

Determination of Germanium Species by Hydride Generation Atomic Absorption Spectrometry: Comparison of Atomizers Based on Diffusion Flame, Heated Quartz Tube, and Dielectric Barrier Discharge Plasma

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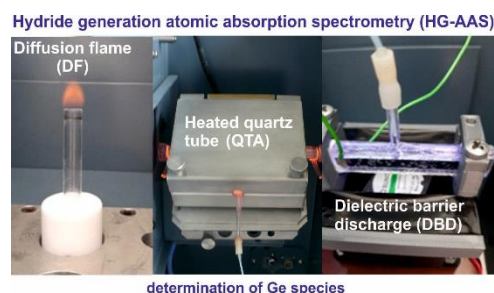
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ABSTRACT: Atomization of three volatile germanium species including germanium hydride (GeH_4) and its two methyl-substituted analogues – monomethyl germanium hydride (CH_3GeH_3) and dimethyl germanium hydride ($(\text{CH}_3)_2\text{GeH}_2$) for their detection by atomic absorption spectrometry after hydride generation was comprehensively investigated. Three types of hydride atomizers based on diffusion flame (DF), multiple microflame quartz tube atomizer (MMQTA) and dielectric barrier discharge (DBD) were optimized for atomization of Ge species. In MMQTA, the supply of air and the use of gas phase dryer are the crucial parameters affecting the sensitivity. The presence of the dryer is essential also for DBD atomizer. Sensitivity was quantified under optimized conditions reaching around $2 \text{ ms ng}^{-1} \text{ Ge}$ in DF and $3 \text{ ms ng}^{-1} \text{ Ge}$ in MMQTA atomizers, respectively. The highest sensitivity of $10 \text{ ms ng}^{-1} \text{ Ge}$ was observed in DBD. When compared to other hydride forming elements the sensitivity observed for Ge species is two orders of magnitude worse in MMQTA, 10-50 times lower in DBD and 5 times worse in DF. In given atomizer type, the sensitivity is comparable for all three Ge species indicating the same atomization efficiency. The fraction of Ge deposited in the DBD and MMQTA atomizers, respectively, after atomization of GeH_4 was quantified to 80%. Fast decay of free Ge atoms and their deposition at the inner walls of the atomizer might explain low sensitivity observed for Ge determination by atomic absorption spectrometry. Effect of L-Cysteine (L-Cys) addition to liquid standards on response of Ge species was also investigated.



INTRODUCTION

Germanium belongs to the recently defined group of Technology Critical Elements (TCE).¹ Although being quite rare in nature, they are increasingly used and vital for modern technologies such as telecommunications, semiconductors, electronic displays, optic/photonic and energy-related technologies.¹ As a consequence, their increased use brings the issue of environmental impact and necessity of analytical methods development to measure their natural levels and assess changes due to anthropological activities.

The methods of analytical atomic spectrometry are generally the first analytical methods of choice for trace and ultratrace determination of elements and especially metals and metalloids.

They include in particular atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS) and inductively coupled plasma (ICP) either with optical emission (OES) or mass spectrometry (MS). These detectors commonly rely on liquid sample nebulization as sample introduction technique. However, the nebulizers employed suffer from relatively low introduction efficiency ranging typically between 5-10%. The sensitivity of any atomic spectrometric detector can be, for some analytes, further improved by using hydride generation (HG) or related volatile species generation (VSG) techniques instead of sample nebulization.^{2,3}

HG and VSG is based on selective analyte conversion to a corresponding volatile compound, typically a hydride or cold vapor. This strategy yields much higher introduction efficiency

which approaches 100% under optimized conditions surpassing thus 10-20 times the efficiency of conventional nebulizers. Moreover, selective analyte conversion from liquid to gas phase by HG or VSG results not only in enhanced analyte introduction efficiency but also in analyte separation from the sample matrix, leading to a reduced risk of interference.^{2,4} The applicability of HG step is restricted to hydride-forming elements only, including eight metals/metalloids such as As, Se, Sb, Bi, Pb, Sn, Te and also Ge.² However, hydride generation step can be applied not only to determine the ionic (inorganic) form of given hydride forming element, e.g. $\text{As}^{3+/5+}$ or $\text{Ge}^{2+/4+}$, but it can be often used also to quantify other “hydride active” species of the same element present in the liquid sample. Thus, also other chemical forms, typically simple organometallic species, e.g. alkylated compounds, could be converted to volatile species.^{4,5} Determination of such species is, by coincidence, important from clinical, toxicological or environmental point of view. Various species of the same element might have different physico-chemical properties that is also reflected in their different toxicity, bioavailability or mobility in the environment. As a consequence, quantification of individual species of given element, *i.e.* speciation analysis,⁶ is preferred to determination of total element content. The most explored speciation analysis methods that benefit from HG step are targeted at arsenic. They allow to perform As speciation analysis in clinical (blood, urine, epithelial cells)⁷⁻⁹ or food (seafood, rice)^{10,11} samples. The “hydride active” species here include: inorganic As (arsenite and arsenate) both converted by HG to arsane (AsH_3) while the alkylated (methylated) As species are derivatized to corresponding methyl-substituted hydrides by HG. Thus, HG from methylarsonate leads to formation of volatile methylarsane (CH_3AsH_2) while dimethylarsinate in the liquid sample gives rise to a gaseous dimethylarsane ($(\text{CH}_3)_2\text{AsH}$). Determination of methylated arsenic species is important from medical and toxicological point of view since these compounds are products of human metabolic pathways of arsenic. Analogous chemical structures of “hydride active” species can be found also for germanium which speciation analysis is important from environmental point of view. Inorganic germanium (Ge^{2+} or Ge^{4+}), monomethyl germanium ($\text{CH}_3\text{Ge}^{3+}$) and dimethyl germanium ($(\text{CH}_3)_2\text{Ge}^{2+}$) are the three major species of germanium present in the environment¹². All these three Ge species can be converted by HG to corresponding volatile species, *i.e.* a hydride (GeH_4) and its methylated analogues CH_3GeH_3 and $(\text{CH}_3)_2\text{GeH}_2$, respectively. Concentration trends of Ge species in the environment and their mutual transformations in (bio)geochemical cycles are now in focus as the industrial consumption of Ge as TCE is increasing. A sensitive method for determination of all these three Ge species based on coupling of HG step with subsequent ICP-MS detection was developed recently¹³ and applied successfully to speciation analysis of Ge in lake water.¹⁴

Coupling of HG step with subsequent AAS detection might be a good compromise when searching for a simple, robust, cheap but

still enough sensitive analytical technique for determination of hydride forming elements and hydride active species. Externally heated quartz tube atomizers (QTA) including their advanced designs, such as multiple microflame quartz tube atomizer (MMQTA), are the most common hydride atomizers in AAS characterized by high sensitivity^{2, 15-17}. Addition of air or oxygen to MMQTA through the outer (auxiliary) gas channel increases sensitivity in case of As,^{18,19} Sn,^{20,21} Se,^{18,22,23} and Te²³ determination benefiting thus from MMQTA construction. The sensitivity reached in QTA/MMQTA is quite comparable among seven hydride forming elements including As, Se, Sb, Bi, Te, Pb and Sn. The dielectric barrier discharge (DBD)^{3, 24} can also be effectively employed for hydride atomization in AAS as proven recently.^{3, 25-27} The first report by Zhu et al. on the use of DBD hydride atomizer dates back to 2006 using the DBD to atomize As hydride and its methyl-substituted analogues.²⁷ Unlike other hydride forming elements, atomization of Ge hydride in a DBD atomizer has never been investigated before to the best of our knowledge. The sensitivity reached for hydride forming elements in DBD atomizers is strongly element dependent. It is comparable with the sensitivity reached in QTA/MMQTA for some analytes such as As,¹⁹ Se,^{22, 23} Sb,²⁸ and Te^{23, 29} while being significantly lower in DBD for the others including Bi^{23, 30} and especially Pb^{23, 31} and Sn.²⁰ Apart from QTA and DBD atomizers the hydride forming elements can also be atomized in the atomizers based on diffusion flame (DF) or graphite tube (GT).^{2, 15} DF is commonly used in AFS rather than AAS since its short optical path is responsible for low sensitivity in AAS leading to 50 times lower signals when compared to QTA or MMQTA.^{2,15,32} The GT atomizer, if employed for hydride atomization, is combined with in-situ preconcentration (trapping) of the volatile hydride directly in the GT.^{2, 15} Atomization of methylated hydrides was studied in detail only for arsenic species showing the atomization efficiency is the same among the volatile species investigated (AsH_3 , CH_3AsH_2 and $(\text{CH}_3)_2\text{AsH}$) in given atomizer as proven for DF,³³ MMQTA,³⁴ and DBD.³⁵

The disproportion of works based on HG-AAS published on Ge compared to other hydride-forming elements as analytes is obvious at first glance. The reason why Ge determination by HG-AAS is so rarely reported is the extremely low atomization efficiency of GeH_4 in both QTA and flame atomizers (air/ C_2H_2 ; $\text{N}_2\text{O}/\text{C}_2\text{H}_2$; air/ H_2) observed already in 1980's and caused most probably due to its tendency to form stable oxide species.^{2,36} Better results were reached when GT atomizer was employed with AAS detection.³⁶⁻³⁸ Nevertheless, even the use of GT atomizer for on-line atomization of GeH_4 or other Ge volatile species has not been widely used since GT atomizer cannot be maintained at atomization temperatures (2600 °C) for prolonged times.² With further development of analytical instrumentation, the AAS detector was replaced by ICP-MS detection of Ge species.^{13, 14} Since new types of hydride atomizers have emerged (*e.g.* MMQTA,^{16, 17} DBD²⁴⁻²⁷) and the hydride atomization processes

were better understood since 1980's³⁹ it is worth to revise the potential of HG-AAS for speciation analysis of Ge.

The objective of this work was to assess the performance of various hydride atomizers based on flame, plasma, and heated quartz tube to determination of three analytically relevant Ge species by HG-AAS in a systematic and comprehensive way. Atomization of GeH₄ (termed as iGe further in the text) and its methylated analogues, (CH₃)GeH₃ (MMGe), and (CH₃)₂GeH₂ (DMGe), in common hydride atomizers was investigated including the (i) MMQTA as advanced construction of QTA; (ii) two configurations of DBD based atomizers and (iii) the diffusion flame (DF). The optimizations were carried out individually for each atomizer and Ge species. In addition to optimizing the atomization step, attention was also paid to the HG step for which the effects of L-Cysteine addition and stability of signal response during the standard ageing were studied. Analytical figures of merit such as sensitivity and limit of detection (LOD) were determined for all Ge species tested in each hydride atomizer under optimum conditions. The extent of interaction of the atomization/decay products of Ge species with the inner surface of the atomizers was quantified by leaching the deposits with subsequent determination of Ge content in the leachate by ICP-MS/MS.

EXPERIMENTAL

Chemicals. All reagents were of analytical grade or higher purity. The solutions and dilutions were made with deionized water (< 0.1 mS cm⁻¹, Ultrapur, Watrex, USA). Tris buffer (termed TRIS-HCl further in the text) was prepared from Trizma® hydrochloride (Sigma Aldrich, Germany) with pH adjusted by NaOH to 6.5. Ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) produced by Lachema, Czech Republic was added into a TRIS-HCl buffer to reach its 0.005 mol l⁻¹ concentration. The reductant was solution of NaBH₄ (Sigma Aldrich, Germany) in 0.1% (m/v) KOH (Lach-Ner, Czech Republic) filtered after preparation and stored frozen. Working standards of Ge species, typically at 1 mg l⁻¹ concentration level, were prepared fresh daily from their 1 000 mg l⁻¹ solutions by dilution with 0.25 mol l⁻¹ TRIS-HCl. A commercial standard of iGe (1 000 mg l⁻¹, Astasol®) was purchased from Analytika, Czech Republic while the solutions of MMGe and DMGe were prepared in the laboratory by hydrolysis and dilution of (CH₃)GeCl₃ and (CH₃)₂GeCl₂, respectively, both purchased from Alfa Aesar, UK. L-Cysteine hydrochloride monohydrate (biochemistry grade, Merck, Germany), further abbreviated as L-Cys, was added at 1% (m/v) concentration into the standards of MMGe and DMGe to enhance their conversion to volatile species. Solid NaOH pellets (p.a., Penta, Czech Republic) were used as a filling of the gas phase dryer (see below). In some experiments also a filling realized by NaOH pearls

(diameter ≥ 2 mm purchased from Lach-Ner, Czech Republic) was employed or a dryer based on a Nafion™ membrane (tube model MD-110-12P, 12" long, 0.11" i.d., Perma Pure, USA) was tested. If explicitly stated, a surface modification (passivation) of the inner surface of the DBD atomizer was performed using a 5% solution of dimethyldichlorsilane (DMDCS) in toluene (Sylon CT solution produced by Supelco). To clean the hydride atomizers prior to their first use or for the purpose of the leaching experiments performed a 3:7 (v v⁻¹) mixture of hydrofluoric acid (38%, Spolchemie, Czech Republic) and nitric acid (65%, Lach-Ner, Czech Republic) was used. The gases used Ar (99.996%), He (99.998 %), N₂ (99.99 %), and H₂ (99.9%) were purchased from SIAD Czech Ltd. (Czech Republic). Air delivered by a compressor in a laboratory was used in the experiments with multiatomizer (see below).

Hydride generator. An in-house made, flow injection hydride generation system based on a peristaltic pump (Ismatec, Switzerland), analogous to that described in refs.^{23, 32} was employed. Standards of Ge species were injected manually by a six port injection valve (V-451, IDEX Health&Science, USA) with a loop of 0.50 ml volume into the flow of the TRIS-HCl buffer (1.0 ml min⁻¹) before mixing with the reductant (1.0 ml min⁻¹). The reaction mixture was merged downstream with a flow of carrier Ar controlled by a mass flow controller (Omega Engineering, USA) and directed to the quartz gas-liquid separator (GLS) with a forced outlet. The liquid waste was drained by the same peristaltic pump from its bottom. Apart from the volatile Ge species generated the gas phase directed from the GLS to the atomizer by a stream of Ar carrier gas, contains hydrogen produced as a side-product of NaBH₄ decomposition and some amount of aerosol/water vapor being co-generated together with volatile analyte species. The amount of co-generated H₂ was 8 ml min⁻¹ as found experimentally. If not stated otherwise, a dryer made of a polypropylene cartridge (100 mm long, 15 mm i.d.), filled with solid NaOH pellets was inserted downstream of the GLS to prevent aerosol and droplets from entering the atomizer. If explicitly stated, other types of gas phase dryers based either on solid NaOH pearls, or Nafion™ membrane (with a drying gas flow rate of 1.0 l min⁻¹ Ar) were tested. No dryer was employed in some of the experiments. The optimum generation conditions for all three Ge species are summarized in Table 1. The hydride generator employed is schematically depicted in Fig. S1.

Hydride atomizers

DBD atomizer designs. Two quartz DBD atomizer designs with a planar configuration of the electrodes, described in detail earlier^{23, 32, 40} were employed. Both had the same T-shaped quartz body consisting of a rectangular horizontal (optical) arm (7 mm × 3 mm inner cross-section) and a length of 75 mm. This arm was adjusted into the optical axis of the AAS spectrometer. Its horizontal and

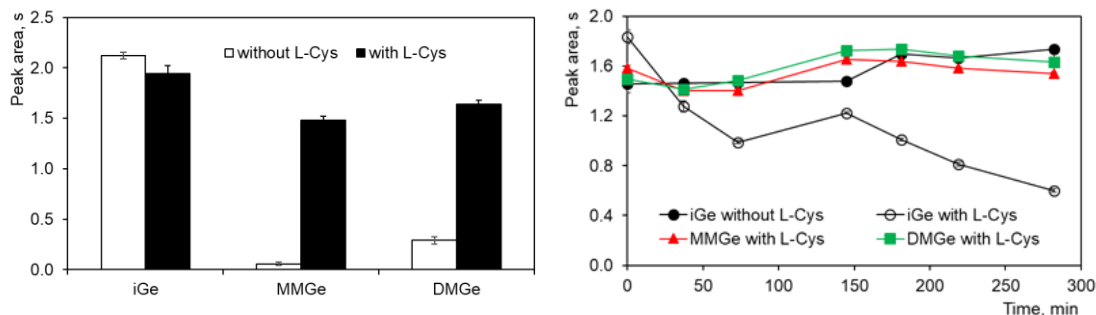


Fig. 1 Effect of L-Cys addition (A) and standard ageing (B) on signal of Ge species. Concentration of Ge species standards $2 \mu\text{g ml}^{-1}$ ($1 \mu\text{g Ge absolute}$). DF atomization conditions as listed in Table 2.

gas phase from the hydride generator containing (i) Ge hydride or its methylated analogues, (ii) carrier Ar (termed as Ar_{HG} in Table 2), and (iii) co-generated hydrogen (from NaBH_4 decomposition). Moreover, an additional flow of Ar was introduced via a T-connector to the side inlet arm of the DF atomizer to support the diffusion flame burning on the top of the support tube. The observation height is defined as the distance from the very top of the support tube to the centre of the optical beam. Observation height of 1 mm was employed in all the experiments. DF atomizer was cleaned prior to its first use or if necessary. The atomizer was turned upside down and the top part of its support tube (ca 20 mm long) was soaked into the polypropylene centrifuge tube filled with a mixture of concentrated HNO_3 and HF (7:3) for 10 minutes. Subsequently, the top part of the tube was flushed by deionized water several times and left to dry.

All the hydride atomizers employed in this work are schematically depicted in Fig. S2.

Atomic absorption spectrometry. A SavantAA atomic absorption spectrometer (GBC, Australia) was employed without background correction. A Ge hollow cathode lamp (Photron Ltd., Australia) operated at 265.2 nm analytical line with 0.5 nm spectral bandpass and a lamp current of 5 mA. Measurements were performed in a flow injection mode. The hydride generator was operated continuously (peristaltic pump running), while the standards of Ge species were manually injected into the carrier liquid (TRIS-HCl buffer) stream 5 s after the recording of the signal had started. A transient signal was recorded. GBC SavantAA software version 3.02b1 was used for evaluation of peak area. Averages from at least 5 replicate measurements were recorded; error bars in the figures represent standard deviation.

Quantification of Ge fraction deposited in the atomizers. Deposition of Ge in the atomizers employed was investigated in order to understand the atomization processes. A series of 50 replicate measurements under optimum atomization conditions was performed in a pre-cleaned atomizer. Subsequently, the atomizers were leached by HNO_3 and HF mixture and the amount

of deposited analyte was quantified by inductively coupled plasma mass spectrometry with liquid nebulization (ICP-MS/MS). Experimental details are provided in Supporting Information (section 1.2).

RESULTS AND DISCUSSION

Preliminary experiments. The preliminary experiments were employed to (i) verify the optimum generation conditions of all three germanium species reported previously¹³ and their adaptation to the current hydride generation system if necessary as well as to (ii) check the stability of the working Ge species standards during the day. For the sake of simplicity, the preliminary experiments were performed with DF as the atomizer (see Table 2 for DF atomization conditions).

The parameters affecting generation of Ge species include: concentration of both the reductant (NaBH_4) and the TRIS-HCl buffer carrier solution, reaction coil length and argon carrier gas flow rate. Their effect on signal response is in detail discussed in Fig. S3 and section 2.1 of Supporting Information.

Addition of L-Cys as reaction modifier has been previously reported¹³ to enhance generation efficiency of Ge species in general. In a follow up study focused on Ge speciation analysis in real samples by HG-CT-ICP-MS two aliquots of the same sample have been measured to determine iGe in absence of L-Cys while MMGe and DMGe were quantified in presence of L-Cys but with no further discussion on such an approach.¹⁴ As a consequence, two sets of experiments were performed to investigate the influence of L-Cys addition together with the effect of standard ageing on response of individual Ge species. In the first experiment the standards of iGe, MMGe and DMGe were prepared with and without the addition of L-Cys being analysed 30 min after preparation. The results are depicted in Fig. 1A showing clearly the presence of L-Cys is essential for generation of methyl-substituted Ge hydrides since the signal of MMGe and

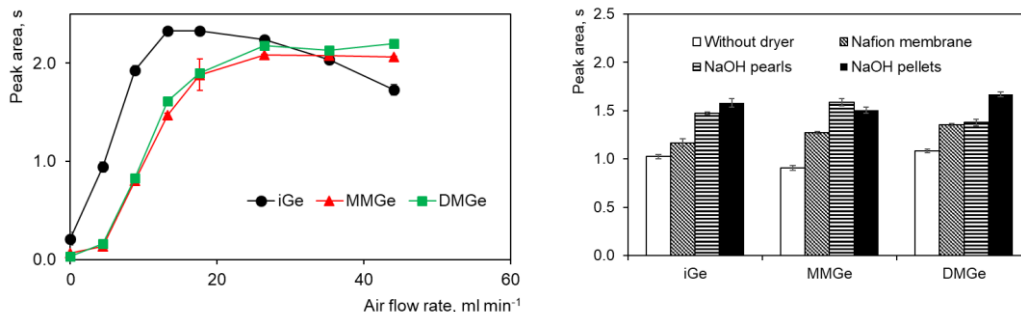


Fig. 2 Effect of outer air flow rate to MMQTA (A) and the dryer (B) on signal of Ge species. Concentration of Ge species standards 2 $\mu\text{g ml}^{-1}$ (1 $\mu\text{g Ge}$ absolute). MMQTA atomization conditions as listed in Table 2.

DMGe in absence of L-Cys is only 4% and 17%, respectively of that in its presence. On the contrary, the role of L-Cys is negligible in case of iGe. However, the presence of L-Cys has a negative effect on signal stability of iGe in time as shown in Fig. 1B resulting in gradual decrease of its signal during the day reaching only 30% of the original value after 5 hours from its preparation. In contrast, the response of MMGe and DMGe working standards with L-Cys added was found constant within the longest period of 5 hours studied. Based on these observations, no L-Cys has been added to iGe standards while L-Cys has been always added to the standards of MMGe and DMGe. Under such conditions the working standards of Ge species could have been used all day long being prepared freshly every morning. The explanation of the mechanism of action of L-Cysteine is beyond the scope of this work. Analogously to studies performed for other hydride forming elements a formation of analyte-(L-Cys) or borane-(L-Cys) complexes can be expected affecting the reaction mechanism and kinetics of volatile Ge species formation and release from the reaction mixture³.

Optimum hydride generation conditions for iGe, MMGe and DMGe are summarized in Table 1.

Diffusion flame. Parameters optimized for DF include the flow rates of H_2 and Ar_{flame} as well as their ratio, observation height and effect of gas phase dryer. Only iGe was used as model analyte to find the optimum atomization conditions in DF. The only exception was the effect of gas phase dryer which was investigated for each of Ge species. Optimization of gas flow rates supplied to the DF, *i.e.* H_2 and Ar_{flame} , and their ratio is discussed in detail in Fig. S4 and section 2.2 of Supporting Information.

The dryers based on Nafion membrane, NaOH pearls and NaOH pellets were tested one by one. The signal of all Ge species, *i.e.* iGe, MMGe and DMGe, was compared in presence and absence of the dryer. When setting the signal of individual Ge species in DF atomizer and in presence of a dryer consisting of NaOH pellets to a reference value of 100%, the signals in presence of other dryers or without any dryer were in the range of $\pm 10\%$ of

this value (see also Fig. S4D). It can be deduced that none of the dryers tested retains the volatile Ge species generated. The compatibility of given dryer with particular analyte has to be always carefully verified. Nafion membranes as inert surfaces were reported not to trap analyte hydrides (Pb, Bi, Se, Te)²³ while the applicability of NaOH based dryers is strongly element dependent. No losses of As¹⁹ and Sn²⁰ hydrides were observed in presence of NaOH dryer whereas a quantitative retention resulting in complete loss of analyte signal was reported for hydrides of Pb, Bi, Se, and Te²³ when employing the same dryer. Both NaOH based dryers as well as the Nafion tube were selected for further testing with MMQTA and DBD atomizers.

Optimum atomization conditions in DF are summarized in Table 2.

Multiple microflame quartz tube atomizer. Outer air and carrier Ar flow rates, atomization temperature and the effect of the dryer were the parameters to be optimized in MMQTA atomizer. The trends observed were analogous for all three Ge species investigated. Ge species cannot be atomized at MMQTA temperature of 600 °C or lower. Ge response is steeply increasing with increased atomization temperature (see Fig. S5A) up to 800 °C reaching a plateau or slightly declining due to gas expansion between 850 and 1 000 °C. Atomization temperature of 900 °C was selected as optimum. The effect of Ar carrier gas on the response of Ge species is shown in Fig. S5B. The signal is decreasing monotonously as the flow rate increases from 50 to 200 ml min^{-1} Ar. At the highest flow rate the signal of iGe and MMGe reaches around 50% and that of DMGe about 75% of the maximum signal (see Fig. S5B). The flow rate of 100 ml min^{-1} Ar was selected as optimum being a compromise between sensitivity and peak shape.

The introduction of outer air improves sensitivity of all Ge species dramatically as shown in Fig. 2A. In absence of outer air the signal of Ge species is almost negligible, increasing significantly up to 15 ml min^{-1} for iGe and 20 ml min^{-1} of outer air in case of MMGe and DMGe reaching a plateau or decreasing

slightly (iGe) at higher supply rates of air. An optimum flow rate of 25 ml min⁻¹ outer air was employed as a compromise for all three Ge species. Analogous behavior, *i.e.* positive effect of outer air supply into the MMQTA on analyte response, was observed previously for hydrides of As^{18,19}, Sn^{20,21}, Se^{18,22,23} and Te²³. The role of outer air resides, in accord with the hydrogen radical theory of hydride atomization³⁹, in enhanced production of hydrogen radicals resulting in higher efficiency of analyte hydride atomization and/or slower decay of its free atoms. Hydrogen radicals are produced in the MMQTA by the reaction between H₂ produced spontaneously in the hydride generator during NaBH₄ decomposition and O₂ supplied to the atomizer in the form of outer air. Interestingly, the signal of Ge species is improved when gas phase dryer is employed (see Fig. 2B). Such an observation is not common for other hydride forming elements and atomizers based on QTA/MMQTA since the hot environment of the atomizer is expected to cope easily with any aerosol or spray droplets co-generated with analyte hydride and transported into the atomizer. The dryer based on NaOH pellets was found as the most effective one followed by NaOH pearls while signals lower by *ca* 20% and even 40% lower, respectively, were observed with Nafion membrane dryer and in absence of any dryer. A gas phase dryer packed with NaOH pellets was chosen for further measurements.

Dielectric barrier discharge plasma atomizers

REF-SIN configuration. Only iGe was employed as a model analyte for optimization studies in the REF-SIN arrangement of the DBD atomizer design since better results in terms of peak shape could be reached in the SE-SW arrangement as discussed below. The only exception were the experiments with gas phase dryers for which standards of all three Ge species were employed. The results are depicted in Fig. S6. The REF-SIN configuration can be operated in various discharge gases including argon, helium, nitrogen, and hydrogen. The highest response was observed in Ar and H₂, but the signal repeatability in H₂ discharge was much worse compared to Ar (see Fig. S6A). The signal in He as discharge gas was about one third lower compared to Ar while the signal in nitrogen was almost negligible (Fig. S6A). As a consequence, Ar was selected as the best discharge gas. Analogous observations regarding the effects of the discharge gas nature on sensitivity have been made previously also for other hydride forming elements including As¹⁹, Sb²⁸, Bi³⁰, Se²², Te²⁹, Sn²⁰ and Pb³¹. Ar flow rate was optimized as shown in Fig. S6B. The discharge is quite unstable at the flow rate of 50 ml min⁻¹ Ar or lower. As a consequence, the response of iGe standard was investigated in the range between 100 and 600 ml min⁻¹ Ar. The Ar flow rate to the DBD was splitted into two streams in these experiments. A flow rate of 100 ml min⁻¹ Ar was added through the hydride generator while the rest (0-500 ml min⁻¹ Ar) was supplied via a polypropylene T-connector downstream the GLS. This arrangement ensures compatibility of the hydride generator with Ar flow. The response of iGe is decreasing monotonously

with increased Ar flow rate due to dilution of free analyte atoms by discharge gas. The flow rate of 100 ml min⁻¹ Ar was selected as optimum for further investigations. The high voltage delivered by the sinusoidal-modulated power supply source was optimized in the Ar driven discharge (see Fig. S6C). The lowest voltage under which the discharge can be sustained was 8.5 kV while the highest value investigated was 35 kV. The signal of Ge is increasing between 8.5 and 25 kV and then reaches a plateau. The optimum setting for the REF-SIN arrangement was thus running the discharge in 100 ml min⁻¹ Ar at 30 kV (Table 2). These values were employed for investigation of the influence of the gas phase dryer on response from all three Ge species. The use of a gas phase dryer has a significant effect on Ge response as shown in Fig. S6D. Although the discharge can be sustained even in absence of any dryer with the plasma appearance looking the same as in its presence, as assessed by the naked eye, the response of all Ge species was negligible in the absence of any dryer. It must be highlighted that a significant amount of water vapor and aerosol is co-generated during HG step. Water molecules present in the DBD possess many rotational and vibrational energetic levels which give the accelerated electrons in the discharge the chance to deposit their energy very efficiently as well as trigger new reaction channels in plasma via formation of highly reactive H₃O⁺ or OH-species. These side reactions may have negative effect on atomization of analyte hydride. The water vapor content can be reduced significantly when employing an appropriate dryer. Water vapor content of 2.0% was determined in a gas phase entering the DBD atomizer by selected ion flow tube mass spectrometry (SIFT-MS) under HG conditions in absence of any dryer while the use of a dryer packed by solid NaOH resulted in decrease of water vapor content down to 0.16%.³⁵ The nature of the dryer, *i.e.* NaOH pearls/pellets or Nafion membrane, does not seem to play a significant role in this work since all of them improve the signal of Ge species equally (see Fig. S6D). When setting the response of Ge species with NaOH pellets-based dryer to 100% the response in presence of other dryers is within ±10% (being +20% for iGe with the dryer based on NaOH pearls). In contrast, the signal for individual Ge species in absence of any dryer was only between 2 to 6% of their signal observed in presence of the dryer based on NaOH pellets (see Fig. S6D). Gas phase dryer based on NaOH pellets was thus employed.

SE-SW configuration. The effect of various parameters on response of all three Ge species was investigated in the SE-SW arrangement of the DBD atomizer. The effect of discharge gas identity was limited to Ar and He only since the plasma cannot be sustained, in contrast to REF-SIN configuration discussed above, in molecular gases such as nitrogen or hydrogen. Higher signals were always observed in Ar with the response in He being at 60% of that in Ar for MMGe and DMGe and 90% for iGe, respectively. These observations are in good agreement with those made earlier in REF-SIN. Argon was thus selected as a discharge gas for further experiments. Its flow rate was optimized individually for each Ge

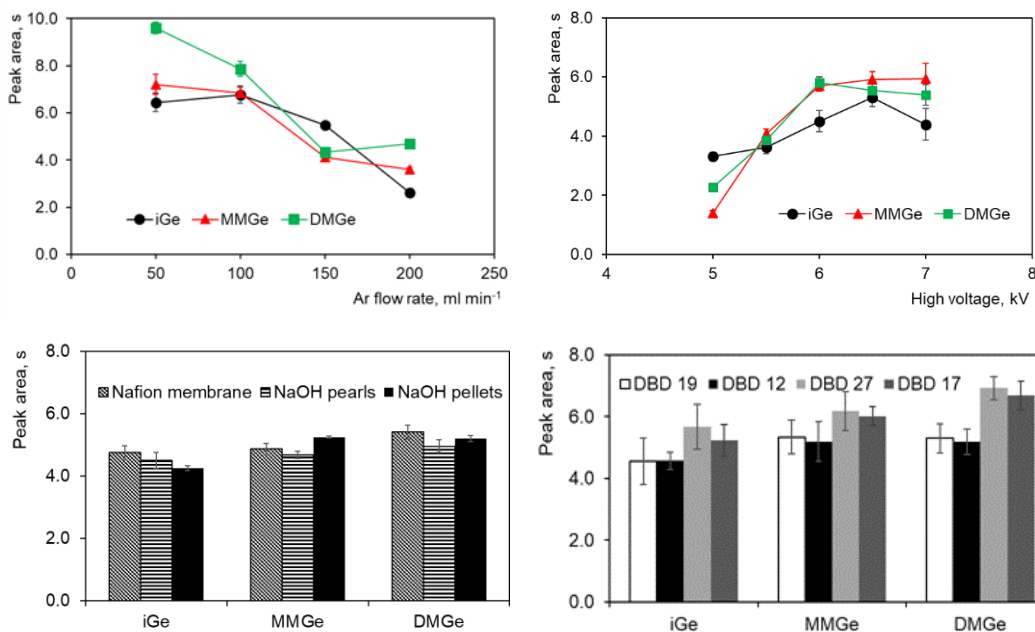


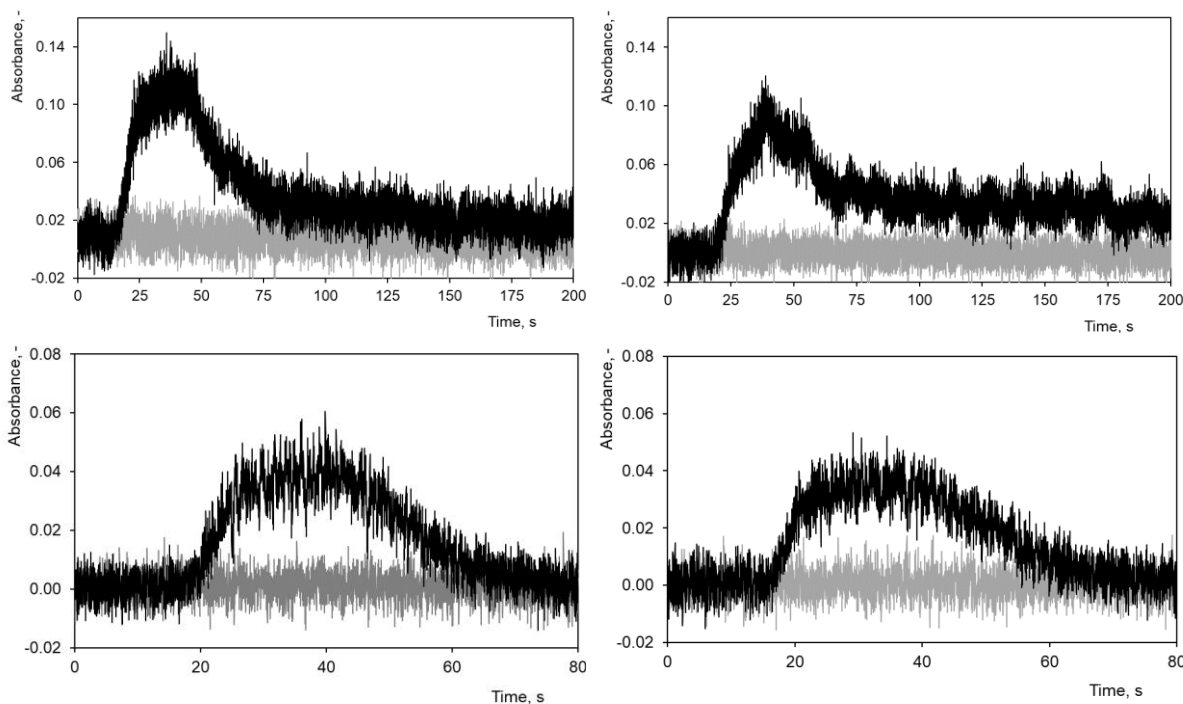
Fig. 3 Optimization of atomization conditions in the SE-SW arrangement of the DBD atomizer. The effect of Ar flow rate (A); high voltage (B) and the dryer (C) on signal of Ge species. Repeatability of determination of Ge species among 4 different pieces of DBD in the same SE-SW design (D). Concentration of Ge species standards $1 \mu\text{g ml}^{-1}$ ($0.5 \mu\text{g Ge absolute}$). Atomization conditions as listed in Table 2.

species with the results depicted in Fig. 3A. The signal of iGe and MMGe reaches a plateau between 50 and 100 ml min⁻¹ Ar followed by signal decrease at higher flow rates. The signal of DMGe is decreasing slightly, by 20%, between 50 and 100 ml min⁻¹ Ar then followed by a steeper decrease. The signal of all Ge species at 200 ml min⁻¹ Ar reaches around 40-50% of their maximum signal. Ar flow rate of 100 ml min⁻¹ was selected as optimum for all three species compromising the sensitivity and peak shape. This value is identical as for the REF-SIN configuration. Employing the square wave modulated power supply source the discharge can be sustained in the DBD between 5.0 and 7.0 kV. The effect of high voltage on the response of Ge species is depicted in Fig. 3B. The signal is increasing for all three species with increase of the voltage from 5.0 to 6.0 kV reaching a plateau for MMGe and DMGe between 6.0 and 7.0 kV while a maximum response for iGe is reached at 6.5 kV followed by a slight decline of the signal. An optimum of 6.5 kV was selected for all species. Although there is a difference in optimum operation voltage between the REF-SIN (30 kV, see Fig. S6B) and SE-SW (6.5 kV) arrangements of the DBD atomizer it has to be highlighted that a signal plateau has been reached for the tested Ge species in both configurations indicating that the voltage supplied is sufficient in both arrangements to reach maximum achievable signal. Since the Ar discharge cannot be operated in absence of the dryer in SE-SW arrangement, only the signals of Ge species in presence of NaOH based dryers (pellets, pearls) and Nafion membrane could have been compared. The results are depicted in

Fig. 3C. Analogously to the REF-SIN arrangement, no significant difference in the response of individual Ge species was observed when different dryers were employed. When setting the signals in presence of the dryer packed with NaOH pellets to 100% the signals in presence of other dryers were within $\pm 12\%$ of the respective reference signals (see Fig. 3C). The dryer based on NaOH pellets was chosen for further experiments. In order to demonstrate repeatability of the results among different atomizer pieces of the same design the response of all Ge species was recorded in four different atomizers at the same day employing the same optimum atomization conditions (6.5 kV, 100 ml min⁻¹ Ar). The results are shown in Fig. 3D. It can be deduced the difference in sensitivity among the atomizers is around 25%. Such an interpiece variance has been reported previously for other hydride forming elements not only for DBD but also for QTA atomizers. When comparing both arrangements of DBD atomizers, *i.e.* REF-SIN and SE-SW, against each other the latter one should be preferred. Although the sensitivity in SE-SW configuration is slightly lower, ca by 15%, compared to the REF-SIN arrangement (see Table 3) the peak shapes and repeatability of peak areas are significantly better in SE-SW arrangement. Pronounced peak tailing was observed in REF-SIN configuration for all three Ge species, being the worst for iGe. In contrast, no peak tailing was observed in SE-SW design of DBD atomizer. See Fig. 4A and 4B for comparison of iGe signals in both arrangements of DBD atomizer. To allow comparison of peak profiles for iGe in all types of atomizers investigated in this work also the signals for $1 \mu\text{g ml}^{-1}$

Table 3 Sensitivity and limits of detection reached for Ge species by HG-AAS in different atomizers

	iGe		MMGe		DMGe	
	Sensitivity (ms ng^{-1})	LOD (ng ml^{-1})	Sensitivity (ms ng^{-1})	LOD (ng ml^{-1})	Sensitivity (ms ng^{-1})	LOD (ng ml^{-1})
DF	1.7 ± 0.5	36	1.7 ± 0.2	19	1.8 ± 0.2	30
MMQTA	2.8 ± 0.7	28	2.7 ± 0.5	43	3.1 ± 0.6	36
REF-SIN	11.0 ± 1.9	127	11.2 ± 1.9	117	13.7 ± 1.1	103
SE-SW	9.5 ± 1.1	171	10.5 ± 0.9	140	10.2 ± 0.7	142

**Fig. 4** Signals for iGe species standard $1 \mu\text{g ml}^{-1}$ ($0.5 \mu\text{g Ge}$ absolute) in the SE-SW arrangement (A), and REF-SIN configuration (B) of the DBD atomizer, DF atomizer (C) and MMQTA (D). Analyte signal response is represented by a black line, grey line corresponds to the blank measurement.

($0.5 \mu\text{g Ge}$ absolute) in DF and MMQTA are shown in Fig. 4C and 4D. Although the sensitivity reached in DBD atomizers is the highest among the atomizers tested in this work, as discussed more in detail below, it is still by several orders of magnitude lower than that observed in DBD atomizers for other hydride forming elements. Modification of the inner surface of DBD's optical arm by passivation (silanization) of reactive OH groups employing dimethyldichlorosilane (DMDCS) was reported earlier to have substantial positive effect on signal response of Bi in the DBD atomizer³⁰. The effect of DMDCS modification on signal response was studied for all three Ge species. The use of DMDCS passivation led to signal enhancement by 30–40%, namely 30% for iGe, 32% for MMGe and even 44% for DMGe. Surface modification was not further used in this work to keep the procedure as simple as possible.

Comparison of analytical performance. The basic analytical figures of merit, *i.e.* sensitivity and limit of detection (LOD), were

determined for each Ge species in all types of hydride atomizers investigated employing the optimized atomization conditions listed in Table 2. The results are summarized in Table 3. It can be clearly seen the sensitivity among the three species, *i.e.* iGe, MMGe and DMGe, is comparable in given hydride atomizer suggesting equal atomization efficiency of these species when accepting their same generation efficiency which is a premise confirmed indirectly by previous work being reflected by the same sensitivity reached for iGe, MMGe and DMGe by ICP-MS and ICP-MS/MS detection, respectively, after HG.^{13,14} Similar behavior was observed for As species in DF,³³ MMQTA,³⁴ and DBD³⁵ atomizers.

The measured values in given atomizer type deviate from those observed for other hydride forming elements, being significantly lower for Ge species, especially in the MMQTA and DBD based atomizers. Therefore, LOD values reached in this work for Ge species are worse than those reported for other hydride forming

elements in the same type of atomizer.

The sensitivity of iGe in the DF atomizer (1.7 ms ng^{-1}) is about five times lower than the values published recently³² for hydrides of Pb, Bi, Se and Te reaching between 6 and 12 ms ng^{-1} . The difference between Ge hydride on one side and the other hydride forming elements on the other is even much more pronounced in MMQTA. Typical sensitivity values reached for other hydride forming elements including Bi^{23,41}, Sb²⁸, As¹⁹, Se^{22,23,42} and Te^{23,32} are reported to be close to 500 ms ng^{-1} ($400\text{--}600 \text{ ms ng}^{-1}$). Lower values but still in the range between $200\text{--}300 \text{ ms ng}^{-1}$ were reported for Pb and Sn hydrides.^{20,23,31,32} The sensitivity found for iGe in MMQTA in this work (2.8 s ng^{-1}) is thus at least two orders of magnitude lower compared to other analytes. LOD is also impaired proportionally. It is as high as 28 ng ml^{-1} for iGe while ranging between 0.03 to 0.6 ng ml^{-1} for other hydride forming elements.^{3,20,23,31} Greater variance in sensitivity values among hydride forming elements was observed in DBD atomizers reaching to $400\text{--}600 \text{ ms ng}^{-1}$ for As,^{19,40} Sb,²⁸ and Se^{22,23,41} around 300 ms ng^{-1} for Te,^{23,29,32} while being significantly lower for Bi ($140\text{--}270 \text{ ms ng}^{-1}$),^{23,30,32,42} Even lower sensitivities, around 50 ms ng^{-1} , were reported for Pb^{23,31,32} and Sn²⁰ hydrides in the DBD atomizers under optimum conditions. However, the sensitivity for iGe found in this work in DBD under optimized conditions is still five times lower than that observed for Pb and Sn and even 50 times worse than that reached for analytes such as As, Sb, Se or Te. The day-to-day sensitivity was satisfactory ($\pm 20\%$) for given atomizer in a horizon of several weeks. Whenever a significant decrease of sensitivity was observed the atomizer was cleaned following the procedure described in Experimental section. Both DBD based atomizers (REF-SIN as well as SE-SW arrangements) seem to be less robust towards sensitivity decrease in time compared to DF and MMQTA atomizers. Typical LOD values reported in DBD were below 0.3 ng ml^{-1} for As,¹⁹ Sb,²⁸ Se,^{22,23} and Te^{23,29} while those for Bi³⁰, Pb³¹ and Sn²⁰ were roughly 10 times higher ranging between 1.0 and 3.0 ng ml^{-1} . The LODs found for Ge species in this work are two orders of magnitude higher reaching between 100 and 130 ng ml^{-1} in REF-SIN arrangement and 140 to 170 ng ml^{-1} Ge in SE-SW configuration, respectively. Both the low sensitivity and high LOD values indicate either poor atomization efficiency of Ge species, or fast decay of free Ge atoms produced in the atomizers. A combination of both cannot be ruled out. A fraction of Ge deposited inside the hydride atomizers (DF, MMQTA, DBD in SE-SW arrangement) under the optimized atomization conditions was quantified by leaching experiments followed by ICP-MS/MS determination of Ge in the leachates (see Supporting Information, section 1.2 for the procedure) in this work. The results of these experiment are discussed below.

Quantification of the deposited fraction of Ge. The results of the leaching experiments provide a very sketchy picture allowing just to distinguish between (i) the fraction deposited in the atomizer that is quantified and (ii) non-deposited fraction leaving

the atomizer boundaries calculated by the difference. The advantage of these experiments is their simplicity. However, information about the spatial distribution of the analyte deposits retained in the atomizer is not available by this approach. The fraction of Ge deposited after atomization of GeH₄ in both MMQTA and SE-SW arrangement of the DBD atomizer was quantified to be around 80% reaching $78 \pm 16 \%$ for MMQTA and $83 \pm 7 \%$ for SE-SW, respectively. These results indicate a fast decay of free Ge atoms by reactions with inner surface of the walls of both atomizers. Deposition of Ge was proven even in the support tube of the DF atomizer, but to a much lower extent, i.e. $7 \pm 2 \%$. Naturally, the flame zone itself is not surrounded by any walls. However, the deposits are formed upstream the flame forming a narrow black ring in the top part of the tube that is heated by the flame ca 3 mm from the top of the support tube as can be seen by naked eye (see Fig. S7 for a photo of a DF with deposited Ge). The mechanism of the deposit formation here can be also explained by decay of free Ge atoms since H radicals were proven to exist not only in the flame but they can even diffuse inside the support tube up to the distance of several millimetres⁴³ which fact agrees well with the position of deposited analyte zone (Fig. S7). An alternative scenario of the deposit formation, i.e. thermal decomposition of Ge hydride, is less likely, although it cannot be completely excluded. The experiments performed reveal the deposits are formed after analyte hydride atomization as a result of decay reactions of free analyte atoms with the inner wall surface of the atomizer. The deposited fraction of Ge is negligible in DF, while being significant in MMQTA and DBD atomizers. Although the mass fraction of Ge deposited in MMQTA and DBD is comparable reaching around 80%, it is worth saying the spatial distribution of the deposits and their effect on atomizer performance might be substantially different. In our previous thorough study focused on atomization of Se hydride in MMQTA and DBD atomizers⁴¹ a significant difference in distribution of the deposits and the deposited mass fraction of Se between these two atomizers was observed. Experiments performed with DBD revealed a higher deposited ($25\text{--}40\%$) and homogeneously distributed mass fraction of Se. On the contrary, the deposited fraction of Se reached 15% only in the MMQTA with the deposits being in the extremities of the MMQTA represented by the unheated ends of its optical arm as found by a radioactive indicator⁴¹. If the area where analyte deposits overlaps with the atomization zone the formation of deposits might affect atomizer sensitivity. This might happen in the DBD atomizer also in case of Ge as an analyte. This hypothesis is indirectly supported by the fact DBD sensitivity was usually decreasing in time and a cleaning procedure was necessary once every few weeks to restore original sensitivity as discussed above. In MMQTA, the distribution of Ge deposits might have the same pattern as in case of Se due to the pronounced temperature gradient along the optical arm. In such a case the central “hot” part of the MMQTA optical arm, where atomization occurs, is free of deposits, resulting in better robustness in day-to-day sensitivity that was observed in MMQTA

for Ge as discussed above. Analyte is deposited very likely outside the atomization zone, *i.e.* in the peripheries of the MMQTA optical arm which temperature is significantly lower than atomization temperature, typically below 400 °C.

Leaching experiments have to be combined with further techniques if understanding the atomization mechanisms is desired. The detailed insights into the mechanism of atomization of Ge species is beyond the scope of this work which was rather targeted on optimization of atomization conditions in individual atomizers and assessment of their analytical performance. Experiments are in progress involving the laser induced fluorescence (LIF) to reveal the spatial distribution of Ge free atoms and quantify the atomization efficiency. Moreover, advanced soft ionization mass spectrometric techniques such as direct analysis in real time (DART-OrbitrapMS) and/or selected ion flow tube MS (SIFT-MS) will be utilized to identify the structure of Ge species leaving the atomizer after atomization step. Scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDS) will be used to characterize the deposited Ge layers.

CONCLUSION

Three types of hydride atomizers based on diffusion flame (DF), heated quartz tube (QTA) and dielectric barrier discharge plasma (DBD) were optimized for atomization of three environmentally important volatile Ge species. Atomization efficiency was confirmed to be comparable among the species in given atomizer. The design of multiple microflame quartz tube atomizer (MMQTA) was found to be more sensitive to Ge species compared to plain QTA since the controlled supply of oxygen (as air) to MMQTA increased analyte response substantially. Also, the use of gas phase dryer improves significantly the sensitivity of Ge determination in both MMQTA and DBD atomizers. According to the expectations the lowest sensitivity was observed in the DF atomizer due to its short optical path. Unlike for other hydride forming elements, the sensitivity in MMQTA was comparable to that observed in DF although the effective optical path of MMQTA with its central part of its optical arm reaching temperature higher than 800 °C,⁴¹ is significantly higher than that in DF - reaching roughly 6 cm and 0.5 cm in MMQTA and DF, respectively. The highest sensitivity was observed in DBD atomizer. However, even the sensitivity reached in the DBD is lower at least by an order of magnitude for Ge species compared to other hydride forming elements indicating either a poor atomization efficiency of Ge species, or fast decay of Ge free atoms. A significant fraction of Ge (around 80%) introduced originally into the atomizer as a volatile hydride (GeH₄) was found deposited in the MMQTA and DBD atomizers providing evidence of fast decay of free Ge atoms. Further experiments are in progress to get deeper insights into the

atomization of volatile Ge species and the fate of free Ge atoms. Although the HG-AAS cannot compete with other spectrometric techniques such as HG-ICP-MS in terms of sensitivity and LOD as demonstrated in this work, comparison of the performance of hydride atomizers based on flame, heated quartz tube and plasma was worth of investigation to bridge the gap in the knowledge of atomization of volatile germanium species.

ASSOCIATED CONTENT

The supporting information (Figs. S1–S7 and Table S1) is available at www.at-spectrosc.com/as/home.

AUTHOR INFORMATION



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Notes

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