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Trace determination of antimony by hydride generation atomic absorption spectrometry with analyte preconcentration/atomization in a dielectric barrier discharge atomizer

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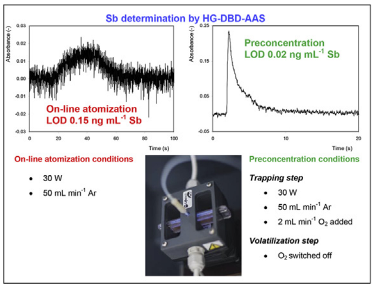
HIGHLIGHTS

- Stibane atomization in a dielectric barrier discharge (DBD) atomizer was optimized.
- DBD atomizer performance compared to that of conventional quartz tube atomizer.
- Limit of detection (LOD) was comparable in both atomizers - 0.15 ng mL^{-1} Sb.
- In situ preconcentration of stibane in DBD atomizer is feasible in presence of O_2.
- Simple and 100% Sb preconcentration in DBD (LOD 0.02 ng mL^{-1} Sb) was reached.

GRAPHICAL ABSTRACT



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ABSTRACT

Atomization conditions for antimony hydride in the plasma atomizer based on a dielectric barrier discharge (DBD) with atomic absorption spectrometric detection were optimized. Argon was found as the best discharge gas under a flow rate of 50 mL min^{-1} while the DBD power was optimum at 30 W. Analytical figures of merit including interference study of As, Se and Bi have been subsequently investigated and the results compared to those found in an externally heated quartz tube atomizer (QTA). The limit of detection (LOD) reached in DBD (0.15 ng mL^{-1} Sb) is comparable to that observed in QTA (0.14 ng mL^{-1} Sb). Finally, possibility of Sb preconcentration by stibane *in situ* trapping in a DBD atomizer was studied. For trapping time of 300 s, the preconcentration efficiency and LOD, respectively, were 103 ± 2% and 0.02 ng mL^{-1}.

1. Introduction

Some elements, including those highly important from toxicological or biological point of view, can be converted to volatile compounds prior to their spectrometric detection employing

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volatile species generation (VSG) as a derivatization and sample introduction technique [1,2]. Generation of binary hydrides (HG) of As, Sb, Bi, Se, Sn, Pb, Te and Ge is the most common approach to VSG for routine analysis [3]. In many cases, VSG minimizes the time and labor consumption during sample preparation. Further benefits of VSG techniques include reduced risk of interference and increased precision. VSG approaches can be combined with virtually any spectrometric detector. Since generation efficiency of hydrides reaches 100% under optimized conditions, HG is capable to improve LOD of given spectrometric detector by a factor of 20 compared to liquid sample nebulization when considering the efficiency of conventional nebulizers to be around 5%. Chemical hydride generation is the most common approach to VSG. It is based on the reduction of analyte ions by $NaBH_4$ to produce volatile species.

Plasma devices based on dielectric barrier discharge (DBD) can be used in many applications in analytical spectrometry as reviewed recently [4,5]. In connection with HG, DBDs are usually used as atomizers in atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS), excitation devices in atomic emission spectrometry (AES), but they may serve also to generate the volatile hydrides [4]. Whereas the first attempts to make use of DBD hydride atomizers in AAS were reported a decade ago using Se, Sb and Sn [6] as well as As [7] as model analytes, externally heated quartz tube atomizers (QTA) and their modifications are the most common atomizers employed since the introduction of HG-AAS in 1970s [3].

The fundamental drawback of the most publications dealing with DBD atomizers of volatile compounds is, with a few exceptions treated below, that they include only optimization of the basic DBD parameters followed by analytical figures of merit quantified for the DBD atomizers only. Neither comparison to any reference atomizer employing the same detector is presented, nor are results of interference studies reported. No effort is made to quantify atomization efficiency in DBD and atomization processes in the DBD plasma are not understood. As a consequence, it is difficult to judge the applicability of the methods reported with such a limited amount of information.

Detailed investigations of DBD atomizers of volatile hydrides have been performed in our laboratory since 2013 to bridge this gap in which atomization performance of DBD in comparison with QTA has been compared for Bi [8], Se [9] and As [10]. Atomization conditions in DBD were optimized individually for each element. The detection limit of Bi in DBD ($1.1\ ng\ mL^{-1}$) is significantly worse than with the QTA ($0.16\ ng\ mL^{-1}$) [8]. On the contrary, the detection limits reached for Se in the DBD ($0.24\ ng\ mL^{-1}$) and QTA ($0.15\ ng\ L^{-1}$) are quite comparable [9]. The same trend was observed for As for which LODs of $0.15\ ng\ mL^{-1}$ in QTA and $0.16\ ng\ mL^{-1}$ in DBD, respectively, were observed [10]. Moreover, a simple procedure of lossless *in situ* preconcentration of arsane in DBD atomizer was developed offering the decrease of detection limit by an order of magnitude [10].

In the only report on DBD application to atomization of stibane (SbH_3) with AAS detection [6], no effort was made to compare the DBD performance with that of a common QTA atomizer.

The aims of this work were to: 1) optimize stibane atomization conditions in a DBD atomizer, 2) compare DBD atomizer performance and analytical figures of merit including interferences with those of a commonly used QTA, 3) evaluate DBD applicability in analytical routine and 4) test the possibility of *in situ* stibane preconcentration in a DBD atomizer.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade or higher purity. Deionized water ($<0.1\ \mu S\ cm^{-1}$, Ultrapure, Watrex, USA) was used to prepare solutions. Working Sb standards were prepared fresh daily from $1000\ mg\ L^{-1}$ Sb stock solution (Fluka, Germany) by dilution in $1\ mol\ L^{-1}$ HCl (Merck, Germany). A blank consisted of $1\ mol\ L^{-1}$ HCl. The reductant was a 0.5% (m/v) solution of $NaBH_4$ (Sigma Aldrich, Germany) in 0.4% (m/v) KOH (Merck, Germany) filtered after preparation and stored frozen. A certified reference materials SRM 1643e (NIST, USA, trace elements in water) and TM-RAIN-04 (fortified rainwater) purchased from Environment Canada (Canada) with defined Sb content were employed to assess the accuracy and precision of the results. KI (≥99.5%, Sigma Aldrich, Germany) and L(+) ascorbic acid (p.a., Riedel-de Haën, Germany) were used for antimony prereduction in the certified reference material. For interference studies, the $1000\ mg\ L^{-1}$ stock solutions of As(III), Se(IV) both purchased from Fluka, Germany and Bi(III) (Sigma Aldrich, Germany) were used to prepare the working solutions in $1\ mol\ L^{-1}$ HCl containing constant Sb concentration as analyte. Hydrofluoric acid (38% (m/v), p.a., Spolchemie, Ústí nad Labem, Czech Republic) and nitric acid (65%, p.a., Lach-Ner, Czech Republic) were used to clean the atomizers if necessary. If explicitly stated, a surface modification (passivation) of the inner surface of the DBD chamber was performed using a 5% solution of dimethyldichlorsilane (DMDCS) in toluene (Sylon CT solution produced by Supelco, USA). Compressed gases Ar (99.996%), He (99.998%), N_2 (99.99%), H_2 (99.95%) and O_2 (99.5%) were produced by SIAD Czech, Ltd. Air was supplied by a local compressor.

2.2. Instrumentation

A GBC model SavantAA atomic absorption spectrometer (GBC, Australia) was employed without background correction. A Photron Sb Superlamp (Photron Ltd., Australia) operated at 217.6 nm line with 0.2 nm spectral bandpass and a lamp current of 15 mA (boost current 8–15 mA).

2.3. Hydride generator

An in-house made, flow injection hydride generation system based on peristaltic pump (Ismatec, Switzerland) was employed together with a 3 ml inner volume gas-liquid separator (GLS) with a forced outlet. Gas flows of a carrier/discharge gas (Ar if not explicitly stated otherwise) for both atomizers as well as other auxiliary gases, if necessary, were controlled by mass flow controllers (Omega Engineering, USA). See Table 1 for optimum experimental conditions for stibane generation and Fig. 1 for schematic diagram of the hydride generator. The gaseous phase at the GLS outlet always contains, apart from the carrier/discharge gas and stibane, also $15\ mL\ min^{-1}$ of hydrogen evolved as a side-product from $NaBH_4$ decomposition as found experimentally. For the sake of simplicity the carrier/discharge gas is termed according to its major gas component, i.e. Ar or He, etc., further in the text even though containing this hydrogen fraction. If explicitly stated a semipermeable polytetrafluorethylene PTFE filter (disc filter 30 mm in diameter, porosity 0.45 μm) produced by Whatman (UK) was inserted downstream the GLS to remove aerosol co-generated in the hydride generator.