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Determination of bismuth by dielectric barrier discharge atomic absorption spectrometry coupled with hydride generation: method optimization and evaluation of analytical performance

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Determination of Bismuth by Dielectric Barrier Discharge Atomic Absorption Spectrometry Coupled with Hydride Generation: Method Optimization and Evaluation of Analytical Performance

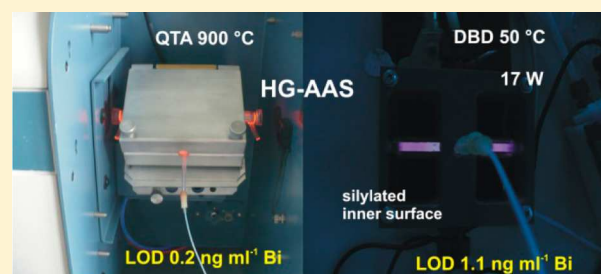Jan Kratzer,*,[†,‡] Jaroslav Boušek,[§] Ralph E. Sturgeon,[‡] Zoltán Mester,[‡] and Jiří Dědina[†]

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S *Supporting Information*

ABSTRACT: Atomization of bismuth hydride in a 17 W planar quartz dielectric barrier discharge (DBD) atomizer was optimized and the performance of this device compared to that of a conventional quartz tube atomizer (QTA) for atomic absorption spectrometry (AAS). Modification of the inner surface of the DBD atomizer using dimethyldichlorsilane (DMDCS) was essential since it improved sensitivity by a factor of 2−4. Argon, at a flow rate of 125 mL min^{-1}, was the best DBD discharge gas. Free Bi atoms were also observed in the DBD with nitrogen, hydrogen, and helium discharge gases but not in air. The detection limit for Bi (1.1 ng mL^{-1}) is worse than with the QTA (0.16 ng mL^{-1} Bi). A poorer detection limit compared to a QTA is a consequence of the shorter optical path of the DBD. Moreover, the lower atomization efficiency and/or faster decay of free atoms in the DBD has to be considered. The performance of the DBD as an atomizer reflects both effects, i.e., atomization efficiency and free atom decay, was estimated to be 65% of that of the externally heated quartz tube atomizer. Nevertheless, this hydride generation DBD-AAS approach can be used for the routine determination of Bi, providing repeatability and accuracy comparable to that reached with a QTA, as demonstrated by analysis of NIST SRM 1643e (trace elements in water). The potential of in-atomizer preconcentration in a DBD atomizer is outlined.

The dielectric barrier discharge (DBD) is an example of a miniaturized plasma source, a useful tool for industrial applications such as surface treatment, plasma coating, thin-film deposition, etc., as well as a powerful atomization, excitation, and/or ionization source for analytical spectroscopy.[1] Its configuration is characterized by the presence of at least one dielectric barrier providing a small gap between two powered electrodes. Apart from using the DBD plasma as a desorption/ionization tool with MS detection, analytical applications of DBDs reside in the field of volatile species generation, employing the DBD as an atomizer for atomic absorption (AAS)[2−4] and atomic fluorescence spectrometry[5−11] as well as an excitation source for atomic emission spectrometry.[12,13] Routine methods have been recently reported coupling generation of hydrides (HG)[14] or cold vapors to DBD atomizers with AAS detection (As, Sb, Se, Sn, and Hg).[2−4] To date, no performance comparison to a quartz tube atomizer (QTA) has been made nor have the atomization mechanisms in the DBD plasma been investigated.

A laboratory-made configuration of a quartz DBD chamber with a custom high voltage generator power supply was used in this work to investigate its application, for the first time, to atomization of bismuth hydride with AAS detection. Sub-sequently, analytical figures of merit in the DBD and a reference QTA were compared.

EXPERIMENTAL SECTION

Chemicals and Standards. All reagents were of A.C.S. grade purity. Deionized water was generated with a Mili-Q system (18 MΩ cm resistivity) and used to prepare solutions. Standard solutions of bismuth were prepared from a 1 mg mL^{-1} Bi stock solution (SCP Science, Montreal, Canada) by dilution in 1 mol L^{-1} HCl (EMD Chemicals Inc.). A blank consisted of 1 mol L^{-1} HCl. The reductant was a 0.5% (m/v) solution of NaBH$_4$ (Sigma-Aldrich, Canada) in 0.4% (m/v) KOH (Anachemia) prepared fresh each day. If explicitly stated, a surface modification (passivation) of the inner surface of the DBD chamber was performed using a 5% (v/v) solution of dimethyldichlorsilane (DMDCS) in toluene (Sylon CT solution produced by Supelco). A certified reference material SRM 1643e (NIST, USA, trace elements in water) with defined Bi content was employed to assess the accuracy and precision

of the results. Concentrated sulfuric acid (p.a., Lachema, Czech Republic) and sodium hydroxide pellets (NaOH, purum, pearls, Lach-Ner, Czech Republic) were used as drying agents to remove residual water from generated bismuthine.

Atomic Absorption Spectrometer. A PerkinElmer atomic absorption spectrometer model Analyst 100 controlled by AAWinLab software (version 2.61) was employed. A Bi hollow cathode lamp (SCP Science, Montreal, Canada) was operated at a current of 10 mA. A spectral bandpass of 0.2 nm isolated the 223.1 nm absorption line. The deuterium background correction system was not employed. Either a QTA or a DBD chamber were located in the optical axis of the spectrometer and employed as the atomizer. Signals were recorded for 60 s, and the peak area as well as peak height response were evaluated for both atomizers.

Hydride Generator and Quartz Tube Atomizer. Similar to that described in ref 15, an in-house continuous flow hydride generation system was constructed based on a Miniplus 2 peristaltic pump (Gilson). A 3 mL internal volume gas–liquid separator with a forced outlet (see ref 16 for a detailed description) was used. Either a DBD atomizer (see description below) or a QTA were used. The QTA was a multiatomizer[17,18] with a blocked auxiliary channel for outer gas. Consequently, the multiatomizer was operated in exactly the same way as a conventional quartz tube atomizer and thus will be simply termed a QTA in the subsequent text. Its 150 mm (i.d. 6 mm) horizontal arm was aligned within the optical path of the spectrometer. The length and i.d. of the inlet arm was 100 mm and 2 mm, respectively. The QTA was heated to 900 °C with the heating unit provided with the spectrometer. A digital thermometer equipped with a K-type thermocouple (BK Precision Corp.) was used to check the atomization temperature prior to the measurements. Gas flows of Ar, He, H_2, N_2, air, and O_2 (all obtained from Praxair, Canada) were regulated by mass flow controllers (Omega Engineering). Table 1 summarizes all liquid and gas flow rates employed.

Table 1. Optimum Generation and Atomization Conditions for QTA and DBD Atomizers

optimum generation conditions		
HCl concentration (mol L^{-1})		1.0
blank/sample channel pump flow rate (mL min^{-1})		3.5
$NaBH_4$/KOH concentration		0.5%/0.4%
reductant channel pump flow rate (mL min^{-1})		1.2
optimum atomization conditions	QTA	DBD
atomizer temperature (°C)	900	45
carrier/discharge Ar flow rate (mL min^{-1})	75	125
plasma power (W)		17
inner surface modification[a]		5% DMDCS

[a]When explicitly stated, also nontreated DBD was tested.

The drying devices consisted of (1) a vessel containing concentrated H_2SO_4, (2) a Nafion dryer tube (MD-110−12FP, Perma Pure, Toms River, N.J., with 2 L min^{-1} N_2), (3) a dryer tube packed with NaOH pellets, and (4) a membrane filter (0.45 μm, LCW916 type, Hach-Lange, Germany). These devices were placed between the outlet of the gas−liquid separator and the inlet to the DBD and each was sequentially investigated to compare the signal with the dryer in place to that without the device.

Dielectric Barrier Discharge Atomizer. A planar configuration of atomizer using a quartz DBD chamber was employed. Its design was based on that recently published by Zhu et al.[2,3] The atomizer was fabricated from two quartz microscope slides (15 mm × 75 mm, 1 mm thickness) and two quartz spacers (3 mm × 3 mm, 75 mm long). All quartz components were purchased from UQG Optics Ltd., England, and fused together. The plasma channel was thus rectangular-shaped with inner dimensions of 7 mm × 3 mm and a length of 75 mm. Two copper electrodes (50 mm long, 12 mm wide, 0.15 mm thick) were attached to the central part of the outer surface of the microscope slides. In order to avoid surface discharge at the outer side of the chamber, the electrode surface was covered with a dielectric layer of epoxy resin. The DBD atomizer was housed in a supporting frame of high-density polyvinyl chloride (PVC). This frame protected the DBD chamber and electrodes from mechanical damage and also facilitated placement of the DBD chamber into the optical axis of the atomic absorption spectrometer. A small computer fan was attached to the bottom of the DBD chamber to provide air cooling. A quartz tube (20 mm long, 2 mm inner diameter, 4 mm outer diameter) was sealed to the center of one of the quartz spacers and served as an inlet arm. A photograph of the DBD atomizer can be seen in Section 1 of the Supporting Information. The DBD and the frame are henceforth termed the DBD chamber. The DBD chamber was coupled to a high-frequency high-voltage generator fabricated by Lifetech (Brno, Czech Republic). The excitation frequency was 25 kHz. To prevent electromagnetic interference, the DBD excitation voltage was fed to the discharge chamber symmetrically, neither electrode was grounded and both were fed with voltage of opposite polarity. The inherent advantage of the generator (necessary for optimization of the experimental conditions) is that the power supplied to the DBD chamber can be controlled over a wide range, typically from approximately 1 to 35 W. Correspondingly, the amplitude of the applied high voltage excitation was approximately 8 kV to 15 kV, depending on the delivered power and gases used in the particular experiment. The temperature of the outer surface of the DBD atomizer was monitored by an IR thermometer (model IR608A, Amprobe). If not explicitly stated otherwise, the inner surface of the DBD atomizer was treated with a 5% solution of dimethyldichlorsilane (DMDCS) in toluene in order to passivate the surface. Silylation was performed following the procedure described in ref 19. Briefly, the ends of the DBD atomizer were closed using homemade plugs comprising Teflon-tape and parafilm. The atomizer was subsequently filled through its inlet arm with the 5% DMDCS solution using a syringe. After 2 min, the silylation reagent was removed and the DBD was rinsed three times with toluene followed by three successive rinses with methanol. The atomizer was then allowed to dry at room temperature prior to further use. The DBD atomizer was cleaned with 10% (v/v) HNO_3 for 10 min prior to applying the silylation procedure.

Externally Heated Planar Quartz Atomizer. For comparative purposes, a T-shaped planar quartz atomizer of the same dimensions as that of quartz body of the DBD chamber was fused together as for the DBD. No electrodes were attached to this atomizer. Thus, a rectangular shaped arm of the atomizer (inner dimensions of 7 mm × 3 mm and length of 75 mm) was placed in the optical axis of the spectrometer, whereas a quartz tube (20 mm long, 2 mm inner diameter, 4 mm outer diameter) served as its inlet arm. The arm placed in the optical axis of the spectrometer was resistively heated by a laboratory power supply source (PS 3065-10 B; E-A, Elektro-Automatik GmbH, Viersen, Germany) to 900 °C. Resistive

heating was realized by a kanthal wire (4.17 Ω m^{-1}, 0.65 mm in diameter). The atomizer arm and the resistive wire were wrapped in a Rescor ceramic fiber blanket (Cotronics Corp.) and overlaid with Al foil to serve as thermal insulation.
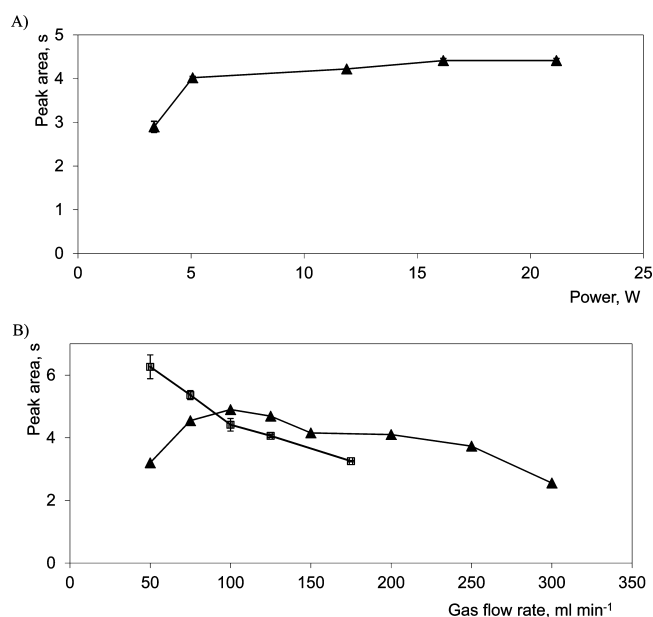
Procedure. Measurements were performed in an online atomization mode. Either blank or standard solution was introduced to the sample channel. The flow rate of hydrogen evolved from decomposition of NaBH$_4$ was experimentally found to be approximately 15 mL min^{-1}. Optimum generation as well as atomization conditions for both atomizers, i.e., QTA and DBD, are summarized in Table 1. Only when explicitly stated was the externally heated planar quartz atomizer used as the atomizer. Averages of at least 3 replicate signals are presented in the figures and in the text with uncertainty expressed as standard deviation (SD).

■ RESULTS AND DISCUSSION

Preliminary Observations. Basic operational parameters of the DBD, such as discharge gas type and flow rate as well as DBD power, were optimized. In the course of these experiments, it was observed that silylation improved the Bi signal under all DBD powers compatible with a stable discharge (5−25 W) for all useful gases (argon, nitrogen, and helium) in a broad range of gas flow rates (50−300 mL min^{-1}) by a factor of 2−4. Therefore, the reported measurements were performed with the DMDCS-modified DBD atomizer. Only if explicitly stated otherwise, experiments made with a nontreated DBD are mentioned.

After a period of nonoperation, once the hydride generator is operational to process a blank solution and the DBD plasma is powered again, it was noted that a transient signal is observed with its height, area, and width not being very reproducible and obviously dependent on the period during which the hydride generator as well as the DBD plasma had been off. Subsequently, replicate measurements of the blank yield a flat baseline signal. It should be noted that both the DBD plasma as well as a hydrogen flow, either from the hydride generator or from the gas cylinder, must be on following any delay in the measurements in order to obtain this prepeak. These prepeaks were also observed in a nontreated DBD and were typically even more pronounced. As well, formation of a black deposit (most probably metallic Bi) was observed in the central part of a nontreated DBD after several days of operation. These observations suggest that (i) there is deposition of Bi species in the nontreated DBD but to some extent also in the surface treated DBD as a result of decay of free Bi atoms on the walls of the atomizer; (ii) the deposited Bi species cannot be removed from the surface of the DBD by the Ar plasma itself, hydrogen must also be present.

Effect of Power. The effect of power supplied to the DDB atomizer was investigated employing an Ar discharge gas introduced upstream of the gas–liquid separator at a flow rate of 125 mL min^{-1} (Figure 1A). It can be seen that the discharge is quite inhomogeneous with a clear filament structure between 2 and 5 W. By contrast, the discharge appears to be homogeneous and fills the entire plasma channel covered by the electrodes for power values above 5 W. The temperature of the central part of the DBD outer surface changed from 28 to 65 °C when increasing the DBD power from 2 to 25 W. The signal increases with increased power up to 12 W, after which it reaches a plateau. A power of 17 W (corresponding surface temperature of 45 °C) was found optimum for further measurements. The effect of power supplied to the nontreated

Figure 1. Effect of power (A) and gas flow rate (B) on Bi signal; DMDCS-modified DBD (30 ng mL^{-1} Bi) with Ar (▲) as plasma gas; fixed discharge gas flow rate 125 mL min^{-1} (A), fixed DBD power supply rate 17 W (B); QTA (900 °C, 10 ng mL^{-1} Bi) with Ar as carrier gas (□).

DBD in Ar and He discharge gases is discussed in Figure S2 (see Section 2 of Supporting Information).

Effect of Gas Flow Rate. The effect of Ar flow rate on Bi response was investigated in the range 50−300 mL min^{-1}. For comparison, the effect of Ar flow rate in a QTA was also studied. Since high gas flow rates through the gas−liquid separator may cause increased aerosol transport to the atomizers, the stream of gas was split into two channels, each separately controlled. The gas flow through the gas−liquid separator was kept constant at 50 mL min^{-1}, whereas the flow of gas added downstream of the gas−liquid separator was varied between 0 and 250 mL min^{-1}.
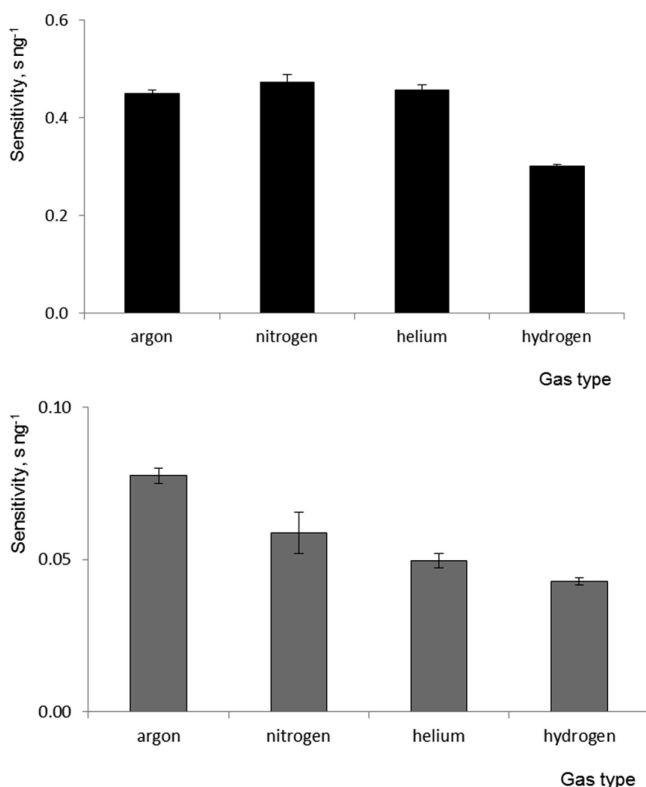
The sum of the gas flows in both channels is plotted in Figure 1B, summarizing its effect on Bi response. In the QTA, the Bi signal decreases with increased Ar flow rate, obviously due to analyte dilution. For subsequent experiments with the QTA, a flow rate of 75 mL min^{-1} was chosen. Analogous to our previous study,[15] this was selected as a compromise between repeatability and sensitivity. However, the dependence of signal on Ar flow rate is different with the DBD atomizer wherein it increases with increased Ar flow rate up to 100 mL min^{-1} followed by a decrease for Ar flow rates above 150 mL min^{-1} (Figure 1B). A flow rate of 125 mL min^{-1} was selected for further experiments with the DBD atomizer.

The effect of gas flow rate on the Bi signal was investigated, analogously to the set of experiments described above, also with a nontreated DBD employing Ar and He as discharge gases. The results are depicted in Figure S3 (see Section 3 of Supporting Information).

In an additional set of experiments (data not shown), the effect of Ar flow rate through the gas−liquid separator was also investigated. The experimental arrangement with two gas channels as described above was employed. Whereas the Ar flow rate to the gas liquid separator was varied from 25 to 125 mL min^{-1}, the flow rate of Ar in the channel downstream of the gas−liquid separator was altered to keep the summed flow rate

in both channels constant at 125 mL min^{-1} in order to maintain the same atomization conditions. It appeared that an Ar flow rate through the gas–liquid separator in this range (25–125 mL min^{-1}) had no effect on the Bi signal. This made it possible to simplify the setup in further experiments by introducing the optimum discharge gas flow rate of 125 mL min^{-1} via the single channel upstream of the gas–liquid separator.

Effect of Gas Type. Argon, helium, nitrogen, hydrogen, and air were investigated as discharge gases to atomize bismuth hydride in the DBD and serve as carrier gases in the QTA, respectively (Figure 2).
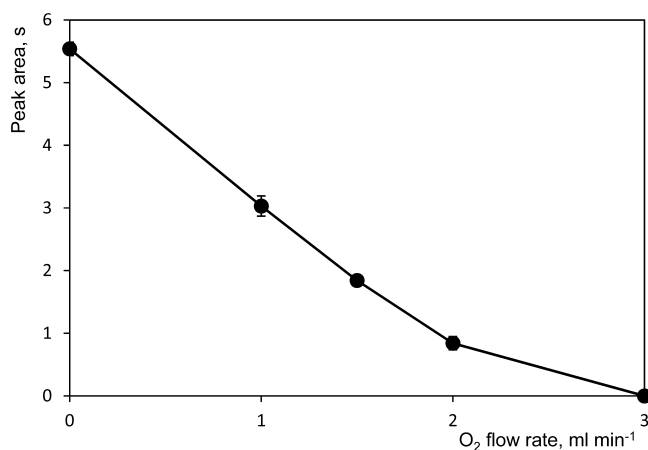

Figure 2. Effect of gas type on sensitivity for Bi in a QTA (black bars) and DMDCS-modified DBD atomizer (gray bars); QTA conditions: 900 °C atomization temperature, gas flow rate 75 mL min^{-1}. DBD atomizer conditions: gas flow rate 125 mL min^{-1}, DBD power supply rate 17 W.

Comparable response in the QTA is obtained using Ar, He, or N$_2$, indicating that the only role of the carrier gas is to transport the hydride efficiently to the optical arm of the atomizer. The nature of the carrier gas does not markedly influence atomization of bismuth hydride and/or the subsequent fate of free atoms in the QTA. Sensitivity in pure H$_2$ in the QTA is only about 65% of that found in Ar, He, or N$_2$. This observation is in accord with our previous observations for Bi[20] as well as with experiments and theoretical calculations performed for Se[21,14] and can be explained by the decrease in the atomic absorption coefficient owing to absorption line broadening in the presence of H$_2$. No Bi signal can be detected using air as the carrier gas since trapping of Bi occurs on the heated quartz surface when an excess of oxygen over hydrogen is present.[15,22] The trapped species are volatilized to produce a transient signal as soon as the carrier air stream is switched off while the hydride generator continues

to operate (generating hydrogen). The amount of hydrogen produced by decomposition of the NaBH$_4$ is sufficient to volatilize the trapped Bi species in the absence of air. Hydride trapping in quartz atomizers under an oxygen rich atmosphere with subsequent volatilization and detection of analyte in a hydrogen rich atmosphere has also been reported for Sb,[23] As, and Se.[24]

By contrast, the signal in the DBD atomizer is significantly dependent on the discharge gas employed (Figure 2), the highest signal being observed in Ar. Analogously to a QTA, no Bi signal was obtained in the DBD with air as the discharge gas. Subsequently, transient signals were observed when the air was replaced by argon during blank generation. This observation indicates that Bi is efficiently trapped in the DBD with air as discharge gas. In subsequent experiments, oxygen was admixed to the discharge Ar flow downstream of the gas–liquid separator. Bi signals decreased by almost 50%, even at an oxygen flow rate as low as 1 mL min^{-1}, and the signal was completely suppressed at 3 mL min^{-1} O$_2$ (Figure 3), i.e., at

Figure 3. Effect of addition of oxygen to Ar discharge gas on Bi signal; DMDCS-modified DBD at 17 W (60 ng mL^{-1} Bi) with 125 mL min^{-1}Ar.

oxygen flow rate much lower than 7.5 mL min^{-1} corresponding to a stoichiometric ratio to hydrogen. Trapped bismuth species can be subsequently volatilized and atomized simply by switching off the oxygen flow, assuming that a blank is simultaneously processed in order to generate hydrogen. The preconcentration efficiency was quantified by comparing the peak areas generated from a 3 ng mL^{-1} Bi standard solution obtained with the DBD in an Ar plasma in (i) the absence of oxygen and (ii) after trapping in an Ar plasma by addition of a 3 mL min^{-1} flow of O$_2$ with subsequent volatilization by introduction of hydrogen from the decomposition of NaBH$_4$ (oxygen flow stopped). The trapping efficiency, estimated from five such consecutive replicates, was 62 ± 5%. No effort was made to improve the trapping efficiency. Quantitative trapping and release of bismuthine can be obtained in quartz tube atomizers[15,22] as already noted above. The concept of in situ trapping of hydride forming elements in the DBD, proven to be feasible in this work for Bi, might also be useful for other elements, especially those for which preconcentration in quartz tube atomizers is incomplete, such as As or Se.[24]

Effect of Water/Moisture Removal. As an example of a low power and low temperature plasma, response from a DBD may be susceptible to introduction of water vapor and droplets

that are cogenerated with analyte hydride and transported to the atomizer. Little or no effect of moisture on atomization of arsine and its methylated analogues was observed when employing a planar DBD atomizer and AAS as a detector.[3] Removal of water increased signals for mercury in the DBD used for excitation of its cold vapors when atomic emission spectrometry was used as the detection technique.[12]

To assess an effect of residual moisture in the DMDCS-modified DBD chamber, several devices were tested, including (1) a vessel containing concentrated H_2SO_4 through which the outflow from the GLS was bubbled, 2) a Nafion dryer tube with $2 \, l \, min^{-1}$ N_2 flow, (3) a dryer tube packed with NaOH pellets and, (4) a 0.45 μm membrane filter. The first three drying devices were found inapplicable since apart from residual water they also completely retained bismuthine. When using a 0.45 μm membrane filter, the Bi signal was registered with a peak area being ~12% lower compared to that without any dryer. As a consequence, no dryer was employed in further experiments.

Analytical Figures of Merit. These were compared for the DBD (DMDCS-modified) and QTA (Table 2) under

Table 2. Figures of Merit

	DBD[a]	QTA[b]
LOD (ng mL^{-1} Bi)	1.1	0.16
m_0 (pg)	52	6.3
CRM 1643e (ng mL^{-1} Bi)	14.2 ± 0.2	14.0 ± 0.1
	certified value 14.1 ± 0.2	

[a] 125 mL min^{-1} Ar discharge gas, 17 W DBD power. [b] 900 °C QTA atomization temperature and 75 mL min^{-1} Ar as carrier gas.
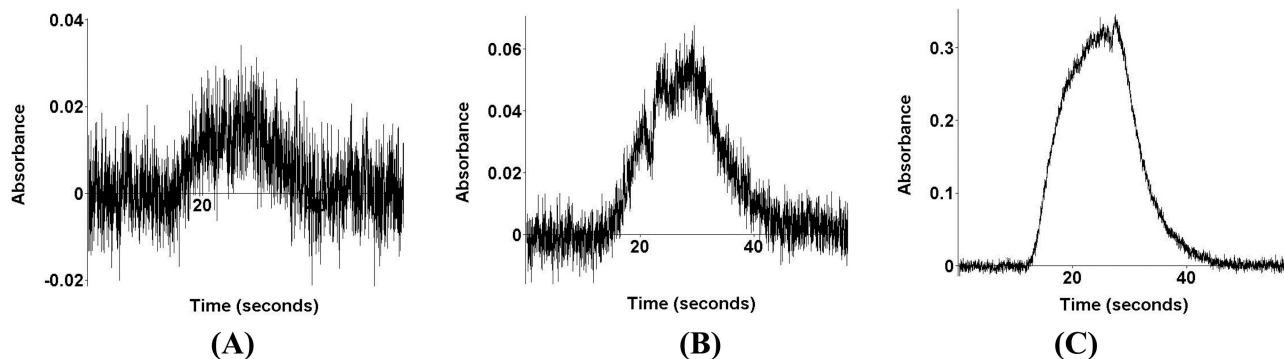
optimum operating conditions (Table 1). Comparison of Bi signals in these atomizers as well as in the nontreated DBD is illustrated in Figure 4. Comparison of detection limits (LOD) and peak area characteristic mass (m_0) for the DBD and QTA, summarized in Table 2, reveals that best sensitivity and LOD are achieved with a QTA: 7- to 8-fold better compared to the DBD. It should be noted that the optimum atomizer conditions (Table 1) include a higher Ar flow rate for the DBD atomizer (125 mL min^{-1}) than for the QTA (75 mL min^{-1}). However, when using an Ar flow rate of 125 mL min^{-1} with the QTA the performance was not markedly impaired in comparison to that obtained in a QTA operating at 75 mL min^{-1}Ar. The LOD and m_0 were 0.19 ng mL^{-1} and 7.3 pg, respectively.

Both atomizers provided sufficient detection power to determine Bi with good accuracy and precision, as demon-

strated by the results of analysis of NIST SRM 1643e (trace elements in water) presented in Table 2. Day-to-day repeatability of the signals with the DBD was satisfactory. The average signal and standard deviation for a 30 ng mL^{-1} standard solution of Bi measured over 10 days randomly undertaken within a 14 day period was 2.77 ± 0.26 s.

Atomization Efficiency. A comparison of analytical figures of merit between the DMDCS-modified DBD and the QTA presented above was performed. Even their optical path length is not comparable.

In order to compare the atomization efficiency of the DBD and externally heated QTA directly, an externally heated planar quartz atomizer was constructed (see the Experimental Section for details), whose shape and dimensions were exactly the same as those of the DBD. The signal from 10 ng mL^{-1} Bi standard was measured ($n = 5$) in both atomizers employing a flow rate of 125 mL min^{-1} Ar. The power for the DMDCS-modified DBD was 17 W whereas atomization temperature in the externally heated planar quartz atomizer was 900 °C. The signal in the DBD was 35% lower (both area and height) compared to the externally heated planar quartz atomizer. Assuming that atomic absorption coefficients are the same in both atomizers, the lower signal in the DBD can be caused by two factors or their mutual combination: the efficiency of conversion of bismuthine to free Bi atoms is lower in the DBD and/or the decay of free Bi atoms is faster in the DBD compared to the externally heated planar quartz atomizer. The evidence for interaction of free Bi atoms with the interior surface of the DBD arises from the substantially improved sensitivity following treatment by DMDCS. Despite the surface modification by DMDCS, its activity and affinity for free atoms of Bi at 45 °C may be higher than that of an untreated quartz surface heated to 900 °C in externally heated planar quartz atomizer. The atomization efficiency of the DBD reflects both effects, i.e., conversion of bismuthine to free Bi atoms and free atom decay, and was estimated to be 65% of that for an externally heated planar quartz atomizer. Although the experimental data do not permit one to discern which of the effects causes lower signal in the DBD, it is possible to estimate the atomization efficiency of bismuthine in the DBD. To the best of our knowledge, this is the first effort to quantify atomization efficiency of any hydride forming element in a DBD ever published.

Figure 4. Comparison of peak areas and profiles for 10 ng mL^{-1} Bi standard (8.75 ng Bi absolute) in nontreated DBD atomizer (A), DMDCS-modified DBD (B), and QTA (C).

CONCLUSIONS

A DBD was employed for the first time as an atomizer for bismuth hydride with AAS detection. Sensitivity was poorer but precision and accuracy comparable to an externally heated QTA. The DBD atomizer can be routinely used for determination of Bi by AAS. An inferior limit of detection compared to QTA can undoubtedly be explained by shorter optical path of the current DBD but also by its lower atomization efficiency, attaining about 65% of that in the QTA.

The substantial increase in sensitivity in the DMDCS-treated DBD atomizer is a unique observation. The use of any silylation agent to improve sensitivity with DBD-based atomizers, either coupled to atomic absorption or atomic fluorescence detectors, has never been reported. This suggests a strong interaction between the surface of the nontreated DBD atomizer and the analyte causing analyte retention in the atomizer and, consequently, signal suppression. The prepeak formation, requiring the presence of hydrogen, indicates that the analyte is, at least partially, retained in the atomizer and that it can be volatilized/atomized only in the presence of hydrogen.

The most significant observation is that of the role of oxygen in the DBD atomizer. In contrast to a QTA, where oxygen must be present in excess over hydrogen to fully trap Bi species,[15,22] the presence of oxygen, even in substoichiometric ratios to hydrogen, decreased or completely suppressed the Bi signal due to analyte trapping in the DBD atomizer. Trapped Bi species can be subsequently volatilized and atomized in the argon plasma in the presence of hydrogen. A preconcentration efficiency of approximately 60% was obtained using a DMDCS-modified DBD, a figure that is open to improvement with further work. Our aim was to simply provide evidence of this concept since hydride trapping in DBD atomizers has not been earlier reported. The potential of in-atomizer preconcentration in a DBD atomizer is worthy of further exploration, especially for those elements for which in-atomizer trapping in the QTA is troublesome and incomplete (As, Se).

ASSOCIATED CONTENT

ⓢ Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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