

*Original Paper*

**Comparison of the cold vapor generation using NaBH<sub>4</sub> and SnCl<sub>2</sub> as reducing agents and atomic emission spectrometry for the determination of Hg with a microstrip microwave induced argon plasma exiting from the wafer**

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**Abstract.** A 2.45 GHz low power microwave microstrip plasma (MSP) exiting the wafer and operated with Ar at atmospheric pressure was used for the optical emission spectrometric determination of Hg with the aid of a miniaturized optical fiber spectrometer with a CCD detector and the cold vapor (CV) generation technique using NaBH<sub>4</sub> and SnCl<sub>2</sub> as reductants. The experimental conditions were optimized with respect to the relative intensity of the Hg I 253.6 nm line and its signal-to-background intensity ratio (SBR). So as to understand the results of the optimization experiments, the excitation temperatures as measured from Ar I lines ( $T_{\text{exc}}$ ) and the electron number densities ( $n_e$ ) for the Ar MSP loaded with Hg vapors were determined and found to be in the range from 5500 to 6300 K and from  $1.4$  to  $2.0 \times 10^{14} \text{ cm}^{-3}$ , respectively. Under the optimized conditions, the detection limit for Hg of the CV-MSP-OES using SnCl<sub>2</sub> as the reducing agent was found to be much lower ( $0.11 \text{ ng mL}^{-1}$ ) than in the case where NaBH<sub>4</sub> was used ( $9 \text{ ng mL}^{-1}$ ). The linearity range was found to be up to  $1 \text{ } \mu\text{g mL}^{-1}$  while the precision was of the order of 0.7–5%. The proce-

dure with SnCl<sub>2</sub> as reductant was used for the determination of Hg at a concentration of  $0.2 \text{ } \mu\text{g mL}^{-1}$  in synthetic water samples containing 1 to 4% (m/v) of NaCl with an accuracy of 3% as well as in a solution of the domestic sludge standard reference material (NIST SRM 2781) with a certified concentration for Hg of  $3.64 \pm 0.25 \text{ } \mu\text{g g}^{-1}$  for which  $3.55 \pm 0.41 \text{ } \mu\text{g g}^{-1}$  was found.

**Keywords:** Microstrip microwave induced plasma; cold vapor generation; SnCl<sub>2</sub>; NaBH<sub>4</sub>; mercury; optical emission spectrometry

The miniaturization of radiation sources for spectrochemical analysis is an important and significant research goal and refers to almost all kind of analytical plasmas [1–3]. Miniaturized microwave induced plasma (MIP) based on microstrip technology for the transmission of the microwave power to the plasma channel have been used for analytical purposes. Indeed, a microstrip plasma (MSP) fully sustained and operated inside the gas channel of different wafer structures has been directly combined with the cold vapor (CV) generation technique and used for the emission spectrometric determination of Hg, when SnCl<sub>2</sub> is used as reductant [4, 5]. Further, also an MSP provided on a substrate, in which the location

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of a microstrip relatively to the open end of the gas channel enables the plasma to exit from the wafer, has been described but its analytical application in combination with a gaseous analyte species generation reaction is still unexploited. Preliminary experiments, however, have shown that this MSP exiting from the wafer [6] can be coupled to chemical Hg CV generation technique even when NaBH<sub>4</sub> is used as reductant and an excess of H<sub>2</sub> is produced. Therefore, it has been decided to compare the analytical performance of the MSP exiting from the wafer for the determination of Hg by the CV generation technique when both SnCl<sub>2</sub> and NaBH<sub>4</sub> are used as reductants in detail. In the latter case volatile hydride forming elements eventually could be determined in the same run and it was expected that the plasma, which exits the wafer can be easily viewed end-on without suffering from space-angle limitations as recently reported [5].

Indeed, although both NaBH<sub>4</sub> and SnCl<sub>2</sub> can be used for the reduction of Hg(II) in acidic solutions to its volatile elemental form, NaBH<sub>4</sub> is very often preferred over SnCl<sub>2</sub> as the reduction of both inorganic and organic Hg is more effective and faster [7]. However, in the reaction using NaBH<sub>4</sub>, the vapors of Hg are accompanied by an excess of H<sub>2</sub>, which may considerably affect the analytical performance, when it is introduced into the radiation source [8, 9]. Therefore, in the present study the MSP exiting the wafer was carefully optimized for OES using a miniaturized optical fiber spectrometer with CCD detection for the determination of Hg by the continuous flow CV generation technique using both NaBH<sub>4</sub> and SnCl<sub>2</sub> (CV-MSP-OES). For both reductants the parameters of the CV-MSP-OES procedures, namely the concentration of the reductants, the concentration of the substances used for a stabilization of the reducing agent solutions, the HCl concentration in the sample, the flow rate of Ar, the flow rate of the reagents, the volume of liquid in the gas-liquid phase separator and the RF power were optimized with respect to maximum net intensities of the Hg I 253.6 nm emission line and its signal-to-background intensity ratios (SBR). The net intensities of the Hg line obtained under different conditions were expressed in relation to the highest intensity in a given series of measurements. So as to understand the results of the optimization experiments, the excitation temperatures, as measured from Ar I lines ( $T_{\text{exc}}$ ), and the electron number densities ( $n_e$ ) both were determined at different concentrations of NaBH<sub>4</sub> and SnCl<sub>2</sub>, flow rates of Ar and forward

powers. Under the optimized conditions for the CV-MSP-OES procedures with SnCl<sub>2</sub> and NaBH<sub>4</sub> the limits of detection for Hg, the linearity range and the precision of measurements were compared. CV-MSP-OES under the use of SnCl<sub>2</sub> as reducing agent was employed for the determination of Hg in synthetic water samples containing NaCl as well as in a domestic sludge standard reference material.

## Experimental

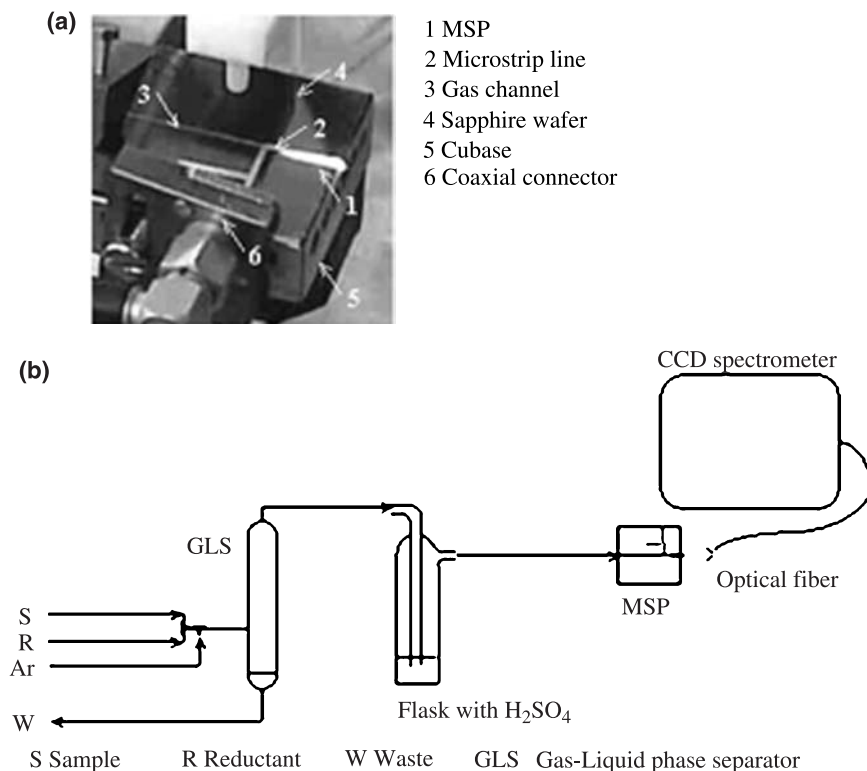
### *Microstrip plasma optical emission spectrometry*

A microstrip plasma (MSP) was operated in a square sapphire wafer with a length of 30 mm and a height of 1.5 mm, in which a straight cylindrical channel (0.64 mm in diameter) for the introduction of the working gas was grown-in. In contrast with the previously described MSP structure [5], the microstrip (0.8 mm in width) on the wafer in the case of the present study extends to the edge of the wafer, by which the plasma exits from the gas channel by about 2–3 mm (Fig. 1a). As before a Cu ground electrode sputtered on the backside of the wafer was connected to a Cu base cooled by a fan. Microwave energy at a frequency of 2.45 GHz were generated with a power oscillator (Dirk Fisher Elektronik, Germany, [www.dfe-online.de](http://www.dfe-online.de)) and transferred to the MSP structure by a coaxial cable and a connector. The MSP was operated with Ar at a maximum forward power of 40 W. The flow of Ar loaded with volatile Hg vapors and other by-products of the CV generation reaction was introduced into the gas channel of the wafer by means of a metal capillary. For controlling the gas flow rates a F-201C-FB-33V Bronkhorst High-Tech (Netherlands, [www.bronkhorst.com](http://www.bronkhorst.com)) mass flow meter was used.

The radiation emitted by the MSP was collected by a COL UV/VIS collimating lens (6 mm in diameter) and transmitted through an FC-UV600-2SR optical fiber (Avantes, U.S.A., [www.avantes.com](http://www.avantes.com)) to a miniaturized USB2000 spectrometer (Ocean Optics, U.S.A., [www.oceanoptics.com](http://www.oceanoptics.com)) equipped with a grating and a Sony ILX511 high-performance 2048-element linear CCD-array detector. The distance between the lens and the wafer was 25 mm. To protect the lens from the gases released by the MSP, a quartz plate was placed between the plasma source and the lens.

### *Cold vapor generation*

For the continuous flow CV generation of Hg, reducing agent solutions containing 0.1% NaBH<sub>4</sub> in 0.04 mol L<sup>-1</sup> NaOH and 4% SnCl<sub>2</sub>·2H<sub>2</sub>O in 0.5 mol L<sup>-1</sup> HCl, respectively, and the analyte solution containing 2 or 0.2 mol L<sup>-1</sup> of HCl were pumped in parallel by a two-channel peristaltic pump at a flow rate of 0.55 or 1 mL min<sup>-1</sup>, respectively. The solutions were mixed in a T-piece where the reaction started and then merged with an Ar flow of 9 mL min<sup>-1</sup> in a second T-piece. The resulting reaction mixture was brought into a small 10 mL cylindrical gas-liquid phase separator (GLS). As compared to a previous system [5], the low dead volume of the present GLS reduces the dilution of the vapors of Hg, what prevents a decrease of the signal heights and their reproducibility. Additionally, for a better separation of the gases and the reaction liquid residue the Ar flow is mixed with the reaction mixture before its introduction into the GLS. The residue of the reaction solution was removed instantly with the aid of a further pump with a such flow rate that constantly 0.5 mL of liquid is present in the GLS. Before entering the MSP, the released vapors of Hg and other



**Fig. 1.** Photograph of an Ar MSP coupled to CV generation (a) and set-up for CV-MSP-OES (b)

**Table 1.** Optimized working conditions of CV-MSP-OES

<i>MSP-OES</i>	
Forward power	40 W
Ar flow rate	$9 \text{ mL min}^{-1}$
Integration time	10 msec
Analytical line	Hg I 253.6 nm
<i>CV generation with <math>\text{NaBH}_4</math></i>	
$\text{NaBH}_4$ concentration	0.1% (m/v) in $0.04 \text{ mol L}^{-1}$ NaOH
Sample acidity	$2 \text{ mol L}^{-1}$ HCl
Reagents flow rate	$0.55 \text{ mL min}^{-1}$
Liquid volume in GLS	0.5 mL
<i>CV generation with <math>\text{SnCl}_2</math></i>	
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ concentration	4% (m/v) in $0.5 \text{ mol L}^{-1}$ HCl
Sample acidity	$0.2 \text{ mol L}^{-1}$ HCl
Reagents flow rate	$1.0 \text{ mL min}^{-1}$
Liquid volume in GLS	0.5 mL

reaction by-products in Ar were dried by passing them through a 10 mL vessel containing concentrated  $\text{H}_2\text{SO}_4$ . The whole experimental set-up for the CV-MSP-OES is shown in Fig. 1b and the optimized operating parameters are listed in Table 1.

#### Reagents and solutions

The reagents  $\text{NaBH}_4$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , NaOH, HCl and NaCl, as well as a stock standard solution of Hg were of analytical grade and supplied by Merck KGaA (Germany, www.merck.de). For the preparation of all solutions doubly distilled water was used and for the microwave assisted digestion procedure "suprapur" concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  were employed. A 0.1% (m/v) solution of

$\text{NaBH}_4$  was prepared daily by dissolving appropriate amounts of the  $\text{NaBH}_4$  powder and solid NaOH in water. A 4% (m/v) solution of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was prepared by dissolving the reagent in a suitable amount of concentrated HCl and diluting with water. The final concentrations of NaOH and HCl in the reducing agent solutions were 0.04 and  $0.5 \text{ mol L}^{-1}$ , respectively. Standard solutions with concentrations of 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2 and  $5 \mu\text{g mL}^{-1}$  of Hg(II) were prepared by diluting the  $10 \text{ mg mL}^{-1}$  stock standard solution. The concentration of HCl in the resulting solutions was brought up to 2 or  $0.2 \text{ mol L}^{-1}$  by the addition of concentrated HCl.

To study the chemical interferences in the CV generation procedure, Merck standard solutions containing  $1000 \mu\text{g mL}^{-1}$  of Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Zn(II), As(V), Bi(III), Sb(III) or Se(IV) individually were added to the  $0.2 \mu\text{g mL}^{-1}$  Hg solutions so that their concentrations amount to 5, 10, 20 or  $50 \mu\text{g mL}^{-1}$ .

#### Sample preparation

A domestic sludge standard reference material (NIST SRM 2781) with a certified value for Hg of  $3.64 \pm 0.25 \mu\text{g g}^{-1}$  was digested in a microwave oven MARS 5 (CEM Corporation, U.S.A., www.cem.com). Therefore, the analyzed material was dried at  $110^\circ\text{C}$  for 2 h, 0.25 g of sample were weighted into the vessels and 5 mL of  $\text{HNO}_3$  as well as 5 mL of  $\text{H}_2\text{SO}_4$  added. Then, a two stage microwave assisted sample digestion procedure was applied. In the first step, a power of 1200 W was used during 5 min, which resulted in a pressure of 35 bars and a temperature of  $140^\circ\text{C}$ . During the second step, the same power was applied to the samples for 40 min, which resulted in a pressure of 35 bars and a reaction temperature of  $190^\circ\text{C}$ . After completing the digestion program, the vessels were cooled and their contents were transferred to pre-cleaned glass beakers with a volume of 50 mL. The mixtures then were heated on a hot plate to remove  $\text{NO}_x$  fumes, as recommended by Saraswati

*et al.* [10]. Finally, the samples were transferred to 50 mL calibrated flasks, 1 mL of concentrated HCl was added and the volumes made up with water. Hg was determined by the CV-MSP-OES procedure with SnCl<sub>2</sub> as reducing agent under the optimized operating conditions and by applying 3 standard additions. Three replicate analyses including the complete analytical procedure were made.

#### Determinations of the excitation temperatures and electron number densities

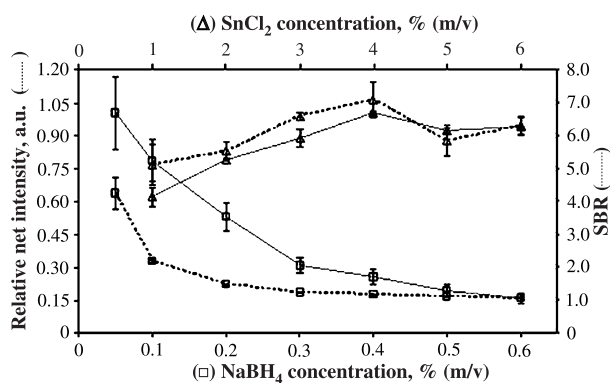
The excitation temperatures ( $T_{\text{exc}}$ ) were measured with Ar atom lines from a Boltzman plot for the Ar I 425.1, 425.9, 426.6, 427.2, 430.1, 433.4 and 434.5 nm lines, as recommended by Cotrino *et al.* [11]. The error of the  $T_{\text{exc}}$  was calculated from the error estimated for the slope of the Boltzman plot and found to be up to 15%. The electron number densities ( $n_e$ ) were determined from the broadening of the  $H_{\beta}$  486.1 nm line, which is accepted to be mainly due to Stark broadening.  $n_e$  was calculated using the equation given by Griem [12] and the precision of the determinations of  $n_e$  was 3–5%.

## Results and discussion

### Influence of the concentrations of the reducing agents

For a plasma at a power of 40 W, an Ar flow rate of 15 mL min<sup>-1</sup>, Hg solutions of 0.2 μg mL<sup>-1</sup> acidified with HCl up to a concentration of 2 and 0.5 mol L<sup>-1</sup>, respectively, and a reagent flow rate of 0.5 mL min<sup>-1</sup>, the influence of the concentration of NaBH<sub>4</sub> in the range of 0.05–0.6% and SnCl<sub>2</sub> in the range of 1–6% on the relative net intensities of Hg I 253.6 nm line and its SBR was studied. The results are given in Fig. 2.

It can be seen that in the case of NaBH<sub>4</sub>, the reagent concentration is critical for the analytical performance. Indeed, when increasing the concentration of NaBH<sub>4</sub> above 0.1%, both the net intensity of the Hg line and the SBR strongly decrease. This is a result of



**Fig. 2.** Effect of the concentrations of NaBH<sub>4</sub> and SnCl<sub>2</sub> · 2H<sub>2</sub>O on the relative net intensity for the Hg line and its SBR. Power: 40 W, flow rate of Ar: 15 mL min<sup>-1</sup>, flow rate of reagents: 0.5 mL min<sup>-1</sup>, concentration of Hg: 0.2 μg mL<sup>-1</sup>. Average ( $n = 3$ ) ± standard deviation

the introduction of the increasing amounts of H<sub>2</sub> into the plasma. Indeed, the amount of H<sub>2</sub> was found to change from 0.3 ± 0.1 mL min<sup>-1</sup> at a concentration of 0.05% NaBH<sub>4</sub> to 5.6 ± 0.3 mL min<sup>-1</sup> at a concentration of 0.6% NaBH<sub>4</sub>. It was also found that then the  $T_{\text{exc}}$  measured with Ar I lines and the  $n_e$  changed from 6100 to 5500 K and from 1.6 to 2.0 × 10<sup>14</sup> cm<sup>-3</sup>, respectively. As even at low NaBH<sub>4</sub> concentrations the efficiency of the CV generation for Hg can be assumed to be rather high [13], the deterioration of the response for Hg found here might be due to changes of the excitation conditions in the MSP as a result of the higher thermal conductivity and the required dissociation temperature of H<sub>2</sub> in comparison to Ar [14]. In compliance with the radiative-recombination excitation mechanism proposed for atmospheric pressure MIPs in gas mixtures containing H<sub>2</sub> [15], it could be expected that although the overall  $n_e$  in the MSP loaded with H<sub>2</sub> increases, the high energy electrons may be involved in the dissociation and the excitation of H<sub>2</sub> and therefore the excitation conditions for Hg may become less favorable.

Despite the fact that with a 0.05% NaBH<sub>4</sub> solution the relative net intensity for the Hg line and the SBR are about 20% higher than in the case of a 0.1% NaBH<sub>4</sub> solution, the repeatability of the analytical signal in this case was poorer. Therefore, in all further experiments a 0.1% solution of NaBH<sub>4</sub> was used.

When performing the CV generation with SnCl<sub>2</sub>, which is known to be a milder reducing agent than NaBH<sub>4</sub> [16, 17], higher concentrations of the reductant were required so as to get a reaction. When increasing the concentration of SnCl<sub>2</sub> · 2H<sub>2</sub>O up to 4%, the relative net intensity of the Hg line was found to steadily increase up to this concentration. For higher concentrations of SnCl<sub>2</sub>, a slight decrease of the response of Hg was observed. The SBR was also found to strongly depend on the concentration of SnCl<sub>2</sub> · 2H<sub>2</sub>O. The  $T_{\text{exc}}$  and  $n_e$ , however, practically remained unchanged at changing concentrations of SnCl<sub>2</sub> and were 6200 K and 2.0 × 10<sup>14</sup> cm<sup>-3</sup>, respectively. Their variation was below 5% within the whole concentration range of SnCl<sub>2</sub> investigated. A solution containing 4% of SnCl<sub>2</sub> · 2H<sub>2</sub>O was used for all further experiments.

### Influence of concentrations of substances stabilizing the reducing agent solutions

NaBH<sub>4</sub> is known to readily decompose in acidic aqueous solutions and therefore alkaline solutions are

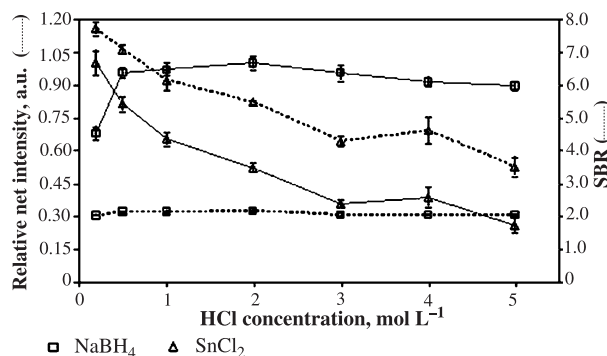
normally required so as to keep this reductant stable. SnCl<sub>2</sub> tends to undergo hydrolysis in aqueous solutions and to form Sn(OH)Cl precipitate. Accordingly, the solutions of SnCl<sub>2</sub> are usually acidified with HCl at moderate concentrations. However, the presence of both substances used for stabilization, namely NaOH and HCl, is also important with respect to the performance of the CV generation reaction and their concentrations were optimized in this study. The influence of the concentration of NaOH used for stabilization of the 0.1% NaBH<sub>4</sub> solution on the response for Hg was investigated in the range of 0.01 to 0.08 mol L<sup>-1</sup>. In the case of HCl added to the 4% solution of SnCl<sub>2</sub> · 2H<sub>2</sub>O, its concentration was varied from 0.1 to 1 mol L<sup>-1</sup>. All other experimental conditions used were as mentioned when describing the influence of the concentrations of the reducing agents.

When changing the concentration of NaOH in the 0.1% NaBH<sub>4</sub> solution from 0.01 to 0.04 mol L<sup>-1</sup> the relative net intensity of the Hg I 253.6 nm line was found to increase from 0.8 to 1.0. At a concentration of 0.08 mol L<sup>-1</sup> of NaOH in the NaBH<sub>4</sub> solution the relative net intensity for the Hg line was found to be about 0.9.

In the case of the 4% SnCl<sub>2</sub> solutions, the highest response for Hg was found when using a concentration of 0.5 mol L<sup>-1</sup> of HCl in the reducing agent solution. Above that concentration the relative net intensity for the Hg line decreases and it is by 25% lower when the solution of SnCl<sub>2</sub> contains 1 mol L<sup>-1</sup> of HCl. Concentrations of HCl in the SnCl<sub>2</sub> solution higher than 1 mol L<sup>-1</sup> were found to be still less favorable as then an oxidation of SnCl<sub>2</sub> to SnCl<sub>4</sub> becomes likely, which is accompanied by a precipitation of Sn(OH)Cl. These observations were well consistent with the results reported in literature, where the molar concentration of HCl is usually from 2 to 5 times higher than this for SnCl<sub>2</sub> [4, 13, 16, 18].

#### *Influence of the concentration of HCl in the sample*

The concentration of HCl in the sample solution also may influence the signal for Hg in CV-MSP-OES, both when using NaBH<sub>4</sub> and SnCl<sub>2</sub>. For this investigation, of which the results are shown in Fig. 3, solutions of 0.1% NaBH<sub>4</sub> in 0.04 mol L<sup>-1</sup> NaOH and 4% SnCl<sub>2</sub> in 0.5 mol L<sup>-1</sup> HCl were used and all other operating parameters were as reported when studying the influence of the concentrations of the reducing agents.



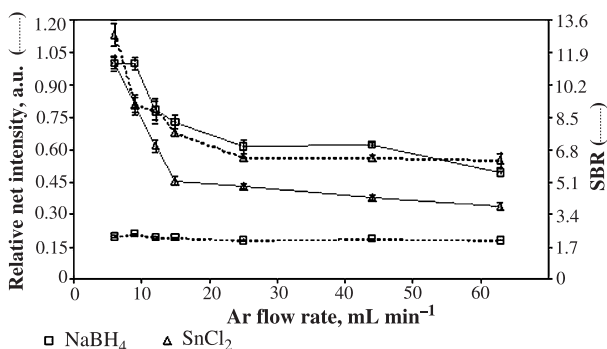
**Fig. 3.** Effect of the concentration of HCl in the sample on the relative net intensity for the Hg line and its SBR. Power: 40 W, flow rate of Ar: 15 mL min<sup>-1</sup>, flow rate of reagents: 0.5 mL min<sup>-1</sup>, reductants: 0.1% NaBH<sub>4</sub> in 0.04 mol L<sup>-1</sup> NaOH and 4% SnCl<sub>2</sub> · 2H<sub>2</sub>O in 0.5 mol L<sup>-1</sup> HCl, concentration of Hg: 0.2 μg mL<sup>-1</sup>. Average ( $n = 3$ ) ± standard deviation

In the case of the CV generation reaction with NaBH<sub>4</sub> it was found that the concentration of HCl in the sample solution over a wide range of acid concentration, namely from 0.05 to 4 mol L<sup>-1</sup>, does not affect the relative net intensity for the Hg line. This was also found to be the case for the SBR for that line, which has a value of 2.1 with a variation below 2.5% over the whole range investigated. In all further experiments, in which the reaction with NaBH<sub>4</sub> was used for the CV generation of Hg, the samples were acidified with HCl to the concentration of 2 mol L<sup>-1</sup>.

When using SnCl<sub>2</sub> in the CV generation, it was found that only at relatively low concentrations of HCl in the sample, namely between 0.2 and 0.5 mol L<sup>-1</sup>, a high net intensity for the Hg I 253.6 nm line and a high SBR were obtained. With a further increase of the concentration of HCl the analytical signal for Hg was found to gradually decrease. This may be understood from a lower efficiency of the reduction of SnCl<sub>2</sub>, which most probably is a result of its oxidation by O<sub>2</sub> under these conditions. Consequently, the concentrations of HCl recommended in the literature [16, 19–21] for the CV generation of Hg under the use of SnCl<sub>2</sub> are close to 0.2 mol L<sup>-1</sup> and a such concentration was also used for all further experiments in this study.

#### *Influence of the Ar flow rate*

Since in CV-MSP-OES Ar both serves to transport the released Hg vapors from the GLS to the plasma, and to support the MSP discharge, it is expected that the flow rate of Ar also largely will influence the perfor-



**Fig. 4.** Effect of the flow rate of Ar on the relative net intensity for the Hg line and its SBR. Power: 40 W, flow rate of reagents:  $0.5 \text{ mL min}^{-1}$ , reductants: 0.1%  $\text{NaBH}_4$  in  $0.04 \text{ mol L}^{-1}$   $\text{NaOH}$  and 4%  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in  $0.5 \text{ mol L}^{-1}$   $\text{HCl}$ , concentration of Hg:  $0.2 \mu\text{g mL}^{-1}$ . Average ( $n = 3$ )  $\pm$  standard deviation

mance of the MSP exiting from the wafer. In the experiments on the influence of the Ar flow rate on the performance of the MSP the latter was operated at the power of 40 W and at a reagent flow rate of  $0.5 \text{ mL min}^{-1}$ . In the CV generation reaction with  $\text{NaBH}_4$  a 0.1% solution of the reducing agent in  $0.04 \text{ mol L}^{-1}$   $\text{NaOH}$  and a sample solution containing  $0.2 \mu\text{g mL}^{-1}$  of Hg in  $2 \text{ mol L}^{-1}$   $\text{HCl}$  were used. In the CV generation with  $\text{SnCl}_2$  a 4% solution of the reductant in  $0.5 \text{ mol L}^{-1}$   $\text{HCl}$  and a solution of  $0.2 \mu\text{g mL}^{-1}$  of Hg acidified with  $0.2 \text{ mol L}^{-1}$   $\text{HCl}$  were used. In addition, the  $T_{\text{exc}}$  as determined with Ar I lines and the  $n_e$  were evaluated under these conditions so as to understand the changes in the analytical performance of the Ar MSP.

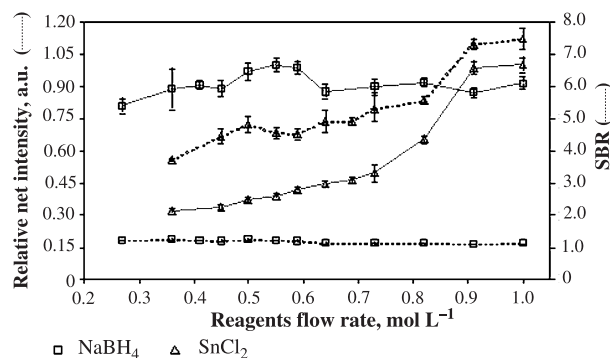
As it can be seen from Fig. 4, the relative net intensities for the Hg I 253.6 nm line at an increase of the flow rate of Ar from 6 to  $63 \text{ mL min}^{-1}$  gradually decreased for a CV generation performed with  $\text{NaBH}_4$  and  $\text{SnCl}_2$  by ca. 50 and 70%, respectively. In a similar way, the SBR in the case of the Hg I 253.6 nm line for the CV generation reaction with  $\text{NaBH}_4$  and  $\text{SnCl}_2$  also decreased over the whole range of the Ar flow rate investigated from 2.3 to 2.0 and from 13 to 6.0, respectively. It was found, however, that the  $T_{\text{exc}}$  as measured from Ar I lines did not change substantially. Indeed, when changing the Ar flow rate from 6 to  $63 \text{ mL min}^{-1}$ , the  $T_{\text{exc}}$  varied between 6100 and 6200 K and between 6000 and 6300 K in the case of the CV generation under the use of  $\text{NaBH}_4$  and  $\text{SnCl}_2$ , respectively. However, there was not a specific trend and  $n_e$  was found to change with the Ar flow rate by about 20 and 10% on the whole for the CV generation with  $\text{NaBH}_4$  and  $\text{SnCl}_2$ , respectively.

Considering the low change of the  $T_{\text{exc}}$  and the  $n_e$  with the Ar flow rate, it was assumed that a deterioration of the response for Hg with the increase of the flow of Ar for the studied MSP does not result from de-excitation through an increase of a number of radiative collisions with neutral Ar atoms, as it could be expected for bulky MIP radiation sources [18, 22]. Most probably, this effect is a consequence of the lower residence time of Hg in the plasma. A very similar behavior has recently been observed for the Ar MSP coupled to CV generation when the plasma is fully sustained inside the gas channel of the sapphire wafer [5]. In all further experiments, a flow rate for Ar of  $9 \text{ mL min}^{-1}$  was used.

#### *Influence of the flow rate of the reagents*

The flow rate of the reagents was expected to influence the rate of the reaction. Additionally, in the case of the CV generation with  $\text{NaBH}_4$  the amount of  $\text{H}_2$  produced and introduced into the MSP may change with the reagents flow rates [23]. Therefore, the influence of this parameter on the response for Hg in the CV generation with the aid of  $\text{NaBH}_4$  and  $\text{SnCl}_2$  was studied. All conditions optimized before were used as such.

Indeed, it was found that with an increase of the flow rate of the reagents from  $0.27$  to  $1.0 \text{ mL min}^{-1}$  the amount of  $\text{H}_2$  produced in the reaction changed from  $2.6 \pm 0.1$  to  $7.6 \pm 0.7 \text{ mL min}^{-1}$ . When the reagent flow rate changes from  $0.27$  to  $0.50 \text{ mL min}^{-1}$ , as it can be seen from Fig. 5, the relative net intensity for the Hg line obtained for the CV generation with



**Fig. 5.** Effect of the flow rate of the reagents on the relative net intensity for the Hg line and its SBR. Power: 40 W, flow rate of Ar:  $9 \text{ mL min}^{-1}$ , reductants: 0.1%  $\text{NaBH}_4$  in  $0.04 \text{ mol L}^{-1}$   $\text{NaOH}$  and 4%  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in  $0.5 \text{ mol L}^{-1}$   $\text{HCl}$ , concentration of Hg:  $0.2 \mu\text{g mL}^{-1}$ . Average ( $n = 3$ )  $\pm$  standard deviation

NaBH<sub>4</sub> was found to increase from 0.8 to 1. Up to the flow rate of 0.59 mL min<sup>-1</sup> the relative net intensity for the Hg line was found to be constant and a further increase of the flow rate of the reagents was found to result in a slight decrease of the response for Hg. These changes also were found to apply for the SBR for the Hg line. Indeed, when using flow rates above 0.59 mL min<sup>-1</sup> the SBR decreased. A flow rate of 0.55 mL min<sup>-1</sup> was found to be optimum.

In the case of the CV generation with SnCl<sub>2</sub>, a steady increase of the relative net intensity for the Hg line and its SBR with the flow rate of the reagents was observed in the range of 0.36–1.0 mL min<sup>-1</sup>. Almost a 3- and a 2-fold increase of the relative net intensity for the Hg line and the SBR was found to occur in this range. A flow rate of the reagents of 1.0 mL min<sup>-1</sup> was found to be optimum and was used in all further experiments.

#### *Influence of the volume in the gas liquid separator*

In all measurements reported, the volume of the liquid in the GLS was kept at a constant level of 0.5 mL. In this way, the pressure inside the low-volume GLS was kept constant. However, the use of other volumes, namely 0.2, 1 and 1.5 mL, also was tested. It was found that the volume of liquid in the GLS only had a slight influence on the Hg signal for both CV generation reactions. In the case of the CV generation with NaBH<sub>4</sub>, the relative net intensity for the Hg line in the case of 0.5, 1 and 1.5 mL was close to 1, whereas for a volume of 0.2 mL a value of 0.9 was found. In the case of the CV generation with SnCl<sub>2</sub>, the relative net intensities for the Hg line with all volumes tested were comparable, however, for volumes of 1 and 1.5 mL higher washing times were required. Therefore, a volume of liquid of 0.5 mL inside the GLS was considered as optimum and used for all further measurements.

#### *Areas of stability*

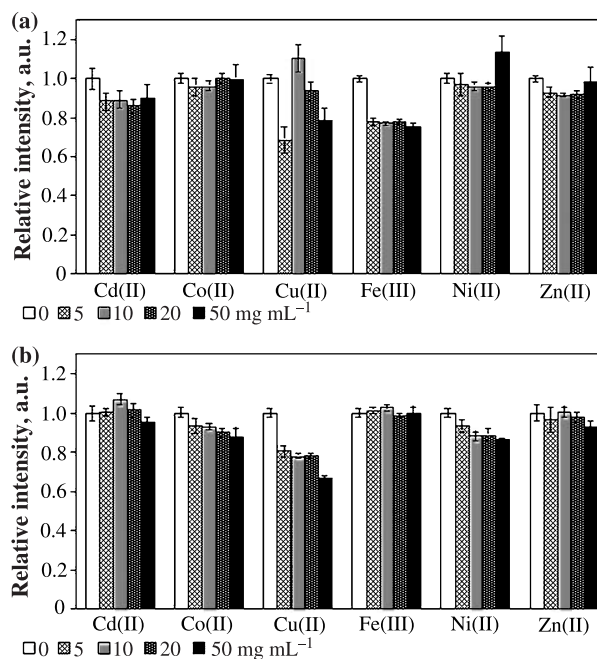
The stability areas for MSPs in Ar loaded with Hg vapors, as obtained with the CV generation reactions using NaBH<sub>4</sub> and SnCl<sub>2</sub>, respectively, were found to be comparable. At an Ar flow rate of 9 mL min<sup>-1</sup>, the MSP was found to be stable at a power between 33 and 40 W under the conditions for optimum CV generation. At lower powers the Ar MSP becomes unstable and extinguishes. When increasing the Ar flow rate up

to 63 mL min<sup>-1</sup>, the power range within which the Ar MSP was stable was reduced to about 35–36 W.

When operating the Ar MSP at a flow rate of 9 mL min<sup>-1</sup> but at a power below 40 W, it was also found that the relative net intensity for the Hg line decreases. Indeed, when the power was decreased to 37 W, the signals for Hg in the case of the CV generation using NaBH<sub>4</sub> or SnCl<sub>2</sub> decreased by about 50 and 30%, respectively. However, the SBR values under these conditions were found to change less than 2–3%. The  $T_{\text{exc}}$  as measured from Ar I lines did not change and was 6000 and 6100 K for the CV generation using NaBH<sub>4</sub> and SnCl<sub>2</sub>, respectively. The respective  $n_e$  therefore was found to decrease from 1.6 to  $1.4 \times 10^{14}$  cm<sup>-3</sup> and from 1.8 to  $1.5 \times 10^{14}$  cm<sup>-3</sup>, respectively.

#### *Chemical interferences*

Under the optimized experimental conditions, the chemical interferences in the determination of Hg by CV-MSP-OES using NaBH<sub>4</sub> and SnCl<sub>2</sub> as reducing agents were investigated. The most commonly known potential interferents were studied and included transition metal ions such as Cd(II), Co(II), Cu(II), Fe(III), Ni(II) and Zn(II) as well as the volatile hydride form-



**Fig. 6.** Effect of the presence of Cd, Co, Cu, Fe, Ni and Zn on the relative intensity for the Hg line in the CV generation reaction performed with NaBH<sub>4</sub> (a) and SnCl<sub>2</sub> (b), respectively. Concentration of Hg: 0.2 μg mL<sup>-1</sup> in 2 mol L<sup>-1</sup> HCl (a) and 0.2 mol L<sup>-1</sup> HCl (b). Average ( $n = 3$ ) ± standard deviation

**Table 2.** Influence of As, Bi, Sb and Se on the relative intensities for Hg when using the CV-MSP-OES procedure under optimized conditions. Concentration of Hg:  $0.2 \mu\text{g mL}^{-1}$ . Average ( $n = 3$ )  $\pm$  standard deviation

	Interferent concentration, $\mu\text{g mL}^{-1}$			
	0	5	10	20
CV generation with $\text{NaBH}_4$				
As(V)	$1.00 \pm 0.02$	$1.02 \pm 0.02$	$0.98 \pm 0.03$	$1.00 \pm 0.02$
Bi(III)	$1.00 \pm 0.03$	$0.96 \pm 0.05$	$0.96 \pm 0.03$	$1.00 \pm 0.02$
Sb(III)	$1.00 \pm 0.04$	$1.04 \pm 0.03$	NM	NM
Se(IV)	$1.00 \pm 0.01$	$0.09 \pm 0.01$	$0.16 \pm 0.05$	$0.11 \pm 0.02$
CV generation with $\text{SnCl}_2$				
As(V)	$1.00 \pm 0.02$	$0.74 \pm 0.02$	$0.74 \pm 0.03$	$0.72 \pm 0.01$
Bi(III)	$1.00 \pm 0.02$	$0.86 \pm 0.07$	$0.76 \pm 0.07$	$0.70 \pm 0.02$
Sb(III)	$1.00 \pm 0.02$	$0.94 \pm 0.01$	$0.96 \pm 0.02$	$0.84 \pm 0.04$
Se(IV)	$1.00 \pm 0.02$	$0.95 \pm 0.05$	$0.78 \pm 0.03$	$0.68 \pm 0.01$

NM Not measured.

ing elements As(V), Bi(III), Sb(III), and Se(IV). For the experiments a concentration of Hg of  $0.2 \mu\text{g mL}^{-1}$  was used, while the concentrations of the potential interferents in the solutions were 5, 10, 20, and  $50 \mu\text{g mL}^{-1}$ . The effects of the presence of transition metals on the response found for Hg in the CV generation using  $\text{NaBH}_4$  and  $\text{SnCl}_2$  are shown in Fig. 6. In Table 2 the results for hydride forming elements are listed. In both cases the relative intensities given were calculated by ratioing the net intensities for the Hg line measured in the case of the solutions containing Hg and the potential interferents to those for the solutions containing Hg only.

In the case of the CV generation using  $\text{NaBH}_4$ , concentrations of  $50 \mu\text{g mL}^{-1}$  of Co, Ni, and Zn as well as As and Bi were found to cause no interferences in the determination of Hg. The interferents concentrations herewith can be 250 times higher than the concentration of Hg ( $0.2 \mu\text{g mL}^{-1}$ ). This could be due to the relatively low concentration of reductant used for the CV generation reaction. For concentrations of  $5\text{--}50 \mu\text{g mL}^{-1}$  of Cd and Fe a suppression of the signals for Hg by about 10 and 20%, respectively, was found. This was not as strong as the effect reported for these metals by Krata *et al.* [7]. The effect of Cu was found to be more complex. At a concentration of  $5 \mu\text{g mL}^{-1}$ , the signal for Hg was depressed, which is most likely caused by an adsorption of the analyte on the reduced Cu [8]. Indeed, brown deposit was found to cover the T-pieces. At a concentration of  $10 \mu\text{g mL}^{-1}$  of Cu the signal for Hg was found to have increased, which is presumably due to some surface-mediated reactions of Hg hydroboron intermediates

with reduced Cu deposited on the surface of the reaction system, as reported by Feng and co-workers [24]. A very strong suppression of the signal for Hg was observed in the presence of Se even at the lowest concentration of this element investigated ( $5 \mu\text{g mL}^{-1}$ ). This effect could be attributed to a formation of HgSe [25]. However, also a competition of the reaction of Se(IV) with  $\text{NaBH}_4$  forming  $\text{SeH}_2$  and the reaction of  $\text{NaBH}_4$  with Hg(II) could be a reason [7, 13]. In the case of Sb, a very intensive Sb I 252.8 nm line was observed as a consequence of the introduction of the  $\text{SbH}_3$  produced by the reaction of Sb with  $\text{NaBH}_4$  into the MSP. As a result of the occurrence of this line the background intensity in the vicinity of the Hg I 253.6 nm line changed, which complicated the measurement of the Hg line intensity.

When using  $\text{SnCl}_2$  for the CV generation of Hg, the investigated metals did not cause any interferences except for Cu and Ni. Their presence at a concentration of  $50 \mu\text{g mL}^{-1}$  results in a reduction of the signal for Hg by about 30 and 10%, respectively. The presence of As, Bi, and Se up to a concentration of  $20 \mu\text{g mL}^{-1}$  was found to cause a decrease of the response for Hg by maximally 30% and the presence of  $20 \mu\text{g mL}^{-1}$  of Sb leads to a depression by 20%. It could be expected that the interferences in the CV generation reaction using  $\text{SnCl}_2$  are due to the formation of different intermetallic compounds with Hg [26].

#### Figures of merit and analytical application

Under the optimized conditions the analytical performance of CV-MSP-OES for Hg was determined. In the case of the CV generation using  $\text{NaBH}_4$ , the calibration curve for Hg was found to be linear up to  $2 \mu\text{g mL}^{-1}$  with a correlation coefficient ( $R^2$ ) of 0.999. The limit of detection for Hg, calculated according to the  $3\sigma$  criterion, was found to be  $9 \text{ ng mL}^{-1}$ . This is better than the one reported in the literature for CV-MIP-OES using analyte preconcentration in a cryogenic trap [8]. The detection limit for Hg can be further improved, as it has been shown in the literature for CV-MIP-OES, by preconcentrating Hg by amalgamation [23] or by removing  $\text{H}_2$  with a special membrane [27] after the reaction with  $\text{NaBH}_4$ . The precision, in terms of the RSD for replicate measurements, was 0.5 and 5% at concentrations of Hg of 2 and  $0.1 \mu\text{g mL}^{-1}$ , respectively.

The analytical performance under the use of  $\text{SnCl}_2$  as reducing agent is better than in the case of  $\text{NaBH}_4$



even after a careful optimization. The sensitivity is almost 12 times higher than the sensitivity obtained with NaBH<sub>4</sub> as reducing agent. The dynamic range, however, was shorter, namely up to 1 µg mL<sup>-1</sup>, but the limit of detection for Hg was as low as 0.11 ng mL<sup>-1</sup>. This is considerably lower than the detection limits of 0.64 and 1.1 ng mL<sup>-1</sup> reported recently for the CV generation with SnCl<sub>2</sub> in the case of Ar and He MSPs, respectively, which were fully sustained inside the gas channel of the microstrip wafer [5], or than the detection limit for Hg obtained in the case of an atmospheric pressure MIP realized in an MPT or a Beenakker cavity coupled with the CV generation under the use of SnCl<sub>2</sub> [18]. RSDs of 0.7 to 5% at concentrations of 1 and 0.05 µg mL<sup>-1</sup>, respectively, were obtained.

CV-MSP-OES under the use of SnCl<sub>2</sub> as reducing agent was used for the determination of Hg in synthetic water samples containing 0.2 µg mL<sup>-1</sup> of Hg and different amounts of NaCl as concomitant [16]. Under calibration with standard solutions containing Hg only, the recoveries for Hg at concentrations of NaCl of 1, 2 and 4% (m/v) were 93 ± 3, 90 ± 4, and 90 ± 4%, respectively.

CV-MSP-OES using SnCl<sub>2</sub> as reducing agent and an MSP exiting the sapphire wafer was also used for the determination of Hg in a domestic sludge standard reference material (NIST SRM 2781). Under a calibration with standard addition a value of 3.55 ± 0.41 µg g<sup>-1</sup> for Hg was found, which is in a good agreement with the certified value (3.64 ± 0.25 µg g<sup>-1</sup>).

## Conclusions

The suitability of the Ar MSP exiting from the sapphire wafer for the determination of Hg by MSP-OES combined to CV generation with both NaBH<sub>4</sub> and SnCl<sub>2</sub> as reducing agents could be shown. With both reductants the MSPs could be stably operated with a low power (33–40 W) and a low working gas flow (9 mL min<sup>-1</sup>). They provided a reasonably fair analytical performance when considering the small dimensions of the plasma. Under the optimized conditions, the detection limit for Hg of CV-MSP-OES in the case of SnCl<sub>2</sub> is 0.11 ng mL<sup>-1</sup>. This is much better than the one obtained with the same experimental set-up under the use of NaBH<sub>4</sub> as reductant (9 ng mL<sup>-1</sup>). In the latter case, the co-generated H<sub>2</sub> in the CV generation reaction was found to deteriorate the excitation of Hg in the Ar MSP, despite the plasma still tolerated the introduction of H<sub>2</sub> at a level of several mL min<sup>-1</sup>. It

should be emphasized however, that the use of miniaturized spectrometers with better performance, including the enhanced sensitivity and the higher signal to noise ratio, would certainly result in an improvement of the power of detection for both procedures described. The MSP exiting from the wafer certainly has no space-angle limitation in the collection of radiation as compared to an MSP sustained inside the gas channel of the microstrip substrate and therewith it seems to be the most promising radiation source for miniaturized analytical systems. When coupling to the CV generation with SnCl<sub>2</sub> as reducing agent its usefulness for the determination of Hg in water samples and in domestic sludge subsequent to sample dissolution could be shown.

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