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Atomization of Bismuthane in a Novel Dielectric Barrier Discharge – A Mechanistic Study

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ABSTRACT:

Atomization of bismuthane in a planar dielectric barrier discharge (DBD) atomizer was investigated using a variety of probes, including atomic absorption spectrometry (AAS) to monitor distribution of free atoms along the optical path and direct analysis in real time (DART) coupled to an Orbitrap mass spectrometer to identify the structure of the species arising from the hydride generator as well as the atomizer. Results obtained with the DBD were compared to those from a conventional externally heated quartz tube atomizer (QTA). Free Bi atoms were essentially absent outside the central part of the DBD atomizer, suggesting their high reactivity. The gas phase analyte fraction transported beyond the confines of the DBD or QTA atomizers, quantified by inductively coupled plasma mass spectrometry (ICP-MS), was less than 10 %. The amount of Bi found in acidic leachates of the interiors of both atomizers, representing the fraction retained on their surfaces, was ca 90 %. These complementary experiments comprising the determination of recovered Bi in the nitric acid leachates from deposition in the atomizer on the one hand and quantification of the Bi fraction transportable outside the atomizer on the other, were in excellent agreement, providing 100 % mass balance of detected analyte. The high fraction of Bi deposited in the atomizers indicates significant reactivity of free Bi atoms, which is in accord with the fact that almost no free Bi atoms exist beyond the physical boundaries of the DBD. The extent of interference from other hydride forming elements (As, Sb, Se) on Bi response by AAS using DBD and QTA atomizers was investigated, with the former atomizer providing superior performance. Compared to QTA, DBD provided two orders of magnitude and one order of magnitude, respectively, better resistance to interference from Se and Sb.

INTRODUCTION

Plasma devices based on dielectric barrier discharges (DBD) [1] can be used in many applications in analytical spectrometry. Depending on their construction and operating conditions, this includes: desorption/soft ionization devices [2] coupled with mass spectrometry (MS); excitation sources for atomic emission spectrometry (AES) [3]; atomizers for atomic absorption (AAS) [4-8] and fluorescence (AFS) spectrometry [9-15] as well as sources for metal vapor generation [16-18]. The increased interest in DBD devices in recent years can be attributed to their universality of use, low power consumption, low cost of fabrication and operation as well as user friendliness. Since DBD atomizers remain rather novel in AAS/AFS, with some dozen publications [4-15] demonstrating their use as atomization sources for volatile compounds, including mercury cold vapor and hydride forming elements [19-21], there has been no work yet focused on a thorough investigation of atomization mechanisms with a single exception of the report published by Abdul-Majeed and Zimmerman [22].

The aim of the present work was to study atomization processes of hydride forming elements in the DBD and to compare them to those for a conventional externally heated quartz tube atomizer (QTA). Generation of volatile hydrides (HG) prior AAS detection of traces of selected analytically useful metals is a favorite sample derivatization technique due to high introduction efficiency of analyte into the detector as well as its superb separation from sample matrix [19-21]. Bismuth was selected as a model analyte since atomization of bismuthane in DBD was thoroughly optimized in our laboratory recently [6]. A variety of spectroscopic detectors was used, allowing detection of free Bi atoms within the DBD atomizer, total Bi species content in the gas phase external to the physical dimensions of the atomizer (including identification of their structure) as well as the fraction of Bi adsorbed within the atomizers. Moreover, the influence of other hydride forming elements on atomization of bismuthane in the DBD atomizer as well as in the QTA was investigated. Insights into the atomization processes and knowledge of the tolerance of the atomizers towards interferences is important not only for further development of the DBD atomizer, but to help ensure accuracy and precision of results generated during routine applications.

EXPERIMENTAL SECTION

Chemicals and standards. All reagents were of analytical reagent grade or higher purity. Deionized water ($< 0.1 \mu\text{S}\cdot\text{cm}^{-1}$, Ultrapure, Watrex, USA) was used to prepare

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3 solutions. Working Bi standards were prepared fresh daily from 1 mg mL⁻¹ Bi stock solution
4 (Fluka) by dilution in 1 mol l⁻¹ HCl (Merck). A blank consisted of 1 mol l⁻¹ HCl. The
5 reductant was a 0.5 % (m/v) solution of NaBH₄ (Sigma) in 0.4% (m/v) KOH (Merck) filtered
6 after preparation and stored frozen. For interference studies, 1 mg mL⁻¹ stock solutions of
7 As(III), Sb(III) and Se(IV) (Fluka) were used to prepare their working solutions in 1 mol l⁻¹
8 HCl containing a fixed concentration of Bi as analyte. Hydrofluoric acid (38% (m/v), p.a.,
9 Spolchemie, Ústí nad Labem, Czech Republic) and nitric acid (65%, p.a., Lach-Ner, Czech
10 Republic) were used to clean the atomizers when needed. A surface modification
11 (passivation) of the inner surface of the DBD chamber was performed using a 5% solution of
12 dimethyldichlorosilane (DMDCS) in toluene (Sylon CT solution provided by Supelco).
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21 **Hydride generator.** Similar to that described in ref.[6], an in-house continuous flow
22 hydride generation system was constructed based on an Ismatec peristaltic pump (model MCP
23 V5.10 Ismatec, Switzerland). A 3 mL internal volume gas-liquid separator with a forced
24 outlet (see ref. [23] for detailed description) was used. Table S1 summarizes conditions for
25 generation of bismuthane employed in this study. A flow of Ar carrier gas was regulated by a
26 mass flow controller (Omega Engineering, USA). The flow rate of hydrogen evolved from
27 decomposition of NaBH₄ was theoretically calculated as well as experimentally determined
28 using a manual volumetric flow meter to be approximately 15 mL min⁻¹. The scheme of the
29 hydride generator is depicted in Figure S1.
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37 **Atomizers.** Either a DBD atomizer or a QTA were used. A planar configuration of a
38 quartz DBD atomizer (see Section S1 of Supporting Information for its dimensions) was
39 coupled to a high frequency, high voltage generator fabricated by Lifetech (Brno, Czech
40 Republic). The complete apparatus setup is described in detail in ref. [6]. The QTA was a
41 multiatomizer [24,25] with blocked auxiliary channel for outer gas. Consequently, it was
42 operated in exactly the same way as a conventional externally heated quartz tube atomizer and
43 thus will subsequently be referred to as a QTA. The QTA was resistively heated to 900 °C
44 (RMI heating unit, Czech Republic). Compressed Ar (99.996 %) produced by SIAD Czech
45 was used as carrier and discharge gas for atomic absorption measurements.
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52 It should be noted that the gaseous phase in both QTA as well as in DBD always
53 contains, apart from the carrier/discharge gas and bismuthane, also 15 mL min⁻¹ of hydrogen
54 evolved as a side-product from NaBH₄ decomposition in the gas-liquid separator. For the sake
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of simplicity the carrier/discharge gas is termed according to its inert gas major component, i.e. Ar or He, further in the text even though containing the hydrogen fraction.

Atomic absorption measurements. A GBC model SavantAA atomic absorption spectrometer (GBC, Australia) was employed without background correction. A Photron Bi boosted hollow cathode lamp (“superlamp”) served as the radiation source at the 223.1 nm analytical line of Bi with a spectrometer spectral bandpass of 0.2 nm (lamp current of 10 mA, boost current 15 mA). Either a QTA or a DBD atomizer was located in the optical axis of the spectrometer. Signals were recorded for 90 s and peak area as well as peak height response were evaluated for both atomizers. The arrangement and the procedure for AA measurements varied according to the purpose of the measurement. For the interference study, standard solutions of Bi at concentration levels of 5 ng mL⁻¹ (QTA) and 10 ng mL⁻¹ (DBD) were employed containing 0, 5, 50, 500 or 5 000 ng mL⁻¹ of As, Sb or Se as interferents. Measurements were performed under generation and atomization conditions as summarized in Table S1. In order to determine the spatial distribution of free Bi atoms in the DBD, two measurement configurations were employed. The first was the conventional AAS setup with the DBD atomizer optical arm aligned to the optical axis of the spectrometer, as schematically depicted in Figure S1A. Analyte concentration was 10 ng mL⁻¹. In the second configuration, the optical arm of the DBD was rotated 90° and adjusted such that the optical axis of the spectrometer passed through the exit end of the optical arm of the DBD, as depicted in Figure S1B. Because of much lower sensitivity observed in this configuration, analyte concentration levels of 250 ng mL⁻¹ to 1 µg mL⁻¹ were employed. Free atoms in the peripheral region of the DBD can only be detected in this configuration.

Cryotrapping was employed in order to investigate the effect of hydrogen on atomization of bismuthane. A cryogenic trap was inserted between the hydride generator and an atomizer. The configuration of the experimental setup is schematically depicted in Figure S1C. An auxiliary gas channel serving for optional introduction of hydrogen gas into the atomizer (15 mL min⁻¹ H₂, 99.95%, SIAD Czech), not shown in the Figure S1C, was connected upstream of the cryogenic trap. The detailed design of the cryogenic trap and the operational procedure can be found in refs. [26,27] and in Section S1 of Supporting Information.

Identification of analyte structure by DART. The commercial direct analysis in real time (DART) ion source (model DART 100, Ionsense, Saugus MA, USA) interfaced to a LTQ Orbitrap mass spectrometer (Thermo Fisher Scientific Inc., Bremen, Germany) was

employed to identify the structure of analyte species released from the hydride generator as well as those leaving the atomizers. See Supporting Information (Section S1 and Figure S1D) for DART settings and detailed description of experimental setup.

ICP-TOF-MS and ICP-MS measurements. These measurements were employed to quantify the relative analyte fraction capable of being physically transported out of the atomizers when in operation, as well as to determine the analyte fraction retained within the atomizer after a defined number of sample replicates had been introduced into the devices. The latter was quantified by leaching the respective atomizer interior surfaces with 10 % HNO₃ and determination of the recovered concentration (mass) of Bi in the leachate.

Two different ICP-MS detectors were employed. An Optimass 8000 orthogonal acceleration time-of-flight ICP-MS (ICP-*oa*-ToF-MS produced by GBC Scientific Equipment Pyt Ltd, Victoria, Australia) was used to quantify the analyte fraction transported outside the DBD atomizer as well as to determine the content of Bi in the leachate arising from the DBD. Detailed description of this instrument, its tuning and optimization have been presented elsewhere [28]. An Agilent 7700x single quadrupole ICP-MS spectrometer was used to quantify the analyte fraction transportable from the QTA atomizer as well as the Bi content in its leachates. Experimental arrangement of the DBD coupling to the ICP-*oa*-ToF-MS is depicted in Figure S1E, whereas Figure S1F shows connection of the QTA to single quadrupole ICP-MS. Operating conditions of both MS spectrometers are summarized in Table S2. See Section S1 of Supporting Information for further detailed description of these experiments.

RESULTS AND DISCUSSION

Interferences. The aim of this study was to compare the performance of two approaches to hydride atomization mated to the same hydride generator (Figure S1A). Interferences from Se, As and Sb on response from Bi were investigated since these hydride forming elements are effectively co-generated [29,30] with bismuthane (generation efficiency $\geq 90\%$). Other hydride forming elements (i.e., Sn and Pb) were not investigated since the generation efficiency of their hydrides under the selected experimental conditions is very low [31,32]. Suppression of the Bi signal by other hydride forming elements is reported to be strong and difficult to control, with Se being ranked as the strongest interferent [19]. This study is significant as it is the first to examine interferences on Bi determination employing

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3 HG-DBD-AAS approach and the second study of interferences in the field of HG-DBD-AAS
4 following that related to the determination of Se by HG-DBD-AAS [8]. Performance with the
5 QTA was taken as the reference for this investigation. No effort was made to distinguish
6 between interferences specifically related to generation or atomization. In any case, even if
7 generation interferences occurred, their impact would be the same for both atomizers as the
8 same generator is employed. Results are summarized in Table 1. Averages of at least 5
9 replicate signals are presented in the figures and in the text with uncertainty expressed as
10 standard deviation (SD). No interference from As was evident with the QTA, even at the
11 highest concentration level of interferent tested ($5\ 000\ \text{ng mL}^{-1}$). Signal suppression of almost
12 25 % was observed in the presence of $500\ \text{ng mL}^{-1}$ Sb whereas Se was found to be the
13 strongest interferent, causing 15 % signal decrease at a concentration of only $50\ \text{ng mL}^{-1}$ Se
14 with the QTA. Interference extents can be conveniently expressed as tolerance limits (defined
15 as interferent concentration responsible for 10 % suppression of the Bi signal) as follows: 45
16 $\pm 5\ \text{ng mL}^{-1}$ Se, $0.3 \pm 0.1\ \mu\text{g mL}^{-1}$ Sb and $> 5\ \mu\text{g mL}^{-1}$ As. These can be compared to the
17 literature. A detailed interference study [33] performed with a batch hydride generator
18 employing a QTA as atomizer reported following tolerance limits: $0.3\ \mu\text{g mL}^{-1}$ Se, $1.3\ \mu\text{g mL}^{-1}$
19 ^1Sb and $>20\ \mu\text{g mL}^{-1}$ As. The absolute values of the tolerance limits found in both studies are
20 naturally different as a consequence of the differing experimental modes of hydride
21 generation (continuous flow versus batch) but the trend, ranking the interferents on Bi as
22 follows $\text{Se} > \text{Sb} \gg \text{As}$, is the same.

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Significant interference by Se on Bi with the DBD did not occur until the highest concentration of $5\ 000\ \text{ng mL}^{-1}$ Se was tested. As a consequence, the atomizer can tolerate two orders of magnitude higher Se concentration levels than the QTA (see Table 1). Resistance of the DBD atomizer to interferences arising from Sb is also better than that of the QTA. Signal suppression caused by Sb was observed only at the highest interferent concentration level. Poorer tolerance towards interference in the DBD compared to the QTA occurred only for As for which response was suppressed by 50 % in the presence of $5\ 000\ \text{ng mL}^{-1}$ As, whereas no interference was found with the QTA under identical conditions. No memory effects were observed for any of the interferents using either atomizer, i.e., no change in signal area or shape compared to the reference signal was observed when an interferent-free standard solution of Bi was measured after a similar solution containing interfering ion was processed.

Interestingly, the manifestation of the interference on the signal shape is different in the QTA and the DBD. This fact is illustrated in Figure 1 showing the influence of Se

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3 interferent. The behavior of As and Sb as interferents is analogous as that of Se. When the
4 interference occurs in the QTA, the shape of the analyte signal remains the same as in the
5 absence of the interferent but its height is decreased according to the interferent concentration,
6 as shown in Figure 1A. Such behavior is commonly reported for interferences in the QTA
7 [19]. As noted above, the DBD atomizer can tolerate up to 500 ng mL⁻¹, regardless of the
8 interfering element (see also Table 1). Strong suppressions of 50-70 % occur at concentrations
9 of 5000 ng mL⁻¹ interferent. Moreover, the signal of Bi is completely distorted in the presence
10 of the interferent using the DBD, as depicted in Figure 1B. It is evident that the Bi signal is
11 actually significantly delayed and appears only when the flow of sample (containing analyte
12 with interferent) to hydride generator is replaced by the flow of the blank solution. Different
13 Bi signal shapes in the presence of high concentrations of interferents might arise as a
14 consequence of different mechanism of the interference in the two atomizers. In principle,
15 interference in the QTA may be due to (i) faster decay of free Bi atoms due to formation of
16 Bi-interferent clusters resulting in shorter Bi free atom lifetimes and/or (ii) loss of H radicals
17 required for atomization of bismuthane as a consequence of their consumption by atomization
18 of the hydride interferent, lowering the atomization efficiency of bismuthane [20]. Both of
19 these mechanisms lead to a decrease of the signal. The fact that the Bi signal “re-appears” in
20 the DBD when switching from the sample solution containing a high content of interfering
21 ions to a blank solution indicates that Bi has been partially trapped (in an unknown form)
22 within the DBD instead of being transported outside the atomizer (as some unknown species)
23 in the presence of high amounts of interferent. The trapped Bi species can be subsequently
24 released and atomized when the flow of the blank solution is introduced to the hydride
25 generator, as illustrated in Figure 1B. Such behavior, i.e., analyte trapping in the atomizer in
26 the presence of excess interferent, has never been reported for the QTA, indicating significant
27 differences in the processes taking place in the two atomizers. Trapping of Bi in a DBD
28 atomizer, reported in our previous study [6], occurs when a flow of oxygen (3 mL min⁻¹) is
29 admixed to the Ar discharge gas. The trapped analyte is released and atomized when
30 switching off the oxygen flow and simultaneously pumping the blank solution (thus
31 generating hydrogen) into the system. Trapping of Bi in the presence of oxygen might be
32 explained by the fact that oxygen reacts with hydrogen radicals. The analyte is thus retained
33 instead of atomized under insufficient concentration of H radicals. Interferences in the DBD
34 might be explained in an analogous way. Bismuth is retained in the DBD since excess of
35 interferent hydride leads to consumption of hydrogen radicals required for atomization of
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3 bismuthane. Once the interferent hydride is removed from the atomizer by switching the
4 sample to the blank, hydrogen radical concentration is restored and the trapped Bi species can
5 be released and atomized. This hypothesis might be supported by the fact that interference in
6 the DBD occurs at the same concentration level for all three interferents tested. Another
7 mechanism is likely responsible for the interference observed in the QTA.
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11 The interference study performed in this work has revealed significant differences in
12 their impact on response from Bi in the QTA and DBD atomizers, indicating dissimilarities in
13 their atomization processes. Understanding the atomization mechanisms is important not only
14 for the development of theory, but also for routine analytical problem solving, such as control
15 of interferences. Further experiments were thus performed to understand the fate of Bi
16 following its atomization in either atomizer.
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22 **Effect of hydrogen.** Hydrogen has been demonstrated to play a key role during
23 atomization of hydride forming elements in QTA atomizers and flames, especially employing
24 arsenic and selenium as model hydride forming elements [34-39]. Hydrogen must be present
25 in these types of atomizers to produce analyte free atoms, which is in accord with the widely
26 accepted concept of atomization mechanism based on hydrogen radicals [19]. Welz and
27 Schubert-Jacobs [38] found a 100-fold drop in sensitivity for Sb, As and Sn in the absence of
28 hydrogen using the HG-cryotrapping-AAS approach with atomization in a QTA. The only
29 work focused on the influence of hydrogen on atomization of hydrides in DBD atomizers was
30 published by Zhu et al. [7], who employed HG-cryotrapping experiments to remove hydrogen
31 from the gas phase introduced into the DBD atomizer. Using arsane as a model hydride, the
32 presence of hydrogen in the DBD was found to be essential for production of atomic
33 absorption signals [7]. No such investigation of the influence of hydrogen on atomization of
34 bismuthane has been performed with DBD atomizers. At first, the preconcentration efficiency
35 of bismuthane was determined experimentally by comparison of the peak areas observed in
36 on-line atomization measurements (without cryogenic trap, see Figure S1A for apparatus
37 arrangement) with those found employing the cryogenic trap (see Figure S1C for
38 experimental setup) using the QTA. A flow of 15 mL min⁻¹ H₂ was added to the QTA through
39 the auxiliary gas channel in the experiment with cryogenic trap to keep the same gaseous
40 phase composition as in the experiment in the on-line atomization mode. The overall
41 preconcentration efficiency was quantified to be 92.5 ± 2.4 % indicating complete collection
42 of bismuthane followed by quantitative release of analyte. Subsequently, two sets of
43 experiments with the cryogenic trap (see Figure S1C for experimental setup) were undertaken
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3 for both the DBD and QTA atomizers; the only difference being that hydrogen (15 mL min^{-1})
4 was added to the atomizer through the auxiliary gas channel in one set of experiments
5 whereas no hydrogen was introduced in the second. In both sets of experiments, bismuthane
6 was quantitatively retained in the cryogenic trap and hydrogen readily separated as it is not
7 condensed at liquid nitrogen temperature (Figure S1C). Trapped bismuthane was
8 subsequently released and introduced into the atomizer; results are summarized in Figure S2,
9 providing clear evidence that hydrogen must be present in both devices to atomize bismuthane
10 as no signal is detected in its absence. The results of these cryotrapping experiments suggest a
11 radical mechanism of atomization even in the DBD atomizer. Results with the QTA in the
12 absence of hydrogen, wherein no signal was detected under these conditions, can be compared
13 with those reported by Welz and Schubert-Jacobs [38] who found a 50 % suppression in the
14 Bi signal the in absence of hydrogen. This discrepancy might be caused by the fact that even
15 traces of hydrogen leaking into the QTA from their gas-liquid separator could result in partial
16 atomization of bismuthane, as also observed in our study (data not shown). The gas-liquid
17 separator was thus carefully flushed with He for 180 s to remove any residual hydrogen (see
18 Section S1 of Supporting Information for details) in our experiments. The means taken to
19 ensure all traces of hydrogen were removed in the studies reported in ref. [38] are not known.
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32 **Spatial distribution of free Bi atoms.** The optical path of the DBD atomizer was
33 rotated 90° such that the beam from the superlamp did not pass through the 75 mm optical
34 path of the DBD atomizer as in the conventional mode of AAS measurement (Figure S1A),
35 but rather through one of the ends of the optical arm (Figure S1B). Measurement
36 configuration depicted in Figure S1A is herein termed a “through DBD” measurement mode
37 whereas the configuration presented in Figure S1B is termed a “through end” measurement
38 mode. The optical path length in the “through end” measurement mode is 3 mm and the beam
39 has to pass through both of the quartz walls of the DBD (1 mm thickness). This leads to
40 significant degradation in the source transmission efficiency. For illustration, the absorbance
41 caused by the presence of the DBD atomizer in the optical axis of the spectrometer
42 (conventional “through DBD” mode of measurement) is ca 0.05, whereas that arising from the
43 “through end” measurement was ca 0.8. Although the increased absorbance in “through end”
44 measurement mode was inevitable, the measurements were feasible. The sensitivity in
45 “through DBD measurement” was $0.16 \text{ s ng}^{-1} \text{ Bi}$ whereas it reached only $9 \times 10^{-4} \text{ s ng}^{-1} \text{ Bi}$ with
46 the “through end” measurement mode, thus being almost 180-fold lower. Taking into account
47 that the ratio of the optical path lengths in both configurations was 25, this experiment
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3 revealed that the fraction of free Bi atoms in the extremities of the DBD is very low,
4 indicating their rapid decay towards the end of the DBD. No analogous experiments were
5 performed with the QTA because of a substantial attenuation of the superlamp beam. An
6 analogous sequence of measurements was also performed with Se analyte using a 250 ng mL⁻¹
7 standard solution in order to compare the result with that of another hydride forming
8 element. In this case, the sensitivity in the “through DBD measurement” was 0.44 s ng⁻¹ (in
9 agreement with the sensitivity recently reported [8]), whereas 32-fold lower sensitivity was
10 obtained in the “through end” measurement, which is close to the predicted factor of 25.
11 Clearly, in contrast to rapidly decaying Bi atoms, Se free atoms have a longer lifetime so that
12 their density in the extremities of the DBD is close to their "longitudinal" density.
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20 Based on the results discussed below (see Section Fate of the analyte after
21 atomization) in which pronounced deposition of Bi in QTA was found, it can be assumed that
22 decay of Bi atoms is fast and the fraction of free Bi atoms in the extremities of the QTA is
23 also very low, analogous to the DBD. DART experiments were performed in order to identify
24 any Bi containing compounds transported in the stream of carrier/discharge gas from both the
25 DBD and QTA atomizers.
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30 **DART measurements.** Identification of the species entering as well as leaving both
31 atomizers was attempted using the DART-OrbitrapMS setup in order to gain further insight
32 into the atomization mechanisms. All DART experiments were performed using a 1 μg mL⁻¹
33 standard solution of Bi employing generation and atomization conditions summarized in
34 Table S1. The gas phase from the gas-liquid separator containing carrier Ar, bismuthane and
35 hydrogen was introduced to the front orifice of the DART source in the first experiment. Soft
36 ionization of volatile bismuth species, likely bismuthane, results in production of Bi⁺ and
37 [Bi(OH)_n] species, where n = 1, 2, 3, as shown in Figure 2A. This is the first attempt to couple
38 the hydride generation technique for binary hydrides with a DART soft ionization source and
39 Orbitrap MS detection. Only volatile organometallic compounds [40] or methylarsane [41]
40 have been earlier investigated using this approach. In the second set of experiments, the gas-
41 liquid separator was connected to one of the atomizers (see Section S1 of Supporting
42 Information for details) but it was not in operation, i.e., the QTA was not heated and the DBD
43 plasma was not powered. No difference occurred in the pattern of the mass spectra, with the
44 same structures being observed as in Figure 2A. The intensities of the signals were about 2-
45 fold lower with the atomizers in-line compared to a direct connection from the gas-liquid
46 separator. This loss of signal may arise as a consequence of the different geometry of the
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3 setup; neither of the atomizers can be physically located as close to the DART source as can
4 the outlet of the PTFE tubing from the gas-liquid separator. Analyte response changes
5 substantially when the QTA atomizer is heated to its operational temperature of 900 °C or
6 when the DBD plasma is ignited: no signal is detected under these conditions using either
7 atomizer. Analyte signal re-appears immediately as the DBD plasma is switched off. The
8 QTA must be cooled down to temperatures below 200 °C in order to detect analyte signals
9 again. The effect of QTA temperature on the Bi signal was studied in detail. QTA heating was
10 switched on and the atomizer temperature slowly increased from ambient to 900 °C over a
11 period of 15 minutes. Heating of the QTA was switched off afterwards and the atomizer was
12 allowed to cool while still inserted in the body of the resistively heated furnace. It required
13 about 35 minutes to cool to less than 150 °C and more than one hour to attain ambient
14 temperature. The hydride generator was running continuously during both heating and cooling
15 phases, alternating every minute between measurements made with either a blank or Bi
16 standard solution. A digital thermometer equipped with a K-type thermocouple (BK Precision
17 Corp., USA) was used to monitor temperature profiles. Results are depicted in Figure 2B,
18 showing that the Bi signal completely disappears when the QTA temperature is higher than
19 200 °C during the heating stage and re-appears as soon as the QTA temperature drops below
20 200 °C in the cooling stage. Since the signal from free atoms can obviously be detected in
21 both atomizers by AAS when they are in operation, as discussed above, the fact that no signal
22 is observed with DART detection may be explained as follows: 1) free Bi atoms or any
23 products of their decay are transported outside the atomizers but they cannot be ionized by the
24 DART or, 2) free Bi atoms or any products of their decay are efficiently retained within the
25 atomizers and are not available for transport outside the atomizers. Further experiments were
26 performed to gain deeper insight into this issue. Coupling of the atomizers to the ICP-MS
27 instruments would directly detect any analyte fraction transportable from the atomizers since
28 the ionization capability of the ICP is much higher than that of the DART, although structural
29 information is then lost. Leaching of the interior surfaces of the atomizers using HNO₃ with
30 subsequent determination of Bi in the leachate was also performed in order to quantify the
31 fraction of Bi retained in the atomizer.
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51 52 **Fate of the analyte after atomization.**

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54 **Quantification of Bi fraction transportable from the atomizers** was performed by
55 ICP-*oa*-ToF-MS for the DBD as described in Section S1 of Supporting Information. A 20 ng
56 mL⁻¹ standard solution of Bi was used for continuous hydride generation. Firstly, reference
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3 measurements in two arrangements were performed. Direct connection of the hydride
4 generator to the ICP-*oa*-ToF-MS was realized as the first reference measurement whereas the
5 DBD atomizer (not in operation) connected between the hydride generator and the ICP-*oa*-
6 ToF-MS comprised the second arrangement. No difference in analytical signals between these
7 two arrangements was noted, indicating no losses of bismuthane occur on the inner surface of
8 the DBD when it is not in operation. By contrast, a significant drop in the signal monitored at
9 m/z 209 was observed immediately after the DBD plasma was switched on. The intensity of
10 the signal was only 7 ± 2 (n=5) % of the reference signal, i.e., signal in the absence of the
11 plasma. Analyte signal returned to its original intensity (of the reference signal) immediately
12 after the DBD plasma was switched off. The fact that such a small fraction of the Bi species
13 introduced into the DBD is detected by the ICP provides support for its efficient retention in
14 the atomizer after atomization. However, the possibility that the Bi species may be lost on the
15 quartz surfaces of the connecting tube between the DBD and the ICP cannot be dismissed.
16 Leaching experiments were thus performed to quantify the fraction of Bi retained in the DBD
17 (see section Quantification of Bi in the leachates).
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28 A resistively heated quartz tube was employed to mimic the QTA for the sake of
29 simplicity as described in detail in Section S1 of Supporting Information. The dimensions of
30 this tube, especially the length of its heated axis as well as i.d., are comparable to those of the
31 optical arm of the QTA. A standard 0.1 ng mL^{-1} solution of Bi was employed. The ICP-MS
32 response with the unheated tube was taken as a reference. A significant decrease in Bi signal
33 was observed when the tube was heated to $900 \text{ }^\circ\text{C}$, the optimum atomization temperature used
34 for bismuthane and many other hydride forming elements. Signal intensity reached only 6 ± 2
35 (n=5) % of the reference value. Moreover, the effect of atomization temperature in the QTA
36 on the breakthrough signal, i.e., analyte fraction being transported outside the quartz tube, was
37 investigated in detail with results summarized in Figure S3. This breakthrough signal steeply
38 decreases at tube temperatures above $200 \text{ }^\circ\text{C}$, reaching ca 30 % of the reference signal at 270
39 $^\circ\text{C}$ and 13 % at $390 \text{ }^\circ\text{C}$. The signal remains below 10 % of the reference signal in the range
40 $400 - 950 \text{ }^\circ\text{C}$, as evident in Figure S3. The reference signal can be restored after cooling the
41 quartz tube to ambient temperature. The observation that the breakthrough signal drops
42 significantly above $200 \text{ }^\circ\text{C}$ correlates well with the DART measurements (see Figure 2B).
43 Based on results from both ICP-MS and DART experiments, it can be concluded that the
44 fraction of Bi released from the QTA atomizer is strongly suppressed at atomizer
45 temperatures above $200 \text{ }^\circ\text{C}$. Analyte retention in the QTA when heated to $900 \text{ }^\circ\text{C}$ was
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3 confirmed by determination of Bi in the leachates, as discussed below. Although Bi species
4 were found not to be transported outside the QTA when heated above 200 °C, it is not
5 expected that atomization of bismuthane occurs at temperature as low as 200 °C. To
6 determine the minimum temperature required for significant atomization of bismuthane,
7 additional experiments were undertaken. A set of experiments with the cryogenic trap and
8 AAS detection was performed employing the addition of H₂ through the auxiliary channel as
9 the temperature of the QTA atomizer was raised from 500 to 900 °C. No signal of free Bi
10 atoms was detected at atomization temperature of 500 °C whereas signals at 600 and 700 °C,
11 respectively, were reaching 30 % and 70 % of the signal at 900 °C. It can be concluded that
12 atomization of bismuthane begins around 550 °C and the Bi signal increases with increased
13 temperature. The decreased response observed in both Figures 2B and S3 in the range of 200 -
14 500 °C is thus the result of analyte losses (retention) in the QTA attributable to thermal
15 decomposition and adsorption of bismuthane onto the atomizer surfaces rather than to its
16 atomization.
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27 **Quantification of Bi in the leachates.** HG-AAS measurements were performed
28 (n=50) providing a sensitivity of $0.52 \pm 0.01 \text{ s ng}^{-1}$ and $0.14 \pm 0.02 \text{ s ng}^{-1}$ with the QTA and
29 DBD, respectively. These values correspond well with those found previously [6] (i.e., 0.45 s
30 ng^{-1} for QTA and 0.08 s ng^{-1} for DBD) showing excellent reproducibility of the results. The
31 interior surfaces of both atomizers were subsequently leached using 10 % HNO₃ for 15
32 minutes. The leachates were diluted five-fold with deionized water and the Bi content
33 determined by solution nebulization ICP-MS with calibration standards prepared in 2 %
34 HNO₃. The mass of Bi in the leachate was compared to the total mass of Bi introduced to
35 either atomizer during the consecutive 50 replicates. The concentration of Bi in the blank
36 experiments was negligible. The fraction of the total amount of Bi introduced into the
37 atomizers found in the leachates corresponded to $94 \pm 1 \%$ in the DBD and $92 \pm 3 \%$ in the
38 QTA. These experiments clearly demonstrate that Bi species are almost completely retained
39 in both atomizers once bismuthane is atomized. The products of free atom decay cannot be
40 transported beyond the atomizer region by the stream of carrier/discharge gas and must be
41 rapidly retained on the interior surfaces. The fraction of Bi found in the leachates, together
42 with the fraction of analyte transported to the ICP accounts for 100 % of the total analyte
43 introduced to either atomizer, as summarized in Table 2. As a consequence, analyte losses to
44 the quartz surfaces of any transport tubing connecting the DBD to the ICP torch discussed
45 above can be neglected. Although the spatial distribution of Bi species was not studied in
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3 either of the atomizers, it may be assumed that atomization of bismuthane occurs in the
4 central part of the atomizers, i.e., the hottest zone of the QTA and the active plasma plume of
5 the DBD, i.e. the atomizer section covered by the electrodes, whereas the products of free Bi
6 atoms decay by retention onto the peripheral zones of the atomizers (colder ends of the optical
7 arms of the QTA and ends of the DBD not covered by the electrodes). The high affinity of Bi
8 species for quartz surfaces following atomization or decomposition of bismuthane can be
9 deduced from Figures 2B and S3. The leaching experiment performed with Bi and the QTA
10 can be compared to the analogous one reported by Welz and Schubert-Jacobs [38] with As,
11 for which 21 % was retained in the atomizer when heated to 900 °C. Moreover, additional
12 spatially-resolved leaching was performed in their study [38] in which very little arsenic was
13 found in the central hot zone of the atomizer with most deposited towards the ends of the
14 QTA heated zone. This comparison clearly demonstrates differences among the hydride
15 forming elements arising from their physico-chemical properties.
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27 CONCLUSIONS

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29 Atomization of bismuthane in DBD and QTA atomizers was examined using a
30 combination of spectroscopic techniques, allowing identification and quantification of the
31 fraction of Bi transported outside the atomizers as well as detection of free analyte atom
32 distribution within the atomizer and, finally, to quantify the analyte fraction retained within
33 the atomizer during on-line atomization of bismuth hydride. Data obtained for Bi are
34 encouraging showing the reliability of the methods employed to investigate atomization of
35 hydride forming elements in these atomizers. Although compromise experimental conditions
36 had to be used in some cases, i.e., analyte concentration with respect to the detection limits of
37 the spectroscopic technique or arrangement of gas introduction, the results obtained by AAS
38 and other approaches are rather consistent. This study can thus be taken as a proof of concept
39 of this approach. Understanding the atomization mechanisms is important not only for the
40 development of the related theory, but to help overcome problems arising from analytical
41 applications. Further experiments are in progress employing the same techniques to
42 investigate atomization of As and Se hydrides in the QTA and DBD atomizers.
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15 ASSOCIATED CONTENT

17 Supporting Information

18 The Supporting Information is available free of charge on the ACS Publications website
19 <http://pubs.acs.org/> at DOI:
20

21 <http://pubs.acs.org/> at DOI:
22 Experimental procedures and setup details.

23 Results of the cryogenic trap experiments.

24 Effect of QTA temperature on Bi signal with ICP-MS detection.
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33 The authors declare no competing financial interest.
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List of Tables

Table 1 Effect of other hydride forming elements on response from Bi in QTA and DBD atomizers; constant analyte concentration 5 ng mL⁻¹ Bi (QTA) and 10 ng mL⁻¹ Bi (DBD)

Table 2 Summary of results obtained using different spectrometric detection techniques for QTA and DBD atomizers

Table 1 Effect of other hydride forming elements on response from Bi in QTA and DBD atomizers; constant analyte concentration 5 ng mL⁻¹ Bi (QTA) and 10 ng mL⁻¹ Bi (DBD)

Interferent	Atomizer	Recoveries (%) in the presence of an interferent concentration (ng mL ⁻¹)				
		0	5	50	500	5000
Se ^{IV}	QTA	100 ± 1.7	103 ± 1.5	85 ± 4.1	56 ± 4.8	36 ± 3.1
	DBD	100 ± 4.8	95 ± 2.8	99 ± 4.4	93 ± 7.0	42 ± 5.5
As ^{III}	QTA	100 ± 0.2	99 ± 0.6	102 ± 0.4	102 ± 1.0	101 ± 2.1
	DBD	100 ± 3.9	100 ± 2.4	103 ± 2.1	103 ± 4.8	48 ± 9.0
Sb ^{III}	QTA	100 ± 0.4	100 ± 1.9	101 ± 1.3	77 ± 1.8	68 ± 0.7
	DBD	100 ± 4.2	101 ± 3.5	106 ± 2.2	103 ± 2.9	31 ± 5.0

Table 2 Summary of results obtained using different spectrometric detection techniques for QTA and DBD atomizers

Bi species <i>detected by</i> atomizer	free atoms	breakthrough signal, %		retained in atomizer, %
	<i>AAS</i>	<i>DART</i>	<i>ICP-MS</i>	<i>Leachates (ICP-MS)</i>
QTA	-	ND	6 ± 2	92 ± 3
DBD	0.16 s ng ⁻¹ ^a 9x10 ⁻⁴ s ng ⁻¹ ^b	ND	7 ± 2	94 ± 1

^a sensitivity in the “through DBD” mode of measurement

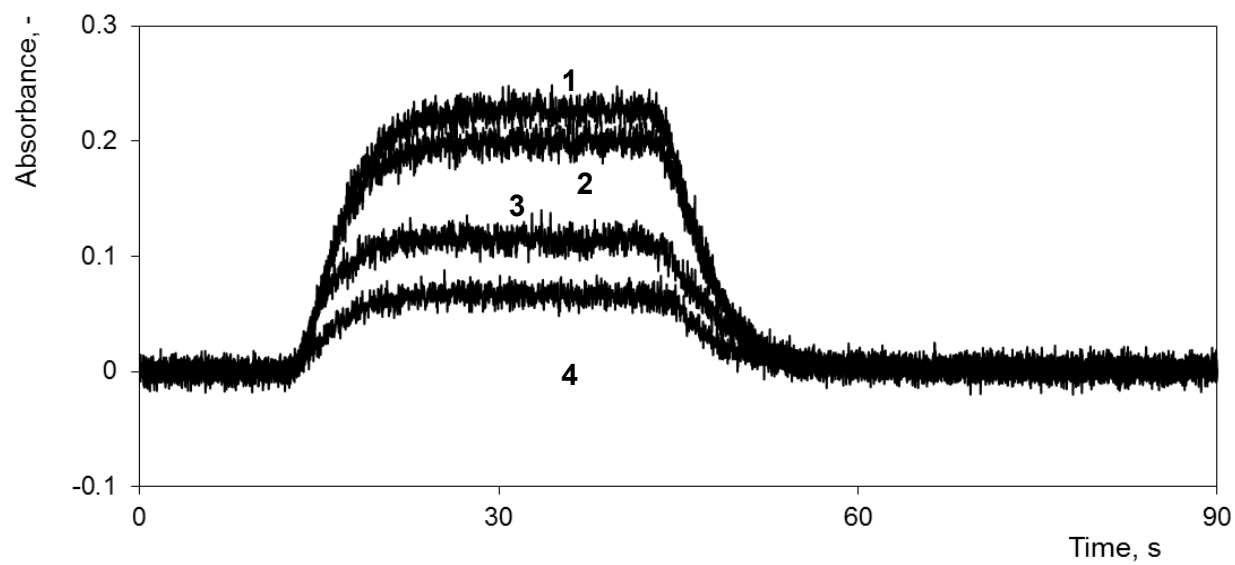
^b sensitivity in the “through end” mode of measurement

Figure Captions

Figure 1 Effect of Se interference on Bi signal in A) QTA and B) DBD; Se concentration 0 ng mL⁻¹ (line 1); 50 ng mL⁻¹ (line 2); 500 ng mL⁻¹ (line 3); 5000 ng mL⁻¹ (line 4);

Figure 2 A) DART mass spectrum arising from bismuthane (1 µg mL⁻¹ Bi standard solution) introduced directly from the gas-liquid separator (DART needle electrode voltage 3.5 kV, 3.5 L min⁻¹ He, gas temperature 100 °C); B) Effect of QTA atomizer temperature on Bi signal (1 µg mL⁻¹ Bi standard solution) using DART (DART needle electrode voltage 3.5 kV, 3.5 L min⁻¹ He, gas temperature 100 °C); temperature profile represented by dashed line; DART signal represented by the bars

A)



B)

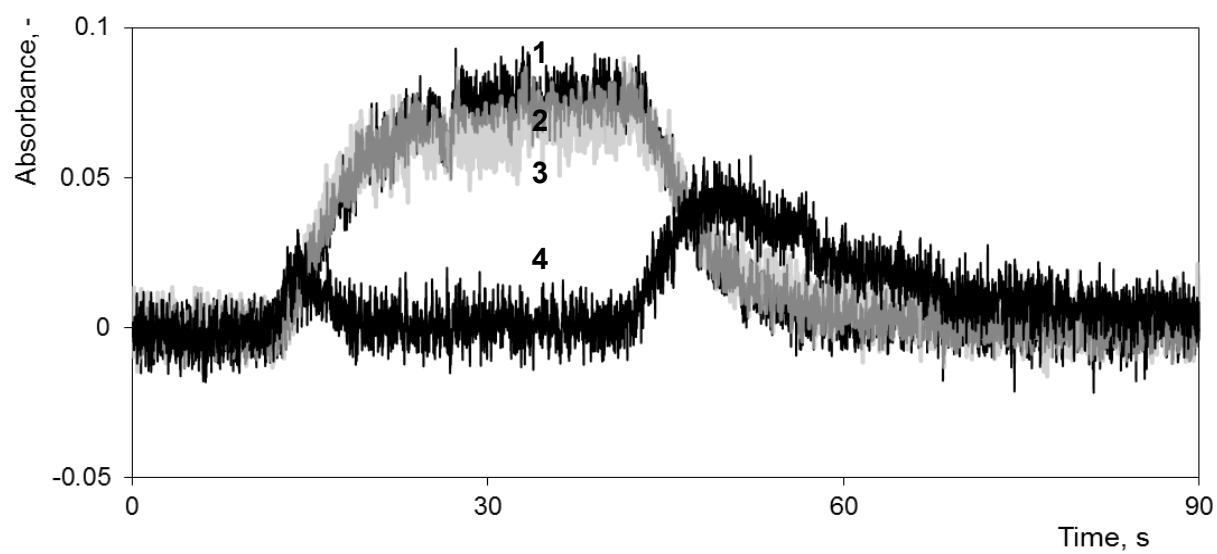


Figure 1

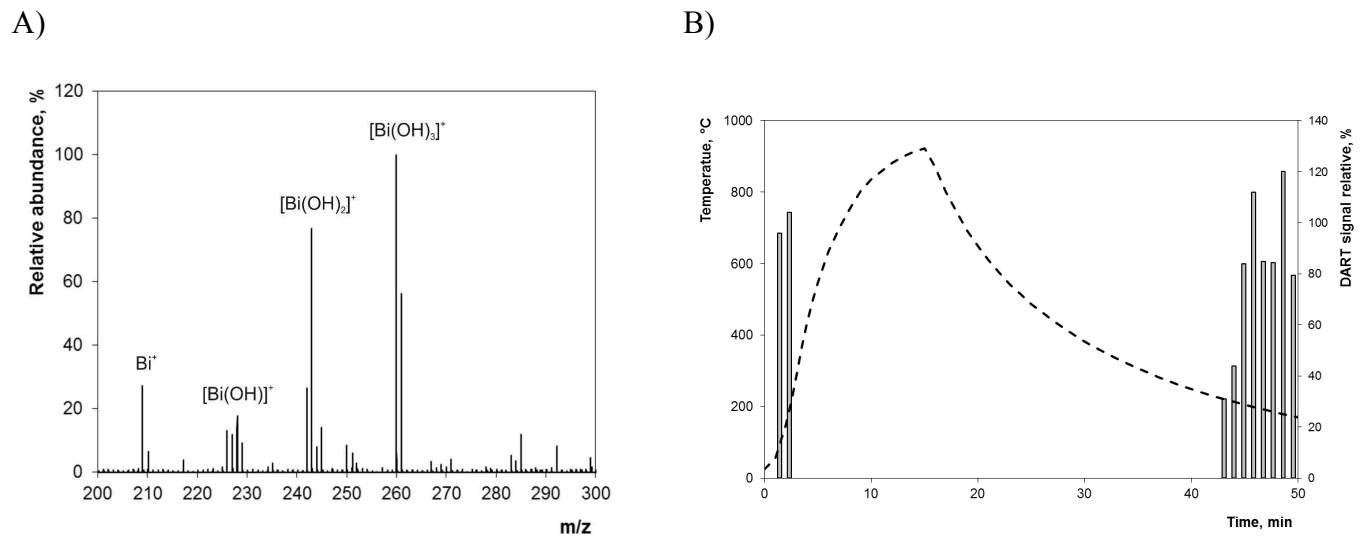


Figure 2

For TOC Only

