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Article

# *In-situ* Trapping of Cd and Se in a Dielectric Barrier Discharge Atomizer after Volatile Species Generation: Optimization of the Preconcentration Step for Atomic Absorption Spectrometry

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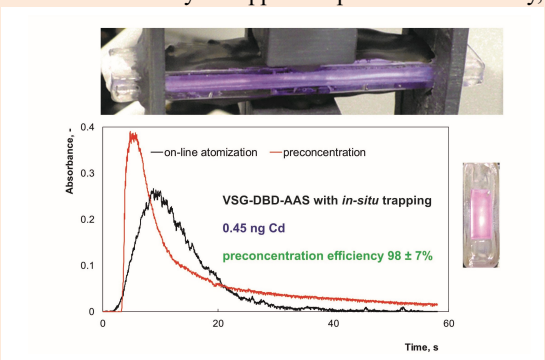
**ABSTRACT:** *In-situ* preconcentration of volatile Se and Cd species in the dielectric barrier discharge (DBD) atomizer for subsequent analyte detection by atomic absorption spectrometry (AAS) was investigated. Quantitative trapping of selenium hydride in the DBD atomizer, followed by incomplete volatilization of trapped analyte species, was previously described in the simplest apparatus arrangement. In this work, two advanced constructions of both the DBD atomizer and its high voltage power supply source were tested to improve the preconcentration efficiency by increasing the volatilization efficiency of trapped Se species. Unfortunately, no significant improvement was found. The overall preconcentration efficiency ranged between 60 and 70% regardless of the apparatus set-up. In contrast to Se, *in-situ* trapping of volatile Cd species in the DBD atomizer for AAS was optimized for the first time in this work. Quantitative Cd trapping was observed at 17.5 kV with 3.5 mL $min^{-1}$ $O_2$ admixed to 300 mL $min^{-1}$ Ar, while complete analyte release was achieved at 25.2 kV with 75 mL $min^{-1}$ Ar. The preconcentration efficiency was quantified to 98 ± 7%. The sample loop volume was optimized to 0.15 mL, as higher sample volumes unfortunately led to a significant decrease in preconcentration efficiency due to analyte loss during the prolonged trapping step.




## INTRODUCTION

Cadmium is one of the most toxic metal elements with a biological half-life ranging from 10–30 years and high accumulation potential.[1] Cadmium and its compounds have been classified as carcinogenic by the International Agency for Research on Cancer (IARC), primarily associated with human lung, prostate, and more recently, pancreatic cancer. Its levels in the environment are increasing due to anthropogenic activities. Therefore, the development of sensitive, accurate, and rapid analytical procedures for Cd monitoring in environmental and clinical samples remains highly desirable.

Selenium is considered an essential element for human health. However, its optimal range of daily intake is fairly narrow since it can cause disease by deficiency, but is toxic at levels less than one order of magnitude higher than those required for health.[2] The detection of total Se content at ultratrace concentrations in environmental, clinical, and food samples should therefore be perceived as a priority task in current trace element analysis.

Sensitive analytical techniques, typically based on atomic spectrometric detectors, are used to determine trace levels of Cd and Se in samples.[3] These include atomic absorption (AAS) or fluorescence (AFS) spectrometry, as well as inductively coupled plasma (ICP) combined either with mass spectrometry (MS) or

optical emission spectrometry (OES). Nebulization of the liquid sample is the most common sample introduction strategy in atomic spectrometry, despite its relatively low introduction efficiency, reaching only 5 to 10%.[3]

Volatile species generation (VSG) comprises a group of techniques based on analyte derivatization to form a volatile compound prior to spectrometric detection.[4-6] Selective analyte conversion from liquid to gas phase results in enhanced analyte introduction efficiency, as well as matrix separation and reduced risk of interferences. Moreover, the VSG step can be utilized during speciation analysis or analyte preconcentration. Hydride generation (HG) induced by a chemical reaction with $NaBH_4$ is the most common approach to VSG yielding quantitative analyte conversion to a volatile hydride, *i.e.* reaching 100% generation efficiency under optimum conditions.[4] Same approach, analyte reduction to volatile species by $NaBH_4$ reduction, can be applied also to other than hydride forming elements, *e.g.*, Hg or Cd. VSG of Cd has been investigated in detail by our group recently, using KCN and $Cr^{3+}$ as additives, reaching the generation efficiency of 60%.[7] VSG is compatible with all atomic spectrometric detectors. Its coupling to AAS is very popular due to the simplicity, reliability, user-friendliness, and low operating costs of this detector. The most popular atomizers of volatile species in AAS are conventional externally heated quartz tubes (QTA).[8,9] However, plasma atomizers based on a dielectric barrier discharge (DBD)[10] have been demonstrated as a promising alternative to QTA.[5,11,12]

An important and useful feature of the DBD atomizer is the fact that efficient *in-situ* preconcentration of hydrides in DBD atomizers prior to detection can be used as a simple and operator-friendly approach to improve the detection limit of HG-AAS.[5] Analyte retention (trapping) occurs in the presence of oxygen admixed to the discharge gas, while analyte release (volatilization) is achieved by switching off the $O_2$ flow in the presence of $H_2$ evolved spontaneously during blank measurement.[5] This phenomenon was first described for arsenic independently and simultaneously by two research groups. [13,14] Preconcentration efficiency reaching 100% was observed in DBD for As[13] and Sb[15] hydrides under the optimum conditions while significantly lower values, ranging between 50 and 70%, were reported for Te[16], Bi[17] and Se[18]. Mechanisms of analyte hydride trapping and its subsequent volatilization were studied in detail in the case of Se employing a $^{75}Se$ radioactive indicator combined with radiometry and image plate autoradiography. Efficient analyte trapping (> 90%) in a small spot in the central part of the DBD optical arm has been proven whereas incomplete analyte release was found responsible for preconcentration efficiency of 70%.[18]

The most common construction of the DBD atomizer is the design with glued electrodes supplied by an AC high-voltage power supply source featuring sinusoidal waveform modulation.[5] Recently, the use of DBD atomizers with sputtered electrodes and power supply sources featuring square-wave high-voltage function modulation was proposed and tested for the determination of hydride forming elements by HG-AAS employing the on-line atomization mode, *i.e.*, with no preconcentration.[19,20] The performance of the new system was element dependent reaching better performance for Pb[20], Ge[21], and Sn[22].

This work aimed to test advanced constructions of DBD atomizers and their power supply sources to improve the overall preconcentration efficiency of Se, especially to enhance volatilization efficiency. Moreover, *in-situ* trapping of volatile Cd species in the DBD atomizer was optimized, to the best of our knowledge, for the first time within this work.

## EXPERIMENTAL

**Chemicals.** All reagents were of analytical grade or higher purity. The solutions and dilutions were made with deionized water (< 0.1 μS $cm^{-1}$, Ultrapur, Watrex, USA). In case of the experiments with Cd as analyte the deionized water was boiled and bubbled (deaerated) for 30 minutes by inert gas (Ar) prior to use. HCl (37%, p.a.) was sourced from Merck (Germany). The reductant was solution of $NaBH_4$ (Sigma Aldrich, Germany) stabilized with KOH (Lach-Ner, Czech Republic), filtered after preparation and stored frozen. Two additives were employed in order to enhance the generation efficiency of volatile Cd species: the first additive was a solution of $Cr^{III+}$ prepared from $Cr(NO_3)_3 \cdot 9\ H_2O$ (≥ 99.99% trace metal basis, Sigma-Aldrich, Germany). KCN (≥ 97.0%, Fluka, Switzerland) was used as the second additive. Working Se and Cd standards were prepared by serial dilution from their 1000 μg $mL^{-1}$ stock solutions purchased from Fluka (Switzerland), and Analytika (Czech Republic). A 3:7 (v/v) mixture of HF (38%, Spolchemie, Czech Republic) and $HNO_3$ (65%, Lach-Ner, Czech Republic) was used to clean the DBD atomizers when needed. Compressed Ar (99.996%) and $O_2$ (99.95%) were purchased from SIAD Czech Ltd. The ERM-CA713 wastewater certified reference material (CRM) produced by European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, Belgium, was used for validation of the method proposed for Cd determination.

**Hydride generator.** The in-house made hydride generation systems based on a computer (WinLab 7.4) controlled flow injection system (FIAS 400, Perkin Elmer, USA) were employed in two arrangements depicted in Fig. 1 and were described in detail earlier.[7,20] Both operated in a flow injection mode with standard/sample being injected automatically by a six port injection valve using an autosampler AS90 (Perkin Elmer, USA) into the flow of the carrier HCl employing 0.5 mL (for Se) or 0.15 mL (for Cd) sample loops. Carrier gas flow rate (Ar) was controlled by a mass flow controller (Cole-Parmer, USA). An in house made

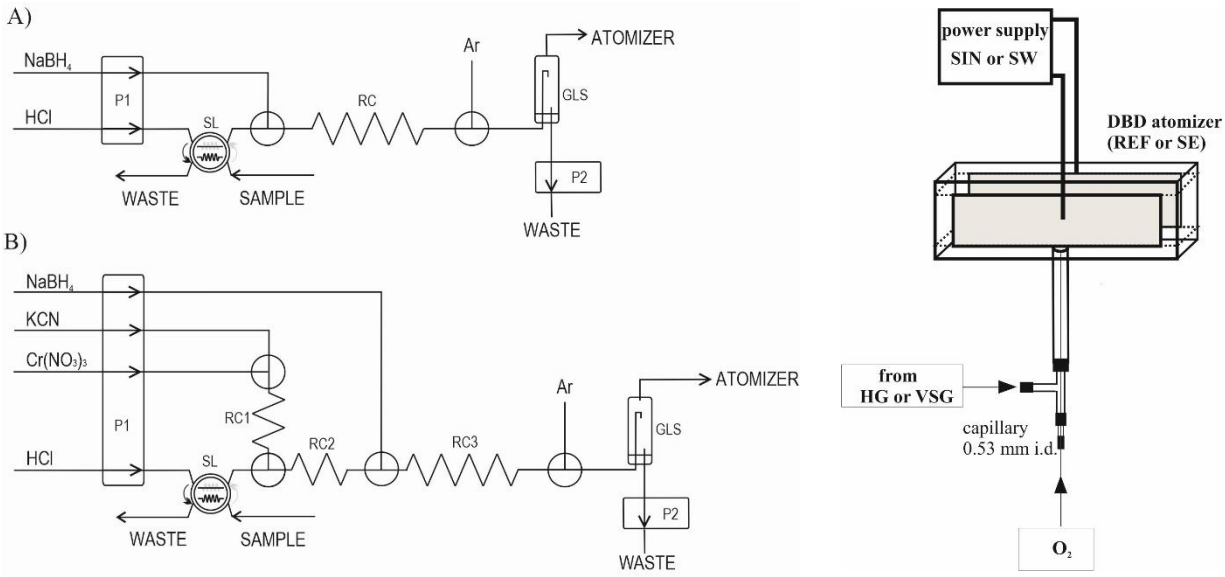



**Fig. 1** The design of the two channel hydride generation system used for HG of Se (A) and four channel volatile species generation system for VSG of Cd (B). P1, 2 – peristaltic pumps, SL- sample loop, RC – reaction coil. Gas phase introduction arrangement into the DBD atomizers (C).

**Table 1.** Optimum HG conditions for Se and VSG for Cd. AAS settings for the determination of Se and Cd

| | Se | Cd |
|---|---|---|
| ***HG/VSG conditions*** | | |
| **HCl concentration, mol $L^{-1}$** | 1.0 | 0.2 |
| **$NaBH_4$ concentration, %** | 0.5 | 5.0 |
| **KOH concentration, %** | 0.4 | 0.4 |
| **Additive 1, ($Cr^{3+}$), mol $L^{-1}$** | - | 0.001 |
| **Additive 2, (KCN), mol $L^{-1}$** | - | 0.1 |
| **Ar, mL $min^{-1}$** | 100 | 75 |
| ***AAS settings*** | | |
| **Wavelength, nm** | 196.0 | 228.8 |
| **Spectral bandpass, nm** | 0.7 | 0.7 |
| **Lamp current, mA** | 290 | 200 |

glass gas-liquid separator (GLS, 3 mL inner volume) with a forced outlet was employed.

A conventional two channel system (Fig. 1B) was used for Se as analyte. The two channels served for HCl (4.0 mL $min^{-1}$) and $NaBH_4$ (1.2 mL $min^{-1}$) introduction, respectively.[20] A four channel system was used for Cd allowing the use of additives.[7] In this arrangement the flow rate in the reductant ($NaBH_4$) and reaction medium (HCl) channels was set to 1.0 mL $min^{-1}$ while that used for both additives was 0.5 mL $min^{-1}$.

The gas phase leaving the GLS was transported through a PTFE tube (1 mm i. d., 15 cm long) to the DBD atomizer described in detail in next section. Liquid phase from the GLS was pumped into the waste.

The optimum generation conditions, adopted from our previous works focused on Se[20] and Cd[7], are summarized in Table 1.

## DBD atomizers and their power supply sources

***DBD atomizer designs.*** Two quartz DBD atomizer designs with a planar configuration of the electrodes, described in detail earlier[13, 15-23] 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 vertical walls were 3 mm and 1 mm thick, respectively. A quartz tube (20 mm long, 2 mm inner diameter, 4 mm outer diameter) was sealed through the centre of the top horizontal wall of the optical arm to form the vertical (inlet) arm of the atomizer serving for introduction of gas phase from the GLS.

The only difference between the designs was thus the way of electrodes attachment, either by gluing or by sputtering (vapor-deposition). The first design with glued electrodes, termed as REF further in the text, had two copper electrodes (50 mm long; 5 mm wide; 0.15 mm thick) glued to the central part of the vertical walls of its optical arm. The second arrangement with sputtered electrodes, termed as SE further in the text, has the electrodes realized by a bottom layer of 20 nm Cr vapor-deposited directly on the quartz surface to act as binding layer over which 200 nm Cu layer was vapor-deposited. The size of the electrodes (50 mm long; 5 mm wide) was exactly the same as in case of REF design. The outer surface of the electrodes in both designs was covered with an insulating layer of multipurpose rubber coating (Plasti Dip International, USA) to avoid parasitic surface discharges at the

outer side of the DBD. Both DBD designs were housed in a supporting frame of high-density polyvinyl chloride (PVC) which protected them from mechanical damage and also facilitated placement of the DBD atomizer into the optical axis of the spectrometer. A computer fan was attached to the bottom of the PVC frame to provide air cooling.

An extra T-connector made of polypropylene (1 mm i.d.) was placed ca. 3 cm upstream of the inlet arm of the DBD atomizer to introduce oxygen into the DBD atomizer separately from the gas phase introduced from the GLS. A deactivated fused silica capillary (Supelco, Germany, 0.53 mm i.d.) was centred inside the inlet arm of the DBD atomizer for that purpose, with its tip aligned with the junction of the inlet arm with the optical arm. Oxygen was introduced through the capillary, whereas all the gases from the GLS were introduced into the inlet arm. See Fig. 1C for an illustration of the gas phase introduction arrangement. Oxygen was introduced only in the first (trapping) step of the two-stage preconcentration procedure, while its flow was stopped in the second (volatilization) step – see next section for details. Its flow rate was regulated by a mass flow controller (Cole-Parmer, USA).

The DBD atomizers were coupled to a high voltage power supply sources operating at 28 kHz excitation frequency having either a sinusoidal (SIN) or square-wave (SW) voltage modulation. The details on both power sources can be found elsewhere[19,20,21]. The DBD atomizer with glued electrodes (REF) was connected to a power source with sinusoidal modulation (SIN). Such a configuration is further termed as REF-SIN in the text to keep consistency with our previous works[20,21]. The high voltage supplied by the SIN source was controlled either manually as in case of Se preconcentration, or automatically as performed for Cd preconcentration (see below for details). The second arrangement investigated was a DBD atomizer with sputtered electrodes (SE) powered by a square-wave (SW) modulated power source. This arrangement will be further labelled as SE-SW.

The DBD atomizers were cleaned regardless of their electrode design prior to their first use or when a significant decrease in sensitivity was observed according to the procedure used previously[13, 15-23]. The outlet of DBD horizontal arm was sealed by Parafilm and the inner volume of the quartz DBD body was filled with a mixture of concentrated $HNO_3$ and HF (7:3) for 10 minutes. Subsequently, the DBD was flushed by deionized water several times and let to dry.

**Atomic absorption spectrometry and measurement procedures.** An AAnalyst 800 atomic absorption spectrometer (Perkin Elmer, USA) equipped with a deuterium background correction and with FIAS 400 flow injection accessory and autosampler AS90 controlled via WinLab 7.4 was used as a detector. Electrodeless discharge lamps (EDL) for Se and Cd were powered by Perkin Elmer EDL System II.

In case of experiments focused on Se preconcentration the voltage of the individual power supply sources tested as well as the flow of oxygen in the trapping step were controlled manually. The flow rate of Ar as discharge gas was not varied between the trapping and volatilization steps for Se.

On the contrary, the preconcentration procedure was automated in case of Cd since more experimental parameters have to be controlled and changed at the same time including the (i) oxygen and (ii) auxiliary Ar flow rates as well as the (iii) high voltage delivered from the SIN power supply source to the DBD (REF arrangement). Different settings of high voltage and auxiliary Ar flow rate were used between the trapping and volatilization steps for Cd. Moreover, the precise timing was necessary to reach good repeatability among the replicates, which could not be achieved with manual control. Two laboratory-constructed relay boxes were built employing relays (43.61-0300, Finder, Italy). The boxes included two relays each and were controlled and programmed via the FIAS 400 (FIAS program). The relay boxes were designated to i) set the voltage of the SIN power supply source to either the trapping or volatilization voltage via resistors, ii) control of oxygen and auxiliary Ar flow rates via two pieces of three-way solenoid valve, both in the open/closed regime. The auxiliary argon flow rate was employed only if the value of 75 mL $min^{-1}$ is exceeded.

The preconcentration mode consisted of two steps: (i) trapping - the analyte was retained in the optical arm of the DBD atomizer; (ii) volatilization - trapped analyte was released, atomized, and detected.

(i) Trapping step: The DBD atomizer was set to a trapping voltage being supplied with a mixture of Ar and oxygen during the whole period of sample and blank introduction. Analyte volatile species were generated from a standard solution of $Cd^{II+}$ or $Se^{IV+}$ after their introduction into the flow injection system via the sample loop.

(ii) Volatilization step: Signal measurement was initiated at the beginning of the volatilization step followed immediately by switching off the oxygen flow and setting the voltage. The volatile species generation from a blank solution was still running, serving thus as a source of hydrogen required for analyte volatilization. Signals were recorded for 60 s by AAS.

Measurements in on-line atomization mode (no preconcentration) were performed in the same apparatus. Analyte standards were introduced via sample loop followed by the introduction of blank. No oxygen was added into the discharge. High voltage supply as well as carrier/discharge gas composition were kept the same as in the volatilization step of preconcentration procedure. Signals were recorded for 60 s by AAS.

In both modes of operation, peak area as well as peak height

response were evaluated. Averages from at least 3 replicates were recorded; peak area of the signals is plotted in the figures; error bars represent standard deviation (SD). To quantify the preconcentration efficiency, the peak areas of the signal in the volatilization step of the preconcentration mode were related to those obtained in the on-line atomization mode under strictly identical experimental conditions (standard concentration and sample loop volume, DBD high voltage, discharge gas composition and flow rate).

## RESULTS AND DISCUSSION

**Selenium.** The feasibility of *in-situ* preconcentration of Se hydride in the DBD atomizer for subsequent Se detection by AAS was investigated in our previous work, resulting in an overall preconcentration efficiency of 70%.[18] The DBD arrangement consisted of the REF-SIN configuration (see Experimental for details), *i.e.*, DBD atomizer with glued electrodes and a power supply source with sinusoidal modulation of the high voltage function. The efficiency of the trapping step was satisfactory, being estimated between 90 and 100% by two independent methods, including either (i) the use of radioactive indicator ($^{75}$Se) with activity determination by radiometry or (ii) comparison of the signals observed in on-line and preconcentration modes with AAS detection.[18] Non-complete volatilization was found to be responsible for lower preconcentration efficiency. The use of the radioactive indicator revealed the redistribution of the analyte between the trapping and volatilization steps. In the trapping step all Se is retained in a relatively narrow zone in the central part of the optical arm, symmetrically to the junction of optical and inlet arm of the DBD atomizer.[18] In the subsequent volatilization step, the released Se is partially transported outside the atomizer (20% fraction) while the rest is redistributed in the optical arm, forming deposits towards its ends. Part of the analyte appears to be non-volatilized being located in the zone of previously trapped Se species, as proven by the autoradiogram.[18] This observation is in agreement with the incomplete volatilization efficiency.

The aim of this work was to improve the volatilization efficiency by testing two apparatus arrangements, SE-SIN and SE-SW. The replacement of glued electrodes by the sputtered ones as well as the use of square-wave modulated high voltage power supply source instead of sinusoidal should minimize the power loss leaving thus more power available for the volatilization step. Testing the SE-SIN and SE-SW apparatus configurations in the on-line atomization mode brought comparable results with REF-SIN arrangement used for a reference, in terms of sensitivity, for Se, Te and Bi, while sensitivity improvement by a factor of two was observed for Pb.[20]

The results were reproduced for Se in this work, reaching the sensitivity between 0.48 and 0.54 s ng$^{-1}$ Se for the three apparatus arrangements as summarized in Table 2. Since quantitative trapping of Se species was reached in the previous work[18], no further optimizations for this step were conducted in this work. Optimum conditions found previously were adopted for trapping: 3.5 mL min$^{-1}$ $O_2$ admixed to 100 mL min$^{-1}$ Ar as discharge gas. Moreover, the trapping voltage was set to 23 kV with the REF-SIN arrangement, 8.4 kV with SE-SIN and 6.5 kV for the SE-SW apparatus set-up. Since no Se signal was observed during the trapping step, further called as breakthrough signal, lossless trapping of Se can be deduced in all tested experimental arrangements under these conditions.

**Table 2.** Comparison of sensitivities reached for Se in different arrangements of the DBD atomizers and the power supply sources in both: (i) on-line atomization mode and (ii) preconcentration mode. Preconcentration efficiency reached for Se in different DBD designs and power supply source configurations

| Arrangement | Sensitivity, s ng$^{-1}$ Se | | |
|---|---|---|---|
| | On-line atomization mode | Preconcentration mode | Preconcentration efficiency, % |
| **REF-SIN** | 0.54 ± 0.03 | 0.38 ± 0.04 | 63 ± 4 |
| **SE-SIN** | 0.48 ± 0.02 | 0.31 ± 0.02 | 66 ± 8 |
| **SE-SW** | 0.51 ± 0.02 | 0.34 ± 0.03 | 65 ± 6 |

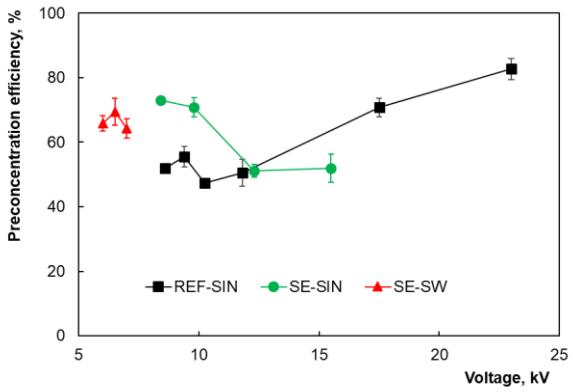



**Fig. 2** Effect of voltage applied in the volatilization step on preconcentration efficiency of Se in different configurations of the DBD atomizer and its power source. HG conditions of Se as listed in Table 1. Standard concentration 2 ng mL$^{-1}$ Se (1.0 ng Se absolute). In all experimental configurations: discharge gas flow rate 100 mL min$^{-1}$ Ar was used in both trapping and volatilization steps; while 3.5 ml min$^{-1}$ $O_2$ was employed in the trapping step. Error bars represent the standard deviation of three replicates.

The voltage in the volatilization step was optimized for each of the three apparatus arrangements tested with the results shown in Fig. 2. The voltage was varied between the lowest value at which a stable plasma could be sustained and the highest value that allowed measurement without the risk of electrode damage. In the

REF-SIN configuration, the signal of Se increased monotonically between 10 and 23 kV. As a consequence, the volatilization voltage of 23 kV was selected as optimum. For illustration, the comparison of peak profiles measured in the preconcentration and on-line atomization modes, respectively, in the REF-SIN arrangement is depicted in Fig. S1 in Supporting Information. The peak profiles observed in SE-SIN and SE-SW apparatus configurations were similar to those shown in Fig. S1. A plateau of maximum signal was observed between 8.5 and 10 kV for the SE-SIN arrangement, followed by a 30% signal decrease at higher voltage values. No significant change in the signal of Se was observed in the volatilization step when using the SE-SW arrangement in the range between 6 and 7 kV. The optimum value chosen for this set-up was thus 6.5 kV.

The optimum values found are in agreement with the assumption lower voltage values will be found as optimum for SE-SIN and SE-SW arrangement owing to the fact power loss, manifesting itself as heat loss occurring at the electrodes, is minimized compared to the REF-SIN configuration. The plateau reached in the SE-SW configuration indicates no further improvement in the volatilization efficiency can be reached. Following a plateau, even a signal decrease, which trend is hard to explain, was observed for the highest voltage values investigated in the SE-SIN apparatus configuration. Neither the use of the SE-SIN, nor the SE-SW arrangements led to higher peak area of Se signals in comparison to REF-SIN configuration. The expectation to improve the volatilization efficiency with SE-SIN and SE-SW arrangements, respectively, was not met.

Under the optimized conditions the sensitivity reached in the preconcentration mode was determined and preconcentration efficiency was quantified individually for all three apparatus configurations tested. No significant differences were found among them as summarized in Table 2. Neither the preconcentration efficiency, nor the repeatability varies among the arrangements. It can be concluded that none of the apparatus set-ups tested can deliver enough power in the volatilization step to release the trapped Se species quantitatively. More fundamental changes in the design of the power supply source and atomizer construction would be needed to reach this aim. Further development of the source focused on the use of higher discharge frequencies up to the MHz range, together with redesigning the DBD chamber to be compatible with higher delivered power rates, is in progress. For practical use, the REF-SIN configuration seems to be the best from the tested arrangements owing to the fact glued electrodes are more resistant to mechanical damage during use or corrosion during occasional cleaning. The results reached in this work, together with those published in our previous study[18], show consistently overall preconcentration efficiency of Se between 60 and 70% using HG-DBD-AAS approach. There are no other works dealing with preconcentration of Se hydride in the DBD for AAS detection. However, using photochemical vapor generation (PVG) of Se followed by *in-situ* preconcentration in a DBD device coupled to AFS detection, Liu *et al.*[24] have reported 100% overall preconcentration efficiency. Some significant differences between the experimental arrangements employed in the recent work and the previous one from our laboratory[18] using HG-DBD-AAS on one side, and the work[24] based on PVG-DBD-AFS on the other, make direct comparison of the results difficult. Firstly, the volatile species of Se generated differ from each other in their chemical form and reactivity. The volatile products of PVG[24] of Se are SeCO and $SeH_2$, while only $SeH_2$ is produced during HG[18]. Moreover, the design of DBD atomizers used is completely different, a volume DBD with a plan-parallel arrangement of the electordes is employed with AAS detection[18], while a tubular design of the DBD was used with AFS detection[24].

## Cadmium

### *On-line atomization*

*Previous study on VSG-QTA-AAS of Cd.* Atomization of volatile Cd species in the DBD atomizer for AAS has never been studied before. However, our recent study[7] addressed optimization of the VSG of Cd and subsequent atomization in a conventional externally heated quartz tube atomizer (QTA). Generation efficiency between 60-70% was confirmed by two independent methods using the same VSG conditions and generator design as in this study. As a consequence, the same efficiency of VSG step is expected in this study. The atomization of volatile Cd species in the DBD atomizer investigated in this study will be compared to that in QTA. For this reason, the most important findings from our previous study[7] are briefly summarized here. The sensitivity in the optimized VCG-QTA-AAS arrangement, employing the atomization temperature of 900 °C in QTA, reached a value of 6.6 s $ng^{-1}$ Cd.[7] Since the signal could be detected even in an unheated QTA, this fact clearly indicates that at least some fraction of the generated Cd species must be free atoms. The effect of QTA temperature on the sensitivity of Cd determination showed an atypical trend. The maximum sensitivity was reached at atomizer temperature of 300 °C, while the sensitivity in unheated QTA and atomizer heated to the maximum investigated value (900 °C) was comparable, being ca 80% of the maximum value.[7] In the case of free atoms as the only volatile analyte form generated, the signal of Cd should decrease with increasing atomizer temperature due to gas expansion showing a sensitivity of about 25% at 900 °C when compared to unheated QTA. The validity of this assumption has been verified using mercury, generated exclusively as cold vapor ($Hg^0$), which sensitivity of determination evolved with QTA temperature exactly according to this model (data not shown). Based on the results observed for VSG of Cd in the QTA, the identity of the generated volatile Cd species was deduced as a mixture of free atoms ($Cd^0$) and some, not yet identified, molecular species.[7]

*VSG-DBD-AAS of Cd.* In this study, we found out that the signal of Cd can be detected in the DBD atomizer in the absence of the plasma, *i.e.*, with the DBD power supply source switched off, analogously to the situation with unheated QTA described earlier[7]. Under such conditions, the sensitivity calculated from the results obtained on three different days within a period of 10 months reached 11.3 ± 0.9 s ng$^{-1}$ Cd. This confirms the fact that free Cd atoms in the ground state are present in the gas phase entering the DBD atomizer. Subsequently, the plasma conditions, namely the voltage applied to DBD and Ar flow rate, were optimized. The results are depicted in Fig. 3. The signal of Cd reaches a plateau between 30 and 100 ml min$^{-1}$ Ar as depicted in Fig. 3A. Employing the flow rates above 100 ml min$^{-1}$ Ar, the signal of Cd drops sharply due to the dilution of free Cd atoms. The effect of high voltage on Cd signal is shown in Fig. 3B. The lowest voltage investigated was 10.2 kV since a stable plasma cannot be sustained below this value. The signal increases sharply up to 17.5 kV, reaching a plateau thereafter. Values higher than 25.2 kV were not investigated to avoid the risk of electrode and power source damage. Under the optimum conditions (75 ml min$^{-1}$ Ar and 25.2 kV), the sensitivity calculated as an average and standard deviation measured on 12 days within a period of 10 months reached 7.7 ± 0.5 s ng$^{-1}$ Cd. Interestingly, the sensitivity of Cd determination by VSG-DBD-AAS with the DBD plasma set to optimized conditions was significantly, roughly by one third, lower when compared to the sensitivity reached in the same system with the only difference the plasma was switched off. The decrease in the Cd signal with the plasma turned on, compared to the atomizer without a discharge, cannot be explained by the thermal expansion of the gas phase, because the plasma temperature is relatively low (550 K). To confirm this, measurements with cold vapors of mercury were performed (data not shown) proving no significant difference in sensitivity in absence and presence of the plasma (25.2 kV, 75 ml min$^{-1}$ Ar). As a consequence, the expected scenarios would therefore be, (i) either no change in the signal in the case of the exclusive presence of free Cd atoms in the gas phase, or (ii) an increase in the signal of Cd in the case of the presence of a molecular structure that would be atomized in the DBD discharge. The observed behavior, *i.e.,* the decrease in the signal in the discharge, can be attributed to a reaction in the plasma consuming free Cd atoms to form a difficult-to-atomize molecular structure. Hydrogen cyanide (HCN), formed in the volatile species generator as a side-product, is the most probable molecule suspected to react with free Cd atoms in the plasma forming a molecular complex. Another hypothesis is the production of excited Cd atoms or even ionization of Cd which processes would decrease the population of ground state Cd atoms.

Elucidating the exact reaction mechanism and explaining this observation, *i.e.,* lower Cd sensitivity in presence of the plasma, is beyond the scope of this work, but it is worthy of further investigation. Cd determination in the on-line atomization mode should preferably be performed with the DBD plasma off to reach

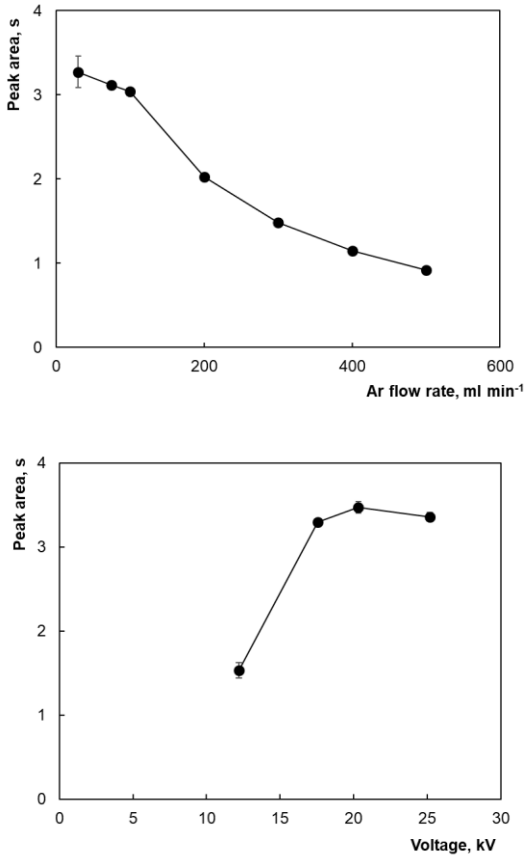



**Fig. 3** Effect of Ar flow rate (A) and voltage (B) on Cd signal. VSG conditions of Cd as listed in Table 1. Standard concentration 3 ng mL$^{-1}$ Cd (0.45 ng Cd absolute). If not subject of optimization, the DBD conditions for atomization were: high voltage of 25.2 kV and discharge gas flow rate of 75 mL min$^{-1}$ Ar. Error bars represent the standard deviation of three replicates.

by 30% higher sensitivity. Since the aim of this work was to study the *in-situ* preconcentration of volatile Cd species, which cannot be performed without the plasma, the above-presented optimization of the on-line Cd determination with the discharge switched on was also performed. For evaluation of the preconcentration performance, the signals reached in the volatilization step of the preconcentration mode are always compared to those recorded in the on-line atomization mode using identical experimental conditions (high voltage settings, gas phase composition and flow rate) – see section 2.4 for details.

### *In-situ preconcentration*

Both steps of the preconcentration procedure, *i.e.,* Cd trapping and subsequent analyte volatilization, were optimized.

*Trapping step.* Three parameters were optimized in the trapping step, including oxygen flow rate, the high voltage supplied to the DBD atomizer and Ar discharge gas flow rate.

*Oxygen flow rate.* Oxygen presence is essential for analyte retention in the atomizer during the trapping step regardless of the element, as proven in our previous studies focused on *in-situ* preconcentration of As[13], Sb[15], Te[16] and Bi[17] hydrides using the same DBD atomizer design. However, the oxygen amount required for efficient trapping is analyte dependent, ranging between 2.0 and 7.0 mL $min^{-1}$ $O_2$ for the above mentioned analytes[13, 15-17] and has to be thus optimized individually for each element. The effect of $O_2$ content in the Ar discharge gas on Cd signal observed in the subsequent volatilization step is depicted in Fig. 4A. When oxygen is not added to the plasma gas (0 mL $min^{-1}$ $O_2$), the experimental conditions correspond to the on-line atomization mode. As a consequence, no Cd trapping occurs, and volatilization signal cannot be detected. Under such experimental conditions, the signal of Cd is registered during the trapping step with peak area and shape identical to the on-line atomization mode. In order to keep consistency with our previous work[13], the Cd signal recorded during the trapping step is termed the breakthrough signal further in the text. The signal of Cd observed in the volatilization step increases steeply with increased $O_2$ flow rate mixed to Ar discharge gas up to 2.0 mL $min^{-1}$ $O_2$ added as can be clearly seen in Fig. 4A, reaching a plateau above 3.0 mL $min^{-1}$ $O_2$. The breakthrough signal, not shown in Fig. 4A, mirrors the course of the Cd signal observed in the volatilization step. It drops sharply between 0 and 2.0 mL $min^{-1}$ $O_2$ being not detectable at oxygen flow rates above 2.0 mL $min^{-1}$, indicating quantitative analyte retention at oxygen flow rates 2.0 mL $min^{-1}$ and higher. The oxygen flow rate of 3.5 mL $min^{-1}$ added to the Ar discharge gas during the trapping step was selected as optimum.

*Trapping voltage.* The effect of high voltage delivered to the DBD atomizer in the trapping step on Cd signal in the volatilization step was investigated, ranging from 10.4 to 25.2 kV with the results shown in Fig. 4B. Lower voltages were not investigated since a stable discharge cannot be sustained below 10.4 kV. A signal plateau is observed between 10.4 and 17.5 kV followed by 10% and 20% signal decrease, respectively, at 20 and 25.2 kV. The slight signal decrease at higher voltage values supplied can be explained by analyte loss at higher voltages caused by incomplete trapping. A trapping voltage of 17.5 kV was selected as optimum in the preconcentration mode.

*Trapping Ar flow rate.* Ar flow rate was the last parameter optimized in the trapping step. Its effect on Cd signal recorded in the subsequent volatilization step is depicted in Fig. 4C. A steep increase of the signal was observed between 30 and 200 mL $min^{-1}$ Ar, reaching a maximum at 300 mL $min^{-1}$ Ar, followed by a slight, *ca* 10%, decrease at higher flow rates of 400 and 500 mL $min^{-1}$ Ar, respectively. Surprisingly, the low volatilization signals observed when using low Ar flow rates, from 30 to 200 mL $min^{-1}$ Ar in the trapping step, were not accompanied by any breakthrough signal, contrary to expectations. The absence of breakthrough signal proves Cd is not transported outside the DBD atomizer at sub-

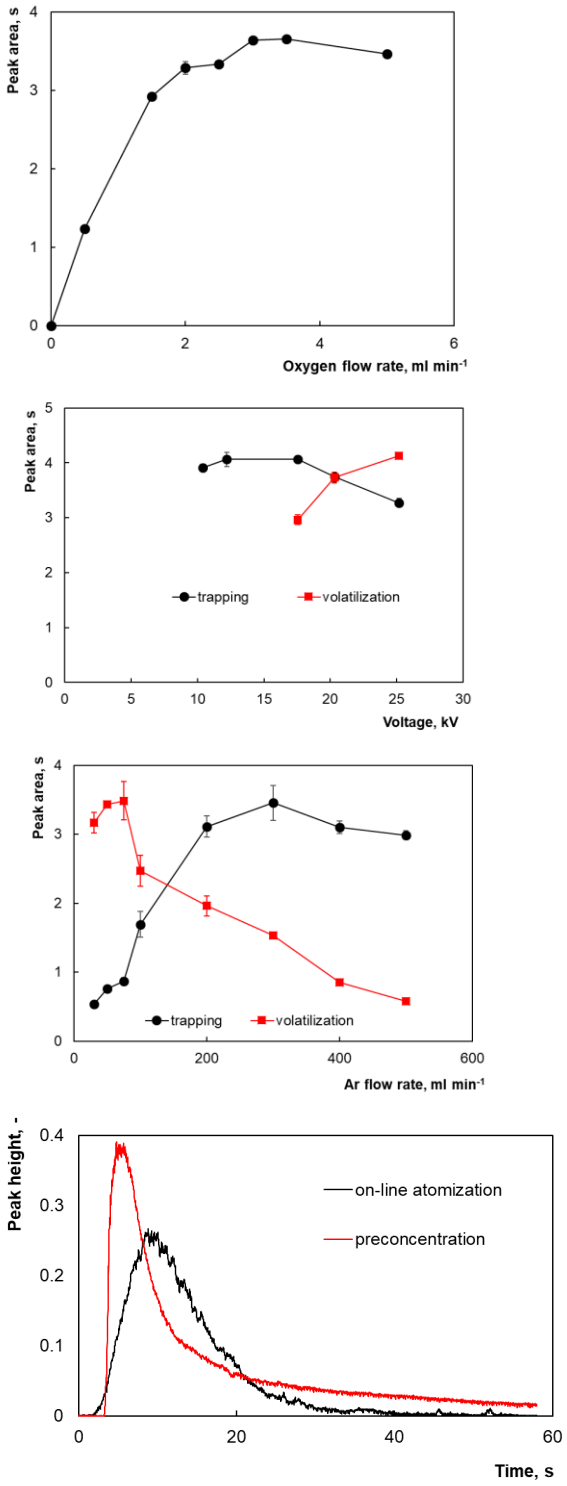



**Fig. 4** Effect of $O_2$ flow rate on Cd signal in the volatilization step (A). Effects of voltage (B) and Ar flow rate (C) applied either in trapping or volatilization steps on Cd signal in the volatilization step. Comparison of Cd signals in on-line atomization and preconcentration modes (D). Standard concentration 3 ng $mL^{-1}$ Cd (0.45 ng Cd). VSG conditions of Cd as listed in Table 1. If not subject of optimization, preconcentration was performed under the following conditions: trapping at 17.5 kV with 300 mL $min^{-1}$ Ar and 3.5 mL $min^{-1}$ $O_2$; volatilization at 25.2 kV with 75 mL $min^{-1}$ Ar. Error bars represent the standard deviation of three replicates.

optimum Ar flow rates in the trapping step. The observations rather indicate that cadmium is trapped in the DBD atomizer even at low Ar flow rates in the trapping step. However, the trapping occurs in such area from where Cd cannot be released efficiently in the subsequent volatilization step. This might happen most likely in a narrow zone in the downstream part of the inlet arm, close to its junction with the optical arm. Reactive species produced in the plasma, sustained in the optical arm of the DBD, can diffuse several millimetres upstream into the inlet arm, especially at low Ar flow rates, to react with volatile Cd species, thus being responsible for Cd trapping. Low peak area observed in the volatilization step is a consequence of the fact the trapped Cd species can hardly be released from this zone outside the active plasma region. The increased Ar flow rate (above 200 mL $min^{-1}$ Ar) in the trapping step limits the diffusion of reactive species inside the inlet arm and ensures at the same time faster and more efficient transport of Cd species up to the plasma plume in the optical arm, where Cd is trapped. Subsequent volatilization is much more efficient since the spot of the trapped analyte is in direct contact with the plasma. A flow rate of 300 mL $min^{-1}$ Ar was selected as optimum for Cd trapping.

*Volatilization step.* The high voltage supplied to the DBD atomizer and Ar discharge gas flow rate were the parameters optimized in the volatilization step of the preconcentration procedure.

*Volatilization voltage.* The effect of high voltage delivered to the DBD atomizer in the volatilization step on Cd signal is depicted in Fig. 4B, showing a monotonous increase. The highest voltage tested was 25.2 kV, which value was also selected as optimum. Higher values might lead to electrode and power source damage and were therefore not investigated. As both the flow rate and the voltage need to be changed between the trapping and volatilization steps, which is demanding to keep the plasma stable, it was not possible to test volatilization voltage values lower than 17.5 kV.

*Volatilization Ar flow rate.* The effect of Ar flow rate in the volatilization step on Cd signal is depicted in Fig. 4C, showing a very similar trend to that observed in the on-line atomization mode, see Fig. 3A for comparison. The signal of Cd in the volatilization step is slightly increasing between 30 and 75 mL $min^{-1}$ Ar while a steep drop of the signal was observed at higher Ar flow rates. Optimum flow rate of 75 mL $min^{-1}$ Ar is identical with that used in on-line atomization mode.

Based on the careful optimization performed in this section the optimum conditions selected for Cd trapping were: 3.5 mL $min^{-1}$ $O_2$ mixed with 300 mL $min^{-1}$ Ar at 17.5 kV voltage; while the volatilization was performed at 25.2 kV with 75 mL $min^{-1}$ Ar. These conditions were chosen for the evaluation of the analytical figures of merit presented in next section.

***Analytical figures of merit***

Preconcentration efficiency calculated during 8 different days within a period of 4 months as a ratio of the signals of 3 ng $ml^{-1}$ Cd standard solution measured the same day in both the preconcentration and on-line atomization modes reached a value of 99 ± 9% indicating quantitative preconcentration of Cd species and a satisfactory day-to-day repeatability.

High sample volumes resulting in longer analyte introduction times should be used for VSG with subsequent preconcentration in order to fully utilize the potential of the preconcentration step. Typically, 10 to 20 mL of the sample can be processed with HG/VSG, corresponding to a several-minute-long generation step, during which volatile analyte species are enriched in the atomizer. Trace amounts of analyte continuously released from the liquid sample during the generation step would not be detectable in the on-line atomization mode since such a signal would be broad and low. In contrast, the same amount of analyte can be detected in the preconcentration mode due to the fact all the analyte is preconcentrated during the trapping step to be subsequently released rapidly in the volatilization step, forming a high and narrow peak. The comparison of the peaks acquired in on-line atomization and preconcentration modes can be found in Fig. 4D. The same standard concentration (3 ng $mL^{-1}$ Cd) and 0.15 mL sample loop were used in both modes. The desired trend of the signal after preconcentration, *i.e.*, a higher and narrower peak, is achieved as evident from Fig. 4D. Even greater contrast between signal shapes in both modes could be achieved if the analyte concentration could be decreased and the volume of the sampling loop increased at the same time. Sample volume or sample introduction time should be selected as a compromise concerning several factors, including sample throughput, stability of trapped analyte, and also potential contamination of reagents used during the VSG step. The effect of sample loop volume on preconcentration efficiency was investigated in this work. The volume of sample loop and the standard concentration were changed while the absolute analyte mass was kept constant (0.45 ng Cd). Preconcentration efficiency of 98 ± 3% was found for 0.15 mL sample loop, while a significant decrease to 31 ± 5% was observed for 1.5 mL volume of the loop indicating unfortunately significant analyte loss with prolonged sample volume due to the instability of the trapped Cd species. Higher sample loop volume was thus not investigated and the volume of the sample loop was limited to 0.15 mL only for further experiments.

A calibration curve was measured in the preconcentration mode under the trapping and volatilization conditions optimized in section of "*In-situ preconcentration*" using standards in the concentration range from 0.5 to 6.0 ng $ml^{-1}$ Cd employing the 0.15 mL sample loop. The preconcentration efficiency was quantified to 98 ± 7% comparing the slopes of the calibration curves measured on the same day in the preconcentration and on-line atomization modes, respectively. The method developed and optimized in this work for *in-situ* trapping of Cd in DBD atomizer

after volatile species generation with subsequent AAS detection was validated using Cd determination in a waste water certified reference material. This CRM was diluted five times and directly measured by the proposed method. Using an external calibration, a 97% recovery was reached. The comparison between the found and certified values, including the measurement uncertainty, is summarized in Table 3 together with other analytical figures of merit of the developed method. The limit of detection (LOD), calculated as 3 × standard deviation of 11 blank measurements divided by the slope of the calibration function, was quantified to 0.22 ng $mL^{-1}$ Cd for the proposed preconcentration method employing the 0.15 mL sample loop. The performance of theproposed method can be compared to other approaches to Cd determination in which Cd preconcentration is involved as summarized in Table 4. The LOD values reported in literature for Cd determination by OES after preconcentration are comparable with LOD reported in this work. LOD values published for AAS detection after VSG of Cd with preconcentration at quartz or metal (W) surfaces are two orders of magnitude better. Additionally, alternative approaches to preconcentration of volatile Cd species for AAS detection were searched for testing gold amalgamators, gold wire and gold nanoparticles (AuNPs) as trapping surfaces. The results are in detail discussed in Text S1 (Supporting information). Briefly, quantitative trapping of Cd in the gold amalgamator was found. However, the inability to release Cd species prevented further testing of this material. Preconcentration of Cd on a gold wire showed poor repeatability of the results. Overall preconcentration efficiency of Cd preconcentration on AuNPs did not exceed 80%. The preparation of the traps with AuNPs is time consuming with low potential for routine use.

**Table 3.** Analytical figures of merit determined for the determination of Cd by the proposed VSG-AAS method with *in-situ* preconcentration in the DBD atomizer. Results of the method validation by analysis of the wastewater CRM

| Parameter | Determined value |
|---|---|
| **Sample loop volume, mL** | 0.15 |
| **Sensitivity, s $ng^{-1}$ Cd** | 7.6 ± 0.2 |
| **Preconcentration efficiency, %** | 98 ± 7 |
| **Wastewater ERM CA 713, ng $mL^{-1}$ Cd** | 4.90 ± 0.10 |
| | *5.09 ± 0.20** |

** Certified value.*

## CONCLUSION

Several configurations of DBD atomizers differing from each other in the way of electrodes attachment were coupled to power supply sources with either sinusoidal or square-wave modulation of voltage in order to find the experimental set-up with the best performance for *in-situ* preconcentration of selenium hydride. The results presented in this work were conducted as a follow-up study to our previous work[18], where the efficient trapping of $SeH_2$ in the DBD atomizer with glued electrodes, coupled to a high-voltage power supply source with sinusoidal modulation of the voltage function (REF-SIN arrangement), was observed. However, subsequent volatilization was found to be incomplete, resulting in overall preconcentration of Se around 70% in this arrangement.[18] Effort was thus made in the recent work to increase the volatilization efficiency of trapped Se species. Either the aforementioned power supply source was connected to the DBD atomizer with advanced, sputter-deposited, electrodes (SE-SIN arrangement) or the advanced atomizer design was coupled to the square-wave modulated power supply source (SE-SW arrangement). Both configurations, SE-SIN and SE-SW, should ensure more efficient power transfer from the source to the plasma, eliminating undesired heat loss at the electrodes. Despite these expectations, the overall Se preconcentration efficiency remained unchanged, reaching around 65% regardless of the experimental arrangement employed.

*In-situ* preconcentration of volatile Cd species in the DBD atomizer for subsequent AAS detection has been investigated for the first time to the best of our knowledge. Quantitative analyte trapping followed by complete release of preconcentrated analyte species was reached under optimized conditions in the simplest and most robust experimental arrangement, *i.e.*, in DBD with glued electrodes coupled to a power supply source with sinusoidal modulation of high voltage (REF-SIN arrangement). Precise and accurate results can be obtained by the proposed method, as validated by Cd determination in a wastewater certified reference material. Although the potential of the proposed method is significantly limited due to its incompatibility with higher preconcentration time/volume due to analyte loss during extended trapping time, the LOD reached can compete with other analytical

**Table 4.** Comparison of LODs reached by AAS or OES for Cd determination after preconcentration

| Analytical method | Approach to preconcentration | Sample volume (mL) | LOD (pg $ml^{-1}$) | Reference |
|---|---|---|---|---|
| **VSG-QTA-AAS** | heated quartz trap upstream QTA | 6.0 | 1.8 | 25 |
| **VSG-QTA-AAS** | heated W-coil | 4.2 | 4.0 | 26 |
| **VSG-ETA-AAS** | *in-situ* trapping in an Ir-coated graphite furnace | 0.5 | 4.0 | 27 |
| **VSG-DBD-AAS** | *in-situ* trapping in DBD | 0.15 | 220 | this work |
| **VSG-DBD-OES** | heated W-coil | 2.0 | 300 | 28 |
| **DBD-OES** | adsorption of $Cd^{2+}$ from solution onto an alumina tube, followed by DBD assisted desorption, vaporization and excitation | 40 | 300 | 29 |

methods reported recently in the literature employing Cd preconcentration. Our future research will focus on modifications in the trapping step to reach higher stability of trapped Cd species in REF-SIN arrangement as well as on testing alternative approaches to preconcentration of Cd species compatible with VSG and AAS detection. Detection of volatile Cd species by AAS in the DBD plasma in the on-line atomization mode, *i.e.*, without preconcentration, revealed an unexpected decrease of sensitivity in the presence of the plasma compared to the "no plasma" mode of the atomizer. The mechanism of this behavior remains unexplained. The hypothesis to be confirmed is the in-plasma reaction of a certain fraction of free Cd atoms generated together with co-generated HCN, whose products, most likely cyanocomplexes of Cd, are difficult to atomize in the DBD. Further investigations will be carried out to explore this phenomenon.

Experiments are in progress to improve the overall preconcentration efficiency for Se by modifications of the DBD power supply source to work in the MHz range as well as to increase the stability of trapped Cd species by modifications of the inner surface of the DBD atomizer to make the preconcentration procedure compatible with larger sample volumes. Once these goals are achieved, a detailed determination of analytical figures of merit will follow, including an interference study.

## ASSOCIATED CONTENT

The supporting information (Fig. S1 and Text S1) is available at https://www.at-spectrosc.com.

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**Notes**

The authors declare no competing financial interest.

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