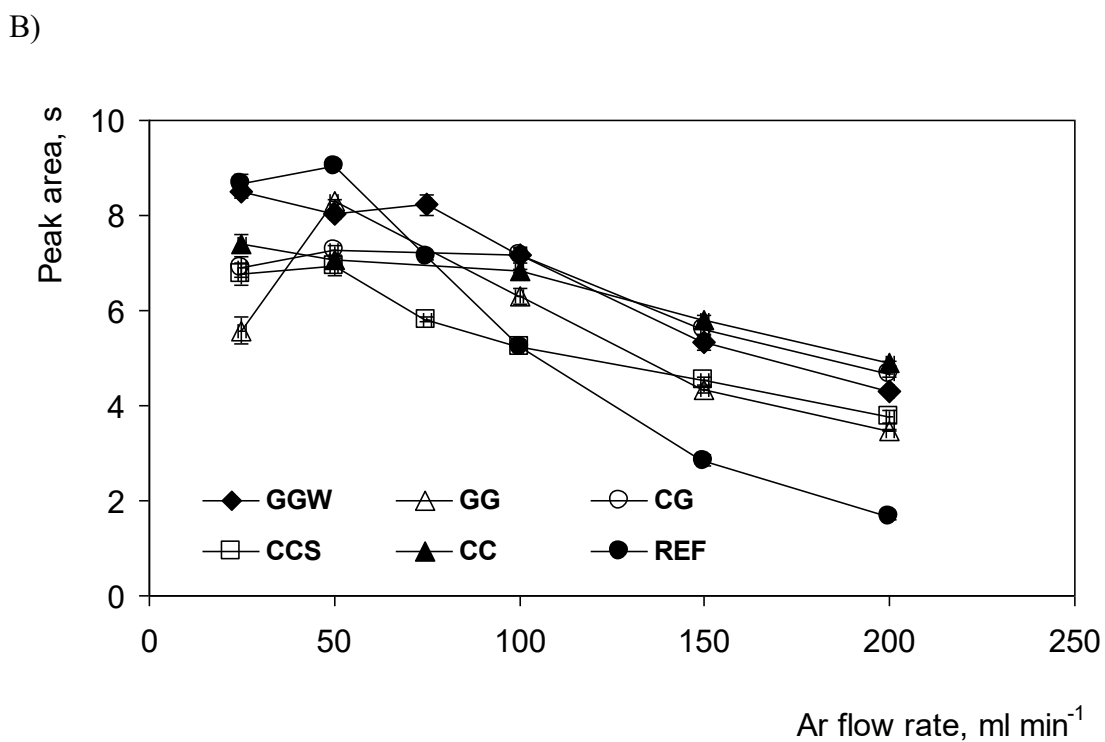
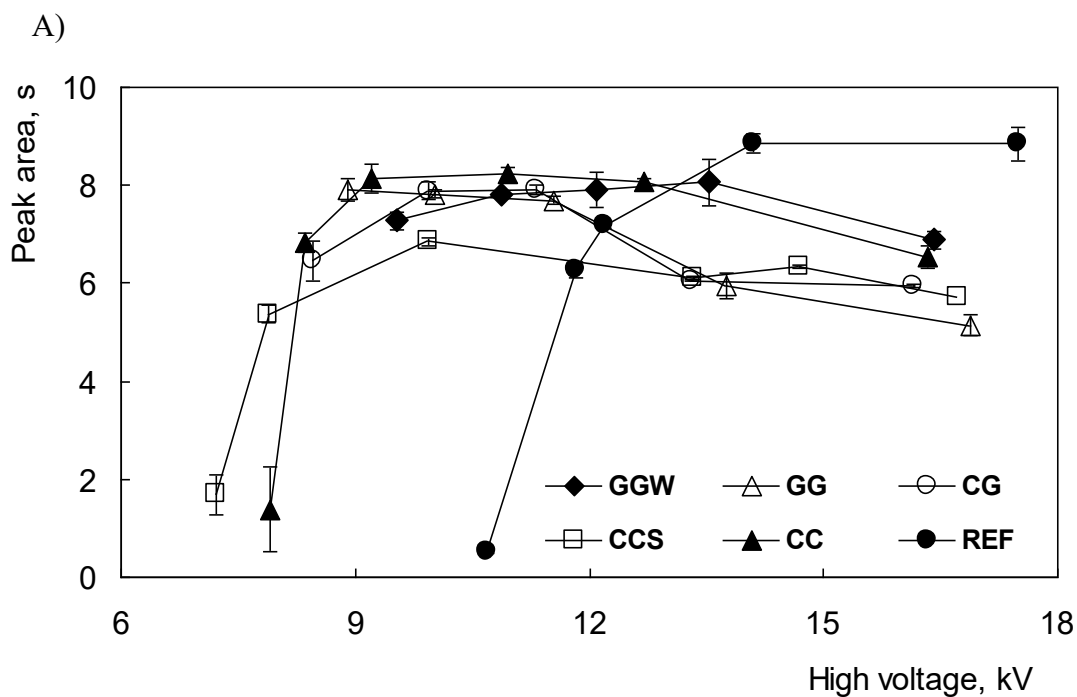


Figure 4.2. Effect of applied high voltage (A) and Ar flow rate (B) on the As signal intensity with various atomizer designs. Applied high voltage was optimized at 50 ml min<sup>-1</sup> Ar flow rate with all the atomizer designs. Ar flow rate was optimized at 11.5 kV (CG, GGW), 10.0 kV (GG), 9.0 (CC, CCS), 17.5 kV (REF). Standard concentration 10 μg l<sup>-1</sup> As.

In conclusion, the way of electrode attachment has the biggest impact on HV requirements. Designs with sputtered electrodes had lower HV requirements than design with the electrodes glued to the body. Electrode shape and surface area had an insignificant effect on the HV requirement. The same sensitivity was achieved with all DBD designs under optimum HV supply rates. This fact indicates that atomization efficiency is the same in all atomizers regardless of their design. The sensitivity reached in DBD atomizers is comparable also to that obtained in MMQTA, the most common hydride atomizer. The sensitivity reached for individual atomizers for As determination is summarized in Table 4.2. Typical limits of detection reached for As in various DBD atomizer designs tested were around  $0.20 \mu\text{g l}^{-1} \text{ As}$ .

Table 4.2. Average sensitivity for As determination for all types of atomizers used under optimum atomization conditions. Standard deviation of sensitivity  $0.02 \text{ s ng}^{-1} \text{ As}$  or better.

	<b>MMQTA</b>	<b>REF</b>	<b>CC</b>	<b>CG</b>	<b>GG</b>	<b>GGW</b>	<b>CCS</b>
Sensitivity (s ng <sup>-1</sup> As)	0.53	0.44	0.44	0.38	0.40	0.40	0.38

### 4.3. AFS detection

The feasibility of AFS detection coupled with DBD plasma atomizers was firstly tested with GG design of DBD atomizer. The beam of the As EDL lamp was pointed into the longitudinal axis of discharge channel. The fluorescence radiation was detected from the side of the atomizer through the center of the grid electrode. Even with the use of interference filter the intensity of radiation emitted by the plasma was too high which heavily increased the baseline signal. As a consequence, the photomultiplier voltage had to be highly reduced and resulted in decreased amplification. This made the detection of low concentration of As impossible.

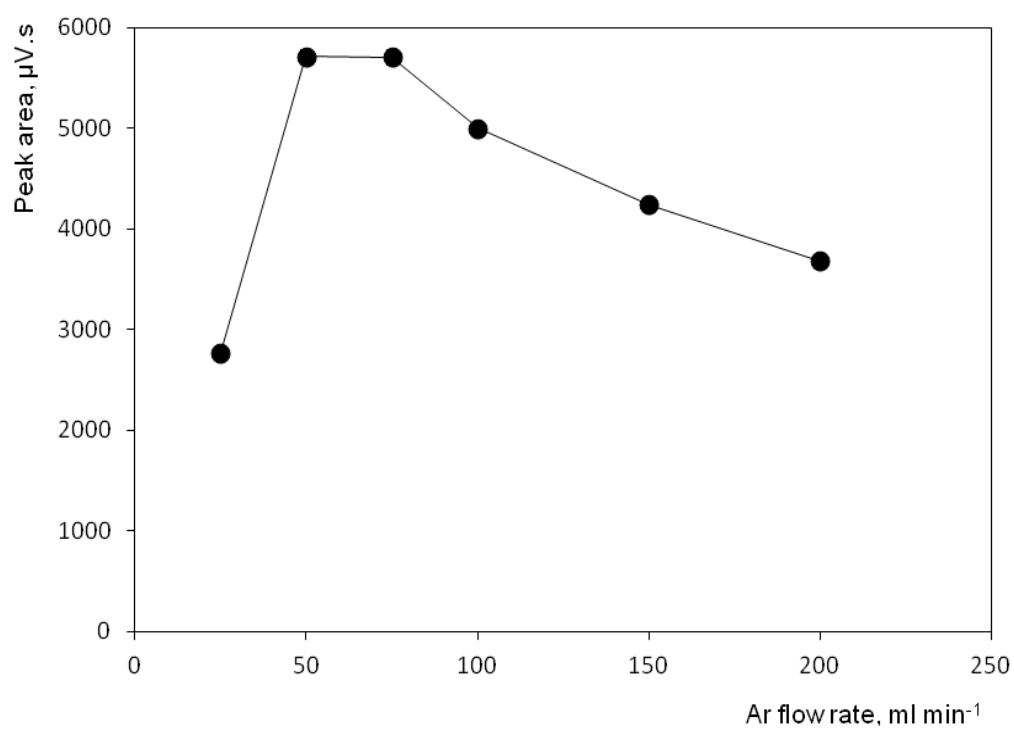
Therefore, a CCS design was used in further experiments with the same position of the EDL lamp and atomizer. The fluorescence radiation was detected through the quartz wall outside the electrode, about 5 mm downstream from the edge of the electrode or about 15 mm from the middle of discharge channel, which was outside of the plasma region. The distant end of atomizer was sealed off with Teflon-tape and parafilm to

prevent unequal sample distribution as the point of detection was only on one end of the optical arm.

The effect of HV supply rate on AFS signal was studied. The signal increased steeply between 7 and 9 kV to reach a plateau and change negligibly between 9 and 14.5 kV. This is analogous to the results achieved with AAS detection. Thus, 14 kV was chosen as optimal. When optimizing Ar flow rate the highest signal was achieved between 50 and 75 ml min<sup>-1</sup> Ar (see Fig. 4.3.A). A slight decrease of signal was observed with higher Ar flow rate due to dilution of analyte. Ar flow rate of 75 ml min<sup>-1</sup> was chosen as optimal and was used in further measurements.

Linear calibration curve was measured with As standard concentrations levels between 0.3 to 10 µg l<sup>-1</sup> As (see Fig. 4.3.B) under optimum conditions (14 kV, 75 ml min<sup>-1</sup> Ar flow rate). A detection limit of 0.05 µg l<sup>-1</sup> As was reached, which is 4 times lower than with AAS (compare with section 4.2). The detection limit could be further improved by modifications of either the optical path of AFS spectrometer or electronic data processing part, which are beyond the scope of this thesis. Nevertheless, the concept of coupling of planar DBD atomizer to AFS detector has been proven.

A)



B)

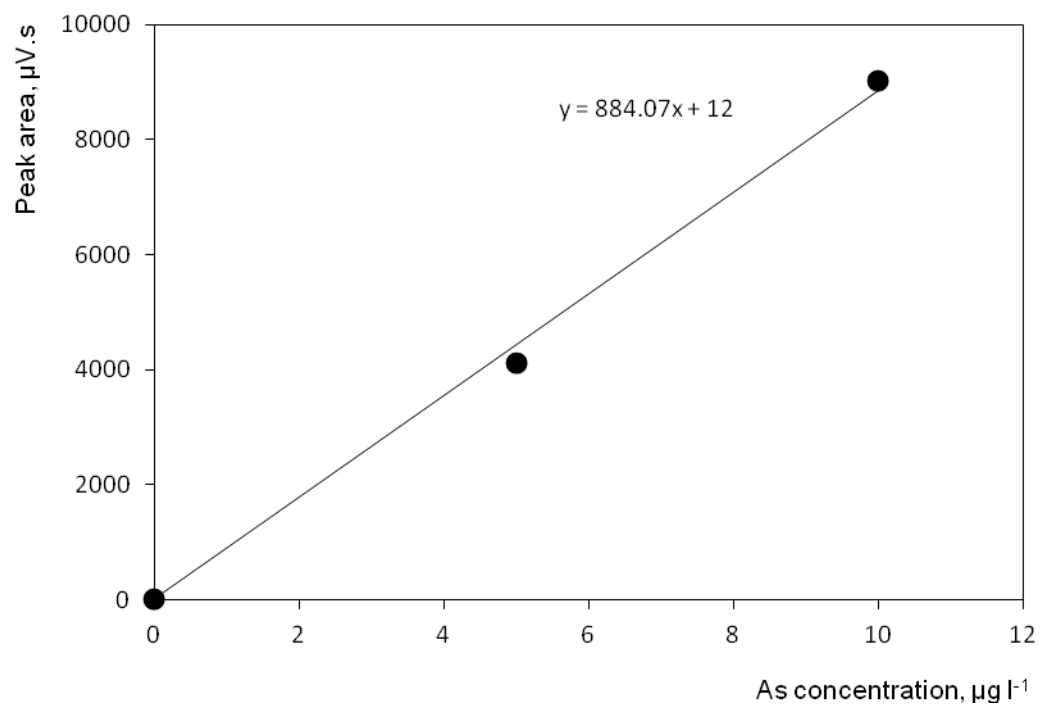


Figure 4.3. Effect of Ar flow rate on the signal intensity in AFS (A). Calibration curve for As measured with AFS detection (B). Ar flow rate  $75\text{ ml}\cdot\text{min}^{-1}$ , HV 14 kV.

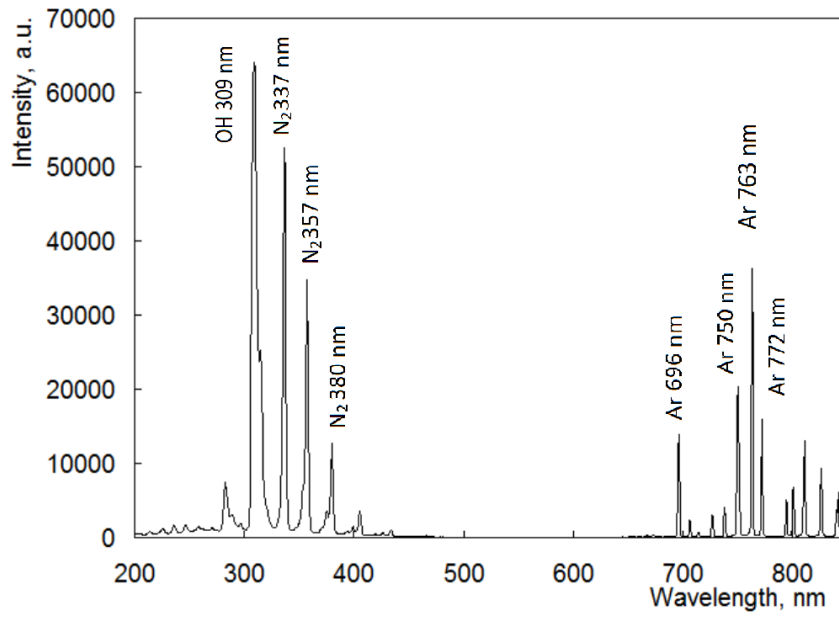
#### 4.4. AES detection

For emission spectra measurements a GG atomizer design was used, for its ability to enable measurements not only “end on” through the optical arm but also from the side of the atomizer through the grid electrode. At first, the effect of hydride generator (HG) on emission spectra was measured. The detection integration time was set to 30 ms with 10 spectra to be averaged. 10 kV HV supply rate was chosen and Ar flow rate was kept at 50 ml min<sup>-1</sup>. With HG turned on, approximately 15 ml min<sup>-1</sup> of H<sub>2</sub> is also supplied to the atomizer. With the HG turned off, a strong emission of Ar lines in the spectrum between 690-850 nm was detected (see Fig. 4.4.A). Also nitrogen impurities with spectral lines at 337.1, 350.7 and 380.5 nm were detected. Despite using the NaOH dryer, emission lines of OH bands at 309 nm were detected being the most intensive (see Fig. 4.4.A). The same pattern of spectra was achieved regardless “end on” or “side on” measurements (through the electrode) were performed.

With the HG turned on a complete suppression of N<sub>2</sub>, Ar and OH spectra lines was detected (see Fig. 4.4.B). Instead broad hydrogen dissociation continuum between 200 and 400 nm was detected. The suppression of N<sub>2</sub>, Ar and OH emission was caused by the presence of H<sub>2</sub> and possibly water vapor which caused quenching of optical transitions. Note the same conditions for measurements depicted in Figs 4.4.A and 4.4.B were used, but the scale on the Y axis is different indicating suppression of Ar emission lines by a factor of ten.



A)



B)

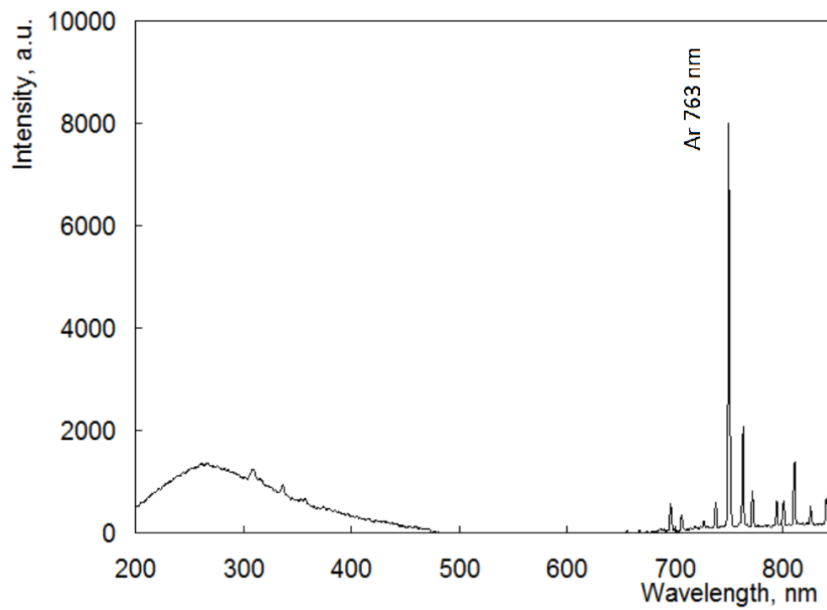
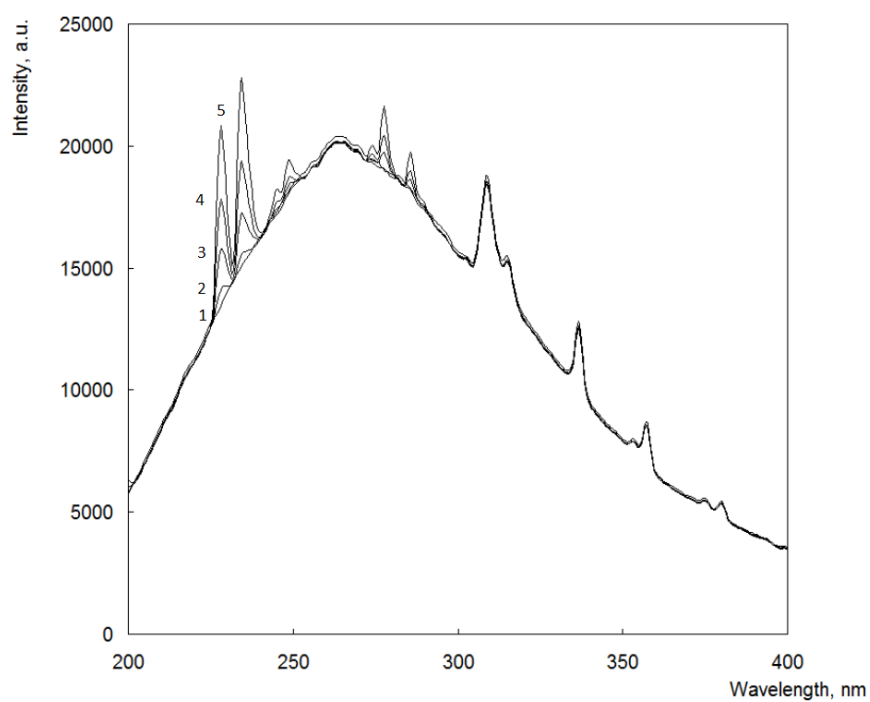


Figure 4.4. Emission spectrum of Ar plasma measured through the optical arm of a GG design DBD atomizer with HG turned off (A) and turned on (B). Applied HV was 10 kV and Ar flow rate was 50 ml min<sup>-1</sup> for both measurements. Detector integration time was 30 ms with 10 spectra to be averaged.

Emission spectra with HG on were measured with various As concentration levels ranging from 100 to 1 000  $\mu\text{g l}^{-1}$  As. Arsenic emission lines at 228 and 234 nm were detected. The rise of intensity of As emission was proportional to the rise in concentration of As. The intensity of emission lines of OH (309 nm) and nitrogen (337.1; 357.7; 380.5 nm) was constant with all measured As concentrations (see Fig. 4.5.). The same pattern was seen in results measured both "end on" (see Fig. 4.5.A), and from the side of the atomizer through the electrode (see Fig. 4.5.B). The intensity of signal decreased over time when measuring through the side. This was probably caused due to the formation of arsenic deposits on the inner surface of the atomizer, which lowered the transparency of the quartz body of the atomizer (see Fig. 4.5.B). The higher the As concentration in the sample, the faster the formation of the arsenic deposits. Despite this phenomenon, measurements through the electrode is important for mechanistic studies and for plasma diagnostics. Such experiment are beyond the scope of this bachelor thesis, however, they will be performed in the laboratory in which this thesis was done. Detection limits for As have been evaluated for both modes of AES detection reaching 30  $\text{ng ml}^{-1}$  As and 100  $\text{ng ml}^{-1}$  As, respectively, for end on and through grid measurements.

A)



B)

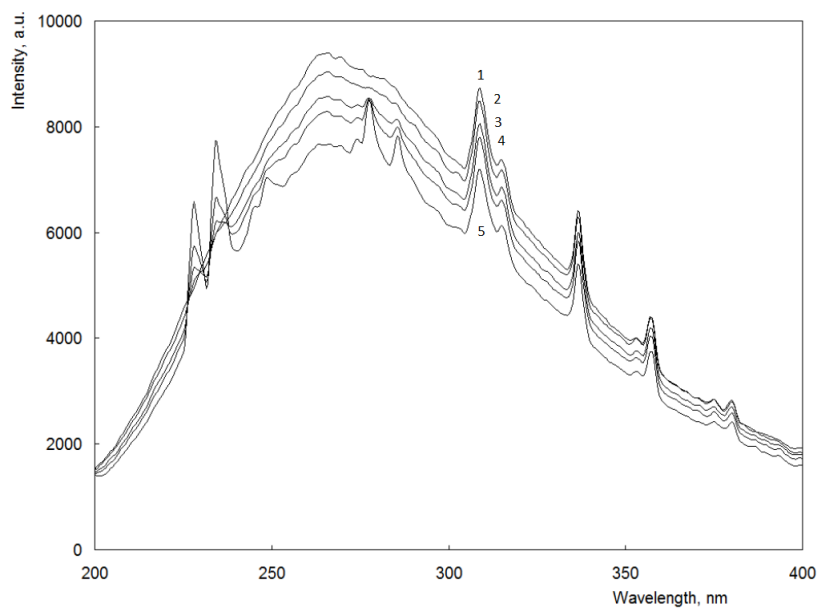


Figure 4.5. Effect of As concentration on emission spectra measured through the optical arm (A) and from the side through the electrode (B). Applied HV 10 kV, Ar flow rate  $50 \text{ ml min}^{-1}$  with HG turned on. Detector integration time was 500 ms (A) and 1000 ms (B) with 10 spectra to be averaged in both cases. Standard concentration was  $0 \mu\text{g l}^{-1}$  (1),  $100 \mu\text{g l}^{-1}$  (2),  $300 \mu\text{g l}^{-1}$  (3),  $500 \mu\text{g l}^{-1}$  (4) and  $1000 \mu\text{g l}^{-1}$  As (5).

## 5. Conclusions

Five novel planar designs of DBD atomizers have been constructed in cooperation with Department of miniaturization, Leibniz Institut für Analytische Wissenschaften – ISAS, Dortmund, Germany. Arsane was employed as a model analyte. The individual designs differed from each other in the way of electrode attachment (glued metal strip electrodes versus sputtered electrodes), electrode shape (compact rectangular-shaped electrodes versus grids) and area. All the designs studied were found compatible with AAS detection giving comparable sensitivity. Although the design with glued metal strip electrodes can be perceived as the simplest and mechanically robust one for routine analytical use, the designs with sputtered electrodes offer the possibility of being supplied by sources with significantly lower power consumption due to better contact between the electrode material and a dielectric barrier. Grid-shaped electrodes have been found ideal for plasma diagnostics allowing spatially resolved measurements. Coupling of selected DBD designs with AAS, AFS and AES spectrometric detectors was found feasible reaching detection limits competitive to those reported in literature. The results were summarized as a manuscript published in *Spectrochimica Acta Part B*.<sup>17</sup>

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