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## Investigation of the direct hydride generation nebulizer for the determination of arsenic, antimony and selenium in inductively coupled plasma optical emission spectrometry

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**Abstract** A direct hydride generation nebulizer (DHGN) was explored for introduction of the sample in inductively coupled plasma–optical emission spectrometry (ICP–OES) using radially viewed mode. This simple hydride generation system was constructed in our laboratory and requires similar plasma operating conditions to conventional nebulizer–spray-chamber arrangements. This work was focused on the optimization of the operating conditions for hydride generation and evaluation of the main analytical figures of merit for the determination of As, Sb and Se. The excitation conditions of the ICP–OES instrument operated with the DHGN were also explored. Results showed that the analytical performance of the new system for the determination of As, Sb and Se was superior to that of conventional nebulization systems. The DHGN also enabled the determination of elements that do not form volatile hydrides, but with less sensitivity than conventional nebulization systems. Evaluation of the plasma robustness showed that gases generated in hydride generation do not significantly affect the plasma discharge. Similar to conventional hydride generation techniques, analysis with DHGN was susceptible to non-spectroscopic interferences produced by transition metals. Finally, the utility of the DHGN in practical ICP–OES studies was demonstrated in the determination of trace elements in an oyster tissue standard reference material.

**Keywords** Direct hydride generation nebulizer · Hydride generation · Inductively coupled plasma optical emission spectrometry · Arsenic · Antimony · Selenium

### Introduction

Today, the use of hydride generation techniques with inductively coupled plasma spectrometry in analytical laboratories is relatively common. Hydride generation methods exhibit potential benefits for the determination of volatile hydride-forming elements such as As, Sb, Bi, Se, Te, etc. compared to traditional nebulizer–spray-chamber arrangements:

1. high analyte transport efficiency into the plasma that allows lower limits of detection (LOD); and
2. separation of analytes from the sample matrix and the solvent that enables the preconcentration of analytes and reduces potential spectral interferences [1].

These attributes are highly attractive in the determination of this selective group of elements in a wide variety of sample types including environmental, geological, industrial and pharmaceutical materials. Thompson et al. [2], were the first to use hydride generation as a procedure of introduction of the sample in an ICP in the simultaneous determination of As, Sb, Bi, Se and Te. The best limits of detection were found at higher RF-power and with 5 mol L<sup>-1</sup> HCl. They found LOD 500 times lower with respect to pneumatic nebulization. Goulden et al. [3] determined As and Se at RF-power of 1400 W in the ICP–OES. They used a torch of larger diameter than usual that provides stability to the plasma discharge. Hwang et al. [4] described a simple continuous flow mode hydride generation system development for ICP–OES. The sample and reductant were continuously pumped into the hydride generator and the waste sample was continuously removed to ensure a constant pressure. Brindle et al. [5] reported a generator–separator in which hydride formation takes place at the outlet of the two capillaries that transport the sample and the sodium borohydride. This hydride generator was used in direct current plasma (DCP) [5] or in an ICP [6] for Se determination. Another form of generating the hydride in a continuous mode is hydride generation by using modified nebulizers [7, 8, 9, 10, 11]. In these systems, the sam-

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ple and the reducing agent supply are integrated to the nebulizer. The reaction of hydride formation is performed within the aerosol, on contact with the small droplets of sample and reductor. Wolnik et al. [9] described a tandem nebulization system that allowed simultaneous determination of elements that form volatile hydrides as well as other elements. With this system LODs were improved 6 to 40 times for the volatile hydride-forming elements without decreasing the sensitivity for those that do not form hydrides. Huang et al. [10] developed a nebulizer-hydride generator system in which large droplets of the acid sample aerosol from the pneumatic nebulizer were trapped by the impact wall of a smoking-pipe shaped hydride generator, and reacted with reductant. The LODs for the hydride-forming elements could be improved over 20 times those obtained with the conventional nebulizer. The LODs of other elements remained unaffected. Feng et al. [11] designed a small concentric hydride generator without gas-liquid separator, which was used with mini-torch for As determination. The Sturgeon group [7, 8] studied a new hydride generator system, based on the insertion of a capillary tube into the sample-introduction channel of a standard nebulizer. In the first design, this device terminated in a 1.5 cm chamber, from the end of nebulizer orifice [7] and they used a gas-liquid membrane separator. With this system, they increased the tolerance limits of transition elements without interference in the selenium determination. The LOD obtained was  $6 \mu\text{g L}^{-1}$ . This LOD was improved 3 times, with a new design [8] in which the chamber was eliminated at the nebulizer outlet and the gas-liquid separator. This was replaced with a conventional Scott type spray chamber. Although they achieved extremely high tolerance levels of the transition metals in selenium hydride generation, the LOD decreased by one order of magnitude with respect to conventional hydride generation techniques [2, 3, 4, 12, 13, 14] and those of similar type [9].

In a recent conference [15], we described preliminary results of the direct hydride generation nebulizer (DHGN) as a sample-introduction system for inductively coupled plasma optical emission spectrometry (ICP-OES). This simple and economical device is a modified V-groove type nebulizer having two solution channels. Preliminary studies with DHGN for Se determination show that this device is very attractive for the determination of volatile hydride-forming elements with low limits of detection, rapid response and low memory effects. In this connection, the principal aim of this work is to investigate the performance of the direct hydride generation nebulizer for the simultaneous determination of As, Sb and Se in ICP-OES. The report includes studies of hydride generation optimization, the determination of the main analytical figures of merit, evaluation of Mg II 280.270/Mg I 285.213 nm data to gauge the robustness of the plasmas and discussions of preliminary results concerning non-spectroscopic interferences produced by transition metals. The potential benefits of DHGN are also explored for the simultaneous determination of elements that do not form volatile hydrides. Conventional nebulization systems were used for comparison purposes. The analytical potential of the DHGN-ICP-OES is demonstrated in the analysis of a biological standard reference material.

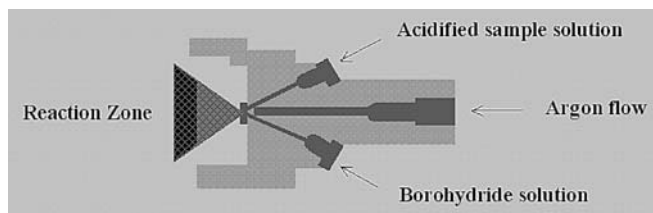
## Experimental

### Instrumentation

The radially-viewed Ar ICP-OES instrument (Thermo Jarrel Ash, Model IRIS HR, Franklin, MA, USA) was used throughout this work. The operating conditions and the working wavelengths are listed in Table 1. These lines were selected based on their sensitivity and freedom from spectral interferences. The sample introduction system was the DHGN coupled with a conventional Scott type spray chamber. Fig. 1 shows a schematic diagram of the hydride generation system. This design was fabricated in home from

**Table 1** Operating conditions for DHGN using radial-Ar ICP OES Instrument

RF Generator	IRIS HR (Thermo Jarrel Ash, Frankling, MA, USA)
Nominal frequency (MHz)	27.12
RF generator type	Crystal controlled
RF power (W)	1350
Dispersive system	Echelle cross dispersion spectrometer: Focal length, 381 mm; F number, F/10; Entrance aperture, 50 $\mu\text{m}$ ; Grating blaze 63.5 degrees; Grating groove density, 54.5 grooves/mm. Resolution, 0.01 nm at 200 nm, 0.02 nm at 400 nm and 0.04 at 600 nm. Full spectral range from 177 to 800, but above 315 there are some gaps in the spectrum.
Detection system	CID (Charge Injection Device) solid-state sensor. Low temperature operation. Array size 512 $\times$ 512.
Outer gas flow rate ( $\text{L min}^{-1}$ )	15
Intermediate gas flow rate ( $\text{L min}^{-1}$ )	1.5
Injector (mm)	1.5
Nebulization systems	DHGN-Scott type spray chamber; Crossflow-Scott type spray chamber and Ultrasonic nebulizer (Cetac, Omaha, NB, USA, The temperatures of the heater and cooler were 110 $^{\circ}\text{C}$ and 4 $^{\circ}\text{C}$ , respectively)
Solution flow mode	Continuous
Integration mode	Random Access Integrator (RAI), Non-destructive read out (NDRO)
Observation height (mm)	8 (Above the last turn of the load coil).
Working wavelengths (nm)	As (I) 189, Ba (II) 455.4, Cd (II) 226.5, Cr (II) 206.1, Cu (I) 324.7, Fe (II) 259.9, Mg (I) 285.2, Mg (II) 285.2, Mn (II) 257.6, Ni (II) 221.6, Sb (I) 206.8, Se (I) 196.1, Zn (II) 202.5



**Fig. 1** Schematic diagram of the direct hydride generation nebulizer (DHGN)

Teflon. It consists of a V-groove nebulizer having two solution channels with 120  $\mu\text{m}$  orifices. Those channels were used for delivery of the borohydride solution and sample solution, respectively. The acidified samples and reductant were simultaneously pumped into the hydride-generation system. In the region of convergence of the two solutions and the carrier gas, sample and sodium borohydride aerosol were generated and a reaction occurred to produce the hydride. For operation of the DHGN, the sample and sodium borohydride solution were delivered using a peristaltic pump (Model Rabbit, Rainin Instrument, Woburn, MA, USA). Crossflow nebulizer-Scott type spray chamber arrangement and ultrasonic nebulizer (Cetac, Omaha, USA) were used for comparison purposes.

#### Reagents

Chemicals and standard used are as follows: sodium borohydride, L -cysteine, potassium iodide, thiourea, hydrochloric acid from Merck (Darmstadt, Germany); sodium hydroxide from Spex Certiprep (Metuchen, NJ, USA); nitric acid and 1000  $\mu\text{g mL}^{-1}$  stock solutions of As, Ba, Sb, Cd, Cu, Co, Fe, Ni, Cr, Mn, Mg, Se and Zn from Riedel-de Haën (Seelze, Germany). All chemicals used were of analytical-reagent grade and distilled, de-ionized water (DDW) was obtained from a Barnstead Nanopure System.

#### Stock solutions

Optimization of hydride generation and the measurement of analytical figures of merit were accomplished by using stock solutions having 1  $\mu\text{g mL}^{-1}$  of the elements prepared by spiking the appropriate amounts of each 1000  $\mu\text{g mL}^{-1}$  standard solution into a volumetric flask and diluting to volume. Non-spectroscopic interferences were conducted by using 1  $\mu\text{g mL}^{-1}$  multielement solutions of As, Sb and Se containing 100  $\mu\text{g mL}^{-1}$  of Cu, Co, Cd and Zn. All sample solutions were acidified with hydrochloric acid to a final concentration of 2.3 mol  $\text{L}^{-1}$ . Sodium borohydride solution containing 0.3% m/v in 0.05% m/v sodium hydroxide was prepared fresh daily immediately prior to analysis. It is important to state that the concentrations of borohydride and hydrochloric acid solutions correspond to optimal values obtained in our previous chemometric study [15]. The optimization of hydrochloric and sodium borohydride concentrations are really important because they a strongly influence in the hydride generation. For studies requiring L -cysteine and EDTA, spiking from stock solution of 20,000  $\mu\text{g mL}^{-1}$  was added to the multi-element solutions of As, Sb and Se to a final concentration of 2000  $\mu\text{g mL}^{-1}$ . On the other hand, for studies requiring potassium iodide and thiourea, similar amounts were added to the borohydride solution to avoid precipitation of the analytes due to reduction process.

#### Sample treatment

Microwave model MDS-2000 (CEM, Mathews, NC, USA) was used to digest the SRM, oyster tissue 1566a from NIST (Gaithersburg MD, USA). The following procedure was used: the 30-mL

**Table 2** Microwave oven program used for the oyster tissue (NIST 1566a)

Step	1	2	3	4	5
Power (W)	300	300	300	300	0
Pressure (psig)	40	85	135	170	20
Time (min)	10	10	6	6	0

Teflon digestion vessels were cleaned with 10 mL concentrated nitric acid and then thoroughly rinsed with twice-deionized water. After weighing 0.1000 g of the dry sample directly into the Teflon digestion vessel, concentrated nitric acid (3 mL) and deionized water (1 mL) were added to each vessel. The samples were digested using the program presented in Table 2. Finally, the digested solutions were transferred to 50 mL volumetric flasks and diluted to volume with hydrochloric acid and twice-deionized water. The final hydrochloric acid concentration in the solution was 2.3 mol  $\text{L}^{-1}$ .

## Results and discussion

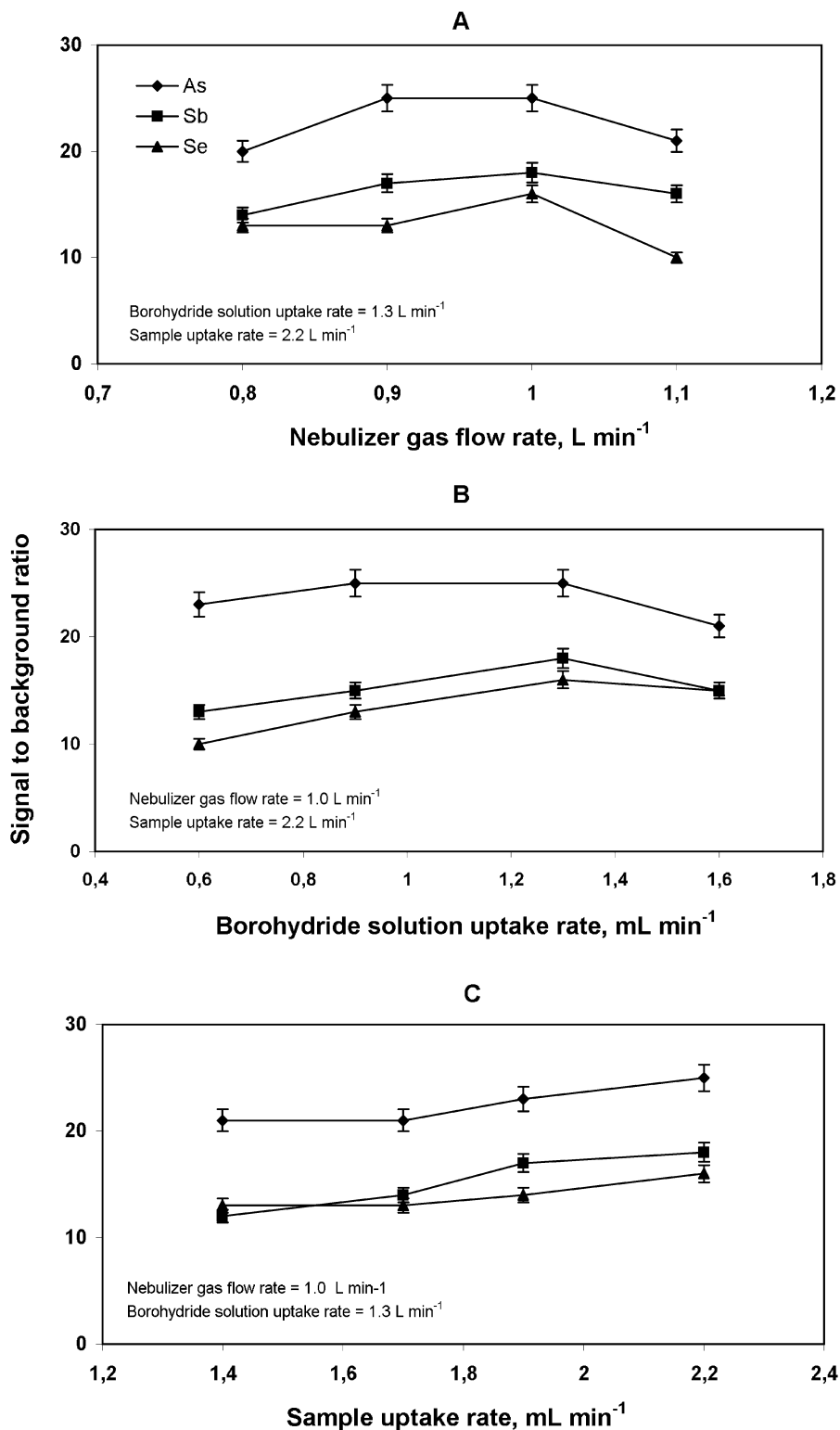
### Optimization of the hydride generation with the DHGN

The efficiency of hydride generation with the DHGN involves the following operational parameters: nebulizer gas flow rate and borohydride and sample solution uptake rates. Accordingly, signal to background ratios for As, Sb and Se were used to obtain the best hydrodynamic conditions for hydride generation. Experiments were conducted using a multi-element solution containing 1  $\mu\text{g mL}^{-1}$  at RF power of 1350 kW. Plots of signal to background ratios are shown in Fig. 2 as a function of nebulizer gas flow rate, sample and borohydride solution using the DHGN. The ratios are the mean of three measurements and the precision was within 5%. Fig. 2A illustrates that signal to background ratios of As, Sb and Se reach a maximum at nebulizer gas flow rate of 1 L  $\text{min}^{-1}$  and Fig. 2B illustrates that highest signal to background ratio for As, Sb and Se are obtained at borohydride solution uptake rate of 1.2 mL  $\text{min}^{-1}$ . In addition, Fig. 2C presents the higher signal to background ratios at 2.2 mL  $\text{min}^{-1}$  of sample uptake rate. In this case, information at higher values was not provided due a significant reduction of the precision of the measurements. In conclusion, the best signal to background ratios are obtained at nebulizer gas flow rate, sodium borohydride solution uptake rate and sample uptake rate of 1 L  $\text{min}^{-1}$ , 1.2 mL  $\text{min}^{-1}$ , and 2.2 mL  $\text{min}^{-1}$ , respectively. These conditions were used in further sections.

### Plasma robustness

The DHGN operates in a continuous mode, i.e., hydrochloric acid and borohydride solutions are continually pumped for hydride generation. This approach results in large amounts of hydrogen, carbon dioxide and water vapor being introduced into the plasma discharge. These products of the chemical reaction may cause instability or even extinguish the plasma [1]. In this connection, exper-

**Fig. 2** Signal to background ratios for As, Sb and Se as a function of: (A) the nebulizer gas flow rate, (B) borohydride solution uptake rate, and (C) sample uptake rate using the DHGN. The plasma RF power is 1350 W



iments are conducted to explore the robustness of the plasma in the presence of the DHGN.

Usually, the efficiency of energy transfer in the plasma is measured by plasma robustness in ICP-OES [16, 17]. Under robust conditions, no significant variation in the analyte signal intensities is observed when the matrix or

reagent composition changes. Applying high RF power and increasing the residence time of the aerosol in the plasma achieve a robust ICP. The intensity ratio Mg II 280.270 / Mg I 285.213 nm is commonly used to estimate plasma robustness, with higher ratios indicating a more robust plasma [18]. This line intensity ratio was not corrected

**Table 3** Experimental values of Mg II 280.270 nm/Mg I 285.213 nm emission intensity ratios using: DHGN, Cross-flow and ultrasonic nebulizers. The DHGN is operated at different borohydride solution uptake rates. The RF-power is 1350 W

Sample introduction system	Solution uptake rate (mL min <sup>-1</sup> )	Nebulizer gas flow rate, (L min <sup>-1</sup> )	Borohydride solution uptake rate (mL min <sup>-1</sup> )	Mg II/Mg I (2% RSD)
Direct hydride generation nebulizer	2.2	1.0	0.0	8.4
			0.3	8.4
			0.6	8.6
			0.9	8.7
			1.3	8.3
Crossflow nebulizer-Scott type spray chamber	1.0	1.0	–	9.0
Ultrasonic nebulizer	0.7	0.9	–	10.3

for differences in Echelle grating efficiency because magnesium lines present the same background emission.

Table 3 presents Mg II/Mg I ratios for radially viewed ICP as a function of the borohydride solution, the RF power and solution uptake rates being kept constant at 1350 W and 2.2 mL min<sup>-1</sup>, respectively. It can be appreciated that all Mg II/Mg I ratios with DHGN-Scott type spray chamber arrangements are close to a mean value of 8.5, thus the plasma operates under robust conditions in the presence of the DHGN. Besides, the Mg II/Mg I ratios for DHGN are slightly lower than ratios of 9.1 and 10.3 provided by a crossflow nebulizer-Scott type spray chamber arrangement and ultrasonic nebulizer, respectively. In conclusion, Mg II/Mg I ratios demonstrated that hydrogen together with other reaction products do not significantly affect the plasma robustness under the selected working conditions of the DHGN.

Sensitivity, detection limit, short-term precision and long-term stability using the DHGN

In this section, typical figures of merit – sensitivity, detection limit and short-term precision – were used to compare the analytical performance of the DHGN with conventional crossflow-Scott type spray chamber arrangement and ultrasonic nebulizer; signal to background ratio was used to express the sensitivity. Determination of limit of detection (LOD) was defined as the concentration of analyte producing a signal equal three times the standard deviation of background fluctuations [17]. Short-term precision was expressed as relative standard deviation (RSD) of the fluctuations in the emission signal around a mean value from a series of 10 replicates [19].

Table 4 presents signal to background ratios (SBRs), detection limits, and short-term precision for As, Sb and Se measured in the radially viewed mode using the direct

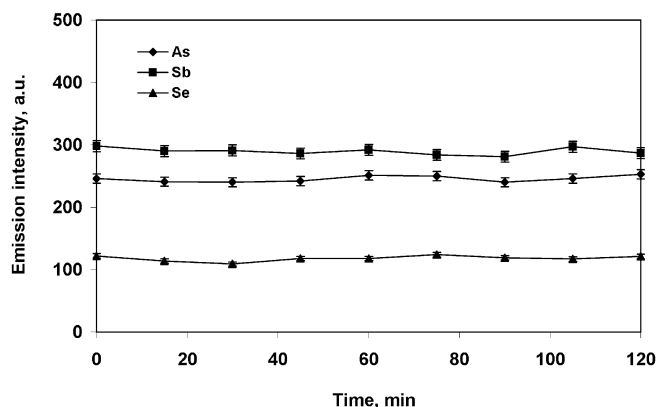
**Table 4** Relative detection limits, sensitivity and precision for the direct hydride generation, crossflow and ultrasonic nebulizers. The RF-power is 1350 W

Nebulizer	Signal to background ratio			Detection limit <sup>1</sup> (ng mL <sup>-a</sup> )			Precision <sup>b</sup> (%RSD)		
	DHGN	Cross-flow	Ultra-sonic	DHGN	Cross-flow	Ultra-sonic	DHGN	Cross-flow	Ultra-sonic
Solution uptake (mL min <sup>-1</sup> )	2.2	1.0	0.7	2.2	1.0	0.7	2.2	1.0	0.7
Nebulizer gas flow rate (L min <sup>-1</sup> )	1.0	1.0	0.9	1.0	1.0	0.9	1.0	1.0	0.9
Elements									
Volatile hydride forming									
As I, 189.0	41.8 (0.2) <sup>c</sup>	0.4	2.2	0.4 (50) <sup>c</sup>	45	5	0.4 (1.5) <sup>c</sup>	0.3	0.7
Sb I, 206.8	19.4 (0.1) <sup>c</sup>	0.2	1.2	2.0 (70) <sup>c</sup>	50	6	0.7 (1.6) <sup>c</sup>	0.2	1.5
Se I, 196.1	29.4 (0.2) <sup>c</sup>	0.4	0.5	0.1 (52) <sup>c</sup>	63	5	0.2 (1.4) <sup>c</sup>	0.3	0.2
Other elements									
Ba II, 455.4	0.5	2.0	12	18	3	0.1	1.4	0.2	0.7
Cd II, 226.5	2.1	4.5	127	3	2	0.4	1.4	0.6	1.2
Cr II, 206.1	1.4	1.7	23	6	5	1	0.9	0.4	1.0
Cu I, 324.7	1.1	1.4	5.6	11	9	0.3	0.7	0.3	0.8
Mg I, 285.2	1.4	1.5	17	9	8	1	0.7	0.5	0.7
Mg II, 280.2	5.4	18	124	3	1	0.1	0.5	0.8	0.6
Mn II, 257.6	3.1	8.6	88	2	1	0.2	1.6	0.7	1.0
Ni II, 221.6	1.4	1.8	23	6	5	1	1.0	0.4	1.0
Zn II, 202.5	4.2	13	156	3	1	0.5	1.5	0.6	1.6

<sup>a</sup>Based on 3 s of the blank solution; measured mass of the analyte

<sup>b</sup>Integration time=30 s and n=10

<sup>c</sup>Figures of merit obtained without sodium borohydride solution



**Fig. 3** Net emission signal as a function of time for As, Sb, and Se using DHGN. Instrument operating conditions are: RF power, 1350 W; borohydride solution uptake rate, 1.3 mL min<sup>-1</sup>; and sample delivery 2.2 mL min<sup>-1</sup>

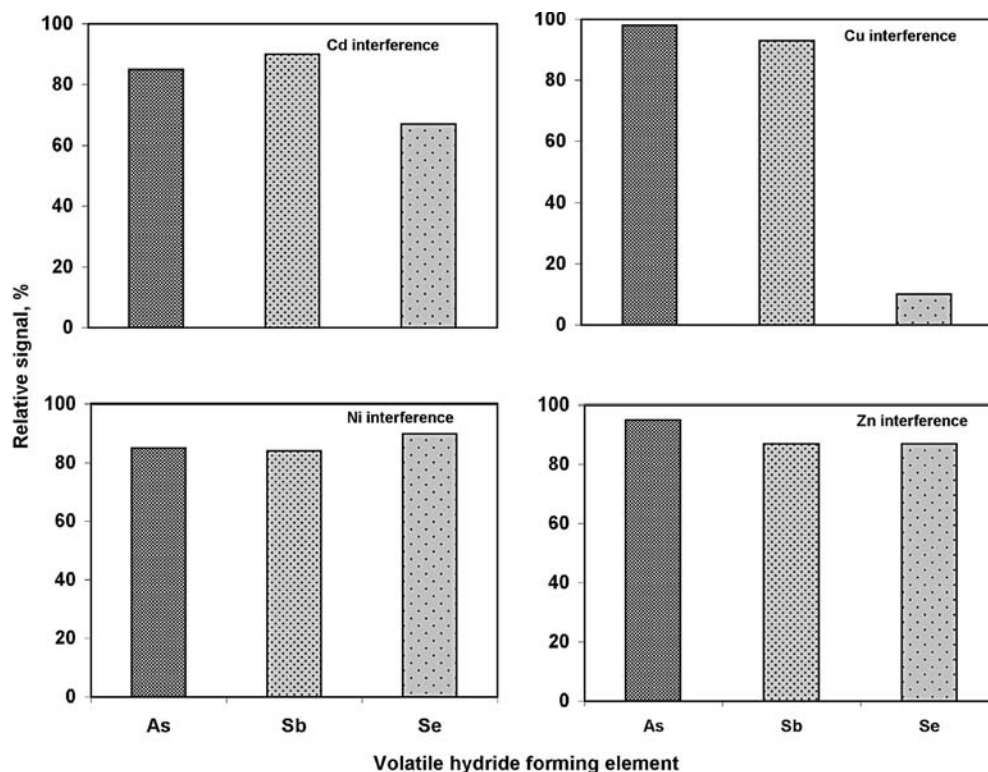
hydride generation, crossflow and ultrasonic nebulizers. The SBRs are reported for a concentration of 1 µg mL<sup>-1</sup>. Generally, SBRs obtained for As, Sb and Se using the DHGN are from 70 to 100 times higher than the values obtained with the crossflow nebulizer and 16 to 60 times higher than the values with ultrasonic nebulizer. However, SBRs without using the sodium borohydride solution were lower than those values obtained using conventional nebulization. DHGN generates hydrides, while keeping the possibility of nebulizing elements that do not form volatile hydrides. Analyzing SBRs obtained for some of these element, it can be appreciated that they are slightly lower than those obtained with crossflow nebulizer and

ultrasonic nebulizer. Limits of detection achieved by the DHGN provide the same conclusion as signal to background ratios. The best results for volatile hydride-forming elements were obtained with the DHGN. Short-term precision values for As, Se, and Sb obtained in DHGN are comparable with conventional nebulization systems. However, the precision for elements that do not form volatile hydrides are a little higher (RSDs close to 1%) than those obtained by the other nebulization systems used in this work (RSDs less than 1%). In conclusion, it is clear that DHGN allows simultaneous determination of both volatile and non-volatile hydride forming elements in ICP-OES. However, the latter group of elements can be determined with less sensitivity and precision than by conventional nebulization.

#### Long-term reproducibility of the DHGN

Measurement of the long-term reproducibility quantifies the degree of drift of the spectrometer. This figure of merit is a prime concern in ICP-OES because the presence of drift implies time-consuming and periodic recalibration [18, 19]. Long-term reproducibility may be illustrated by plotting the signal intensity as function of time. In this sense, Fig. 3 presents the emission intensity signal for As, Se and Sb over a period of 2 h after a warm-up time of 30 min. The figure shows a typical drift of the ICP-OES. The average of all RSD values are 1.0; 0.7 and 0.8 for As, Sb and Se, respectively.

**Fig. 4** Effect of some transition metals on the emission intensity signals of As, Sb and Se. The plasma using DHGN is operated with RF power, 1350 W; borohydride solution and sample uptake rates, 1.3 mL min<sup>-1</sup> and 2.2 mL min<sup>-1</sup>, respectively. The concentration of each transition metal in the solution is 100 µg mL<sup>-1</sup>



### Interferences from transition metals using DHGN-ICP-OES.

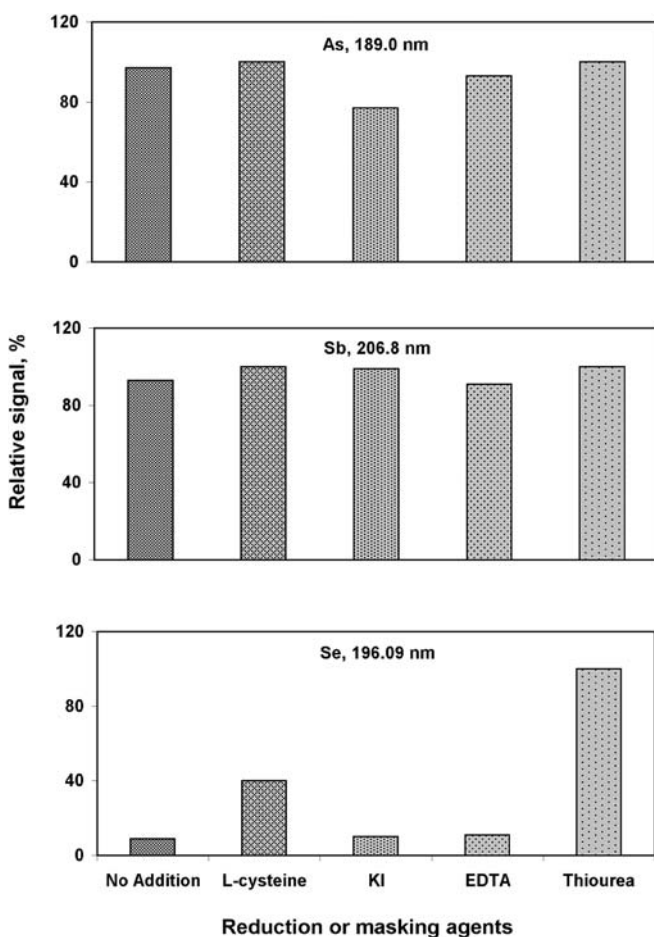
Hydride generation is not free from non-spectral interferences. Strong oxidants, interference of transition and noble metals and other species, including ions of other volatile hydride-forming elements can produce deleterious effects on hydride generation [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, 21, 22, 23, 24]. It is well known that interferences of transition metals are the most severe and therefore must extensively studied. A number of workers overcome these non-spectral interferences by means of selective reactions. For example, the use of reduction agents/masking agents [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, 21, 22, 23, 24], such as potassium iodide, thiourea, L-cysteine, and EDTA, has been commonly employed to reduce interferences from transition metals. With this type of idea in mind some experiments were conducted to evaluate the effects of some transition metals in the determination of As, Sb and Se by using the DHGN. Solutions containing  $1 \mu\text{g mL}^{-1}$  of As, Sb and Se

in the presence of  $100 \mu\text{g mL}^{-1}$  Cd, Cu, Ni and Zn were selected for this purpose.

Figure 4 presents the relative emission signal (with and without the presence of the transition metals) for As, Sb and Se using the DHGN-Scot type spray chamber arrangement. In brief, the emission signal of selenium is the most significantly affected by the presence of transition metals and it is clear that copper has the most severe effect on the emission signal of this element (over 90% of reduction of the signal). On the other hand, As and Sb are not significantly affected by transition metals. They exhibit only a reduction of the signal from 10 to 20%. The depletions of the signal in the presence of these interferences are similar to other reports that studied the effect of transition metals [7, 8, 20, 21, 22, 23, 24].

The effects of some reductant and masking agents such as L-cysteine, potassium iodide, EDTA and thiourea on the relative emission signal of As, Sb and Se in the presence of  $100 \mu\text{g mL}^{-1}$  of copper are shown in Fig. 5, copper was selected because this element generates a significant negative effect on hydride generation. First, it is possible to observe that only thiourea can help in the total recovery of the emission signal of Se, without affecting the As and Sb signal, in other words thiourea seems to be the recommended reductant/masking agent in the presence of a high concentration of transition metals such as copper. Again, these results are in agreement with literature. For example, Lund et al. [23, 24] report in their studies that thiourea is a more efficient masking agent for copper interference. Meanwhile, L-cysteine can help slightly in the recovery of Se. However, this masking agent is very useful for As and Sb. It is clear that the selenium signal is not significantly recovered in the presence of potassium iodide and EDTA. Thiourea and then L-cysteine seems to be the best masking agents.

Even though thiourea is the best reductant or masking agent for the determination of As, Sb and Se using the DHGN, this reagent significantly decreases the sensitivity of the selenium. This fact can be appreciated in Table 5 where signal to background ratios for As, Sb and Se are presented with and without the presence of thiourea and L-cysteine in an aqueous solution without the addition of any potential interferent agents. It is possible to observe that thiourea decreases the signal to background ratio of Se from 29.4 to 10.5 (64.3% lower). In addition, L-cysteine dramatically decreases the signal to background ratio of As and Se 64 and 20%, respectively. This contrasts with the sensitivity of Sb that it is not significantly affected by the presence of the reductant/masking agents used in this work. The depletion of hydride generation for selenium in presence of thiourea was previously reported by Lund et al. [23]. Even though a significant depletion of SBR for As, Sb and Se is found as a consequence of elimination of interference effects of transition metals by thiourea, the values of SBR are still better than those values obtained by conventional nebulization (Tables 4 and 5).



**Fig. 5** Effect of some reductant or masking agents on the emission intensity signals of As, Sb and Se in the presence of  $100 \mu\text{g mL}^{-1}$  of copper. The plasma using DHGN is operated with RF power, 1350 W; borohydride solution and sample uptake rates,  $1.3 \text{ mL min}^{-1}$  and  $2.2 \text{ mL min}^{-1}$ , respectively

**Table 5** Signal to background ratios for As, Sb and Se with and without the presence of L -cysteine and thiourea in aqueous solution without the addition of any potential interferent agent. Instrument operating conditions are: RF-power, 1350 W, borohydride solution uptake rate, 1.3 mL min<sup>-1</sup> and sample delivery 2.2 mL min<sup>-1</sup>. The ratios are the means of three measurements and the precision is within 2%

Element and wavelength (nm)	Signal to background ratios		
	No addition	L -Cysteine	Thiourea
As I, 189.0	41.8	26.8	35.5
Sb I, 206.8	19.4	20.1	19.4
Se I, 196.1	29.4	1.50	10.5

**Table 6** Trace elements in oyster tissue (NIST 1566a)

Element and wavelength (nm)	Concentration (µg g <sup>-1</sup> )	
	Found <sup>a</sup>	Certified <sup>b</sup>
As 189.042	15.2±0.6	14.0±1.2
Se 196.090	2.4±0.4	2.21±0.24
Fe 259.9	543±13	539±15
Mn 257.6	12.4±0.2	12.3±1.5
Zn 206.200	826±13	830±57

<sup>a</sup>Mean±standard deviation for six digest solutions

<sup>b</sup>Uncertainty expressed as 95% tolerance limits

#### Analysis of the standard reference material.

To investigate the analytical viability of the DHGN as a sample-introduction system, the standard reference material NIST 1566a was analyzed. The SRM 1566a consists of oyster tissue sample with known amounts of trace element concentrations. Results are shown in Table 6 for the determination of As, Se, Fe, Mn and Zn. The DHGN provides results comparable with the certified values at 95% confidence level.

#### Conclusions

The direct hydride generation nebulizer was successfully coupled to a radially viewed ICP-OES spectrometer. The plasma required the same conditions as those required for a conventional nebulizer-spray chamber arrangement for operation under robust conditions. The values of Mg II 280.270 nm/Mg I 285.213 nm ratios indicate robust plasma with the DHGN. This device provides better signal-to-background ratios, detection limits, and precision for the determination of As, Sb and Se than crossflow and ultrasonic nebulizer. In contrast analytical figures of merit for the nebulization of elements that do not form volatile hy-

drides were lower than for conventional nebulization systems. Studies of matrix effects produced by transition metals showed that the emission signal of selenium was significantly depleted by the presence of copper. In this case, reduction or masking agents such thiourea are recommended to take care of the loss of sensitivity produced by this agent in hydride generation. Further experiments are planned for future work. Our interest is to improve the design of DHGN to produce better figures of merit for the determination of major elements of the sample with a significant reduction of interferences from transition metals, in the determination of volatile hydride-forming elements.

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