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## Dual nebulizer sample introduction system for simultaneous determination of volatile elemental hydrides and other elements

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**Abstract** A dual sample introduction system was explored for volatile hydride generation in inductively coupled plasma-optical emission spectrometry (ICP-OES) performed in the radially viewed mode. The system consists of two pneumatic nebulizers connected to the conventional spray chamber of the instrument via a simple adaptor. This configuration permits hydride generation but still allows other elements to be determined by pneumatic nebulization. This work was focused on the optimization of the plasma operating conditions for the determination of As, Hg, Sb and Se and other elements. The excitation conditions of the ICP-OES instrument operated with the dual sample introduction system were also explored. Results showed that the analytical performance of the dual system for the determination of As, Hg, Sb and Se was superior to those of conventional nebulization systems. The dual system also enabled the determination of elements that do not form volatile hydrides, but with less sensitivity than conventional nebulization systems. An evaluation of the plasma robustness showed that the gases generated in the hydride reactions did not significantly affect the plasma discharge. Similar to conventional hydride generation techniques, the analysis was susceptible to nonspectroscopic interferences produced by transition metals. Finally, the applicability of the dual nebulization system to practical ICP-OES studies was demonstrated by determining the trace elements in an oyster tissue standard reference material.

**Keywords** Dual nebulization · Hydride generation · Inductively coupled plasma-optical emission spectrometry · Arsenic · Antimony · Mercury · Selenium

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### Introduction

Today, the use of chemical vapor generation techniques with inductively coupled plasma spectrometry is relatively common in analytical laboratories. Specifically, volatile hydride generation methods: improve the analytical figures of merit obtained for the determination of As, Bi, Ge, Sb, Pb, Sn, Se, Te, etc. compared to traditional nebulizer-spray chamber arrangements; increase analyte transport efficiency into the plasma, which allows lower limits of detection (LOD) to be obtained; make it possible to separate analytes from the sample matrix and the solvent. This fact permits the preconcentration of analytes and reduces potential spectral interferences [1].

Volatile hydrides and cold vapor generation systems based on sodium tetrahydroborate acid reductor are normally used for vapor generation [2]. Generally, two approaches are used, either *continuous* or *batch* methods. In the methods of continuous generation, the reagents are constantly pumped by a multiple-channel peristaltic pump into a mixer channel, where the acid–borohydride reaction takes place. The volatile hydrides are then swept into a gas–liquid separator, where the liquid is drained and the gas mixture is directed into the torch of the ICP. In the *batch* methods, an aliquot of acid solution containing the analyte elements is mixed rapidly with an aliquot of borohydride reagent. The resulting volatile hydrides are then swept directly into the plasma discharge. Also, modern analytical applications include the use of flow injection analyses to provide rapid sample throughput, lower sample consumption, and easy automated approaches to mixing the plug of sample with the flowing reagent stream [1, 3].

New approaches to generating the hydride based on modified nebulizer–spray chamber arrangements have recently been reported [4–12]. In these continuous mode systems, the sample and the reducing agent are integrated into the nebulizer–spray chamber arrangement. Reactions to form hydrides are performed within the aerosol, on contact with the small droplets of sample and reductor. The generation of the volatile hydrides using this arrangement

provides the following analytical benefits in ICP–OES: i) the sample introduction systems act as an efficient gas–liquid separator; ii) detection limits are comparable to those obtained with traditional hydride generation systems; iii) increased transition metal ion tolerance concentrations due to the very short reaction time and the rapid separation of gaseous products; iv) no significant effect of the plasma discharge produced by the generation of gases such as hydrogen, and; iv) these devices take advantage of hydride generation while maintaining the ability to determine other elements by pneumatic nebulization.

Several papers illustrate the use of nebulizer–spray chamber systems for hydride generation. Wolnik et al. [4] described a tandem nebulization system in which a concentric Meinhard nebulizer is mounted in a Teflon spray chamber, joined to a crossflow nebulizer and fitted to a spray chamber connected to the ICP torch. Huang et al. [5] 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. Watling and Collier [6] reported continuous hydride generation using a dual platinum grid nebulizer. Hwang et al. [7] described a simple continuous flow mode in situ nebulizer / hydride generation system. Schramel and Li-Qiang [8] presented a system that consists of two peristaltic pumps connected to a mixer disk, and this was connected to a spray chamber and to the ICP torch. Fengzhou et al. [9] developed and integrated a nebulizer–hydride generator system in which the spray chamber for pneumatic nebulization was modified for hydride generation. Ding and Sturgeon [10] reported an approach based on the insertion of a capillary tube into the sample introduction channel of a concentric Meinhard nebulizer. The sample and the reagent are mixed at the end of the nebulizer orifice and nebulization occurs into a tubular spray chamber. Tao and Sturgeon [11] described a new hydride system in which a concentric Meinhard nebulizer was modified by the insertion of a capillary tube into the sample introduction channel. Moor et al. [12] examined a crossflow nebulizer that had a Teflon tube inserted into the nebulizer tip to provide a small well-defined mixing zone for hydride generation reaction. Brindle et al. [13] reported a multimode sample introduction system (MSIS) in which hydride formation takes place at the outlet of the two capillaries, located in a modified cyclonic spray chamber, that transport the sample and sodium borohydride solutions. Carrion et al. [14] and Rojas et al. [15] used a modified V-groove with one additional channel to introduce the hydride solution. Finally, Zoltan et al. [16] studied a modified crossflow-type nebulizer coupled with a conventional Scott double-pass spray chamber. In this case, they adapted two new channels into the nebulizer in order to introduce the hydride and acid solutions separately.

This work explores the analytical benefits of a dual nebulizer sample introduction system for volatile hydride generation. The use of two sample introduction systems

operating in parallel has been reported in relation to the following studies in plasma spectrometry: calibration in laser ablation [17]; a standard tandem calibration technique [18]; improvement of sensitivity and reproducibility in double-focusing sector field ICPMS [19]; hydride generation [4]; as well as in fundamental studies of, for example, the charge transfer mechanism and matrix effects [20, 21]. The system to be examined here consists of two pneumatic nebulizers connected to the conventional spray chamber of the ICP–OES using a simple adaptor. The nebulizers were used to aspirate the acidified samples and the borohydride solution, respectively. Experiments were focused on optimizing the operating parameters of the plasma and evaluating the main analyte figures of merit for the determination of As, Sb, Se and other elements.

## Experimental

### Instrumentation

A 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. Figure 1 presents the dual nebulizer system used for volatile hydride generation. It consists of a crossflow nebulizer and concentric conventional Meinhard pneumatic nebulizers connected to the conventional double-pass spray chamber of the instrument using a simple T-shaped adaptor; in other words, no special nebulizer or spray chamber design was necessary. The dual system operates in a continuous mode in which acidified sample and borohydride solutions are continually pumped for hydride generation using the crossflow and concentric nebulizers, respectively. The chemical vapor is generated when the small droplets of sample and reductor react in the convergence region in the adaptor. In contrast with direct hydride nebulizers [10–16], the dual configuration allows the the aerosols used for hydride generation to be optimized by changing the solution uptake rate and gas flow of both nebulizers independently. A crossflow nebulizer–Scott-type spray chamber arrangement and an ultrasonic nebulizer (Cetact, Omaha, NE, USA) were used for comparison purposes.

### Reagents

The chemicals and standards used were as follows: sodium borohydride, thiourea, hydrochloric acid, perchloric acid from Merck (Darmstadt, Germany); sodium hydroxide from Spex Certiprep (Metuchen, NJ, USA); nitric acid and 1000 µg mL<sup>-1</sup> stock solutions of As, Ba, Sb, Cu, Hg, 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.

**Table 1** Operating conditions for the inductively coupled plasma instrument

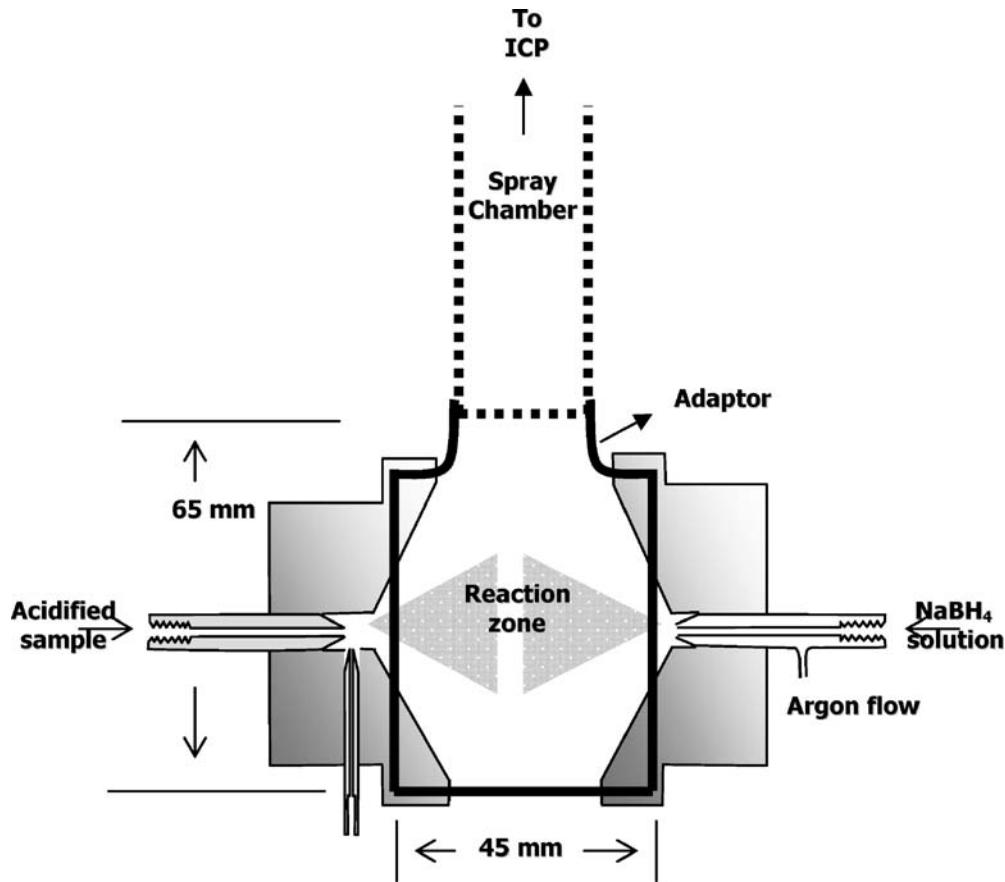
RF Generator	IRIS HR (Thermo Jarrel Ash, Franklin, MA, USA)
Nominal frequency (MHz)	27.12
RF generator type	Crystal controlled
RF power (W)	1350
Dispersive system	Echelle cross-dispersion spectrometer: Focal length, 381 mm; F number, F/10; Entrance aperture, 50 $\mu\text{m}$ ; Grating blaze 63.5 degrees; 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 512×512
Outer gas flow rate ( $\text{L min}^{-1}$ )	15
Injector (mm)	1.5
Nebulization systems	Dual system–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 °C and 4 °C, respectively)
Solution flow mode	Continuous
Integration mode	Random Access Integrator (RAI), Nondestructive readout (NDRO)
Observation height (mm)	8 (above the last turn of the load coil)
Working wavelengths (nm)	As(I) 189, Ba(II) 455.4, Cu(I) 324.7, Hg(I) 184.9, Mg(I) 285.2, Mg(II) 257.6, Mn(II) 257.6, Zn(II) 202.5

Stock solutions

Optimization of hydride generation and measurement of analytical figures of merit were both accomplished using

stock solutions that contained 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. Nonspectroscopic interferences were

**Fig. 1** Schematic diagram of the dual nebulization system



tested by using  $1 \mu\text{g mL}^{-1}$  multielement solutions of As, Sb and Se containing  $100 \mu\text{g mL}^{-1}$  of Cu. All sample solutions were acidified with hydrochloric acid to a final concentration of  $2.3 \text{ mol L}^{-1}$ . Sodium borohydride solution containing 0.2% m/v in 0.05% m/v sodium hydroxide was prepared fresh daily immediately prior to analysis. The hydrochloric acid and sodium borohydride concentrations are very important because they have a strong influence on vapor generation. The borohydride concentration used in this study corresponds to a value that allows the nebulizer to run without any risk of clogging and the hydrochloric acid contents correspond to optimal values obtained in our previous studies [14, 15]. For studies requiring thiourea, an appropriate amount of a stock solution of concentration  $20,000 \mu\text{g mL}^{-1}$  was added to the borohydride solution to give a final concentration of  $1000 \mu\text{g mL}^{-1}$ . The thiourea was not combined with the multielement solutions in order to avoid precipitation of the analytes due to reduction.

### Sample treatment

A microwave (model MDS-2000, CEM, Mathews, NC, USA) was used to digest the SRM, oyster tissue 156 from NIST (Gaithersburg, MD, USA). The following procedure was employed: 30-mL Teflon digestion vessels were cleaned with 10 mL of concentrated nitric acid and then thoroughly rinsed with deionized water. After weighing 0.5000 g of the dry sample directly into the Teflon digestion vessel, concentrated nitric acid (3 mL), perchloric acid (1 mL) and deionized water (4 mL) were added to each vessel. The samples were digested by following the recommended program of the microwave guidebook. Finally, the digested solutions were transferred to 25 mL volumetric flasks and diluted to volume with hydrochloric acid and deionized water. The final hydrochloric acid concentration in the solution was  $2.3 \text{ mol L}^{-1}$ .

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## Results and discussion

### Optimizing the hydride generation using the dual system

The efficiency of vapor generation depends on the nebulizer gas flow rates, the borohydride and the sample solution uptake rates. The gas and liquid flows were carefully adjusted in both nebulizers to ensure that a fine aerosol was produced while the plasma was not overloaded when the argon flow was increased. In other words, the plasma becomes unstable and prone to being extinguished if the argon flow and liquid uptake increases too much. Therefore, the excitation conditions of the plasma were optimized by monitoring the plasma robustness while changing the gas and liquid flows until both robust plasma and reproducible aerosol were achieved. It is important to note that the robustness of the plasma discharge can also be affected by the generation of hydrogen, carbon dioxide and water vapor produced during hydride generation. The

robustness of the plasma was obtained using the intensity ratio Mg(II) 280.270 nm/ Mg(I) 285.213 nm, with higher ratios indicating more robust plasma [21, 22]. This line intensity ratio was not corrected for differences in echelle grating efficiency because the magnesium lines exhibit similar background emission. On the other hand, the reproducibility of the aerosol was evaluated using the relative standard deviation of the Mg(II) 285.213 nm emission signal.

Figure 2 presents the Mg(II) 280.270 nm/ Mg(I) 285.213 nm ratio and the RSD of the Mg(II) signal as functions of the nebulizer gas flow rates and solution uptake rates. The borohydride concentration was kept constant at 0.2% m/v in order to avoid nebulizer clogging. The RF power was 1350 W. The ratios are the means of three measurements and the precision was to within 3%. It is clear that all of the Mg(II)/Mg(I) ratios increase to a value of 11 when both nebulizer gas flows are  $0.35 \text{ L min}^{-1}$ . The plasma becomes less robust as the nebulizer gas flows are increased; it may become overloaded by the argon flow and/or the gas generation could have a significant effect on the discharge. The best Mg(II) 280.270 nm/ Mg(I) 285.213 nm ratios were obtained at sample and borohydride solution uptake rates of  $0.62 \text{ mL min}^{-1}$  and  $0.31 \text{ mL min}^{-1}$ , respectively. Also, Fig. 2 shows that the emission signal precision was lower than 1% RSD when the best excitation conditions were obtained. In conclusion, the results demonstrate that plasma can operate under robust conditions and that a reproducible aerosol/emission signal can be obtained for hydride generation using the dual nebulization system. Also, it is evident that hydrogen, together with the other reaction products, does not significantly affect the plasma excitation conditions. Accordingly, Table 2 presents the plasma operating conditions for hydride generation using the dual nebulization system. These values are contrasted with typical operating conditions used with a conventional crossflow nebulizer-spray chamber arrangement. It is clear that the nebulizer gas flows need to be reduced in the dual nebulization mode in order to avoid plasma overload, and this fact may produce a significant effect on the aerosol generation; in other words, a significant reduction in sensitivity should be expected for elements that do not form volatile hydrides. It is important to note that the auxiliary gas flow was also reduced in the dual nebulization mode in order to reduce blowing effects in the plasma.

### Sensitivity, detection limit, short-term precision and long-term stability obtained using the dual system

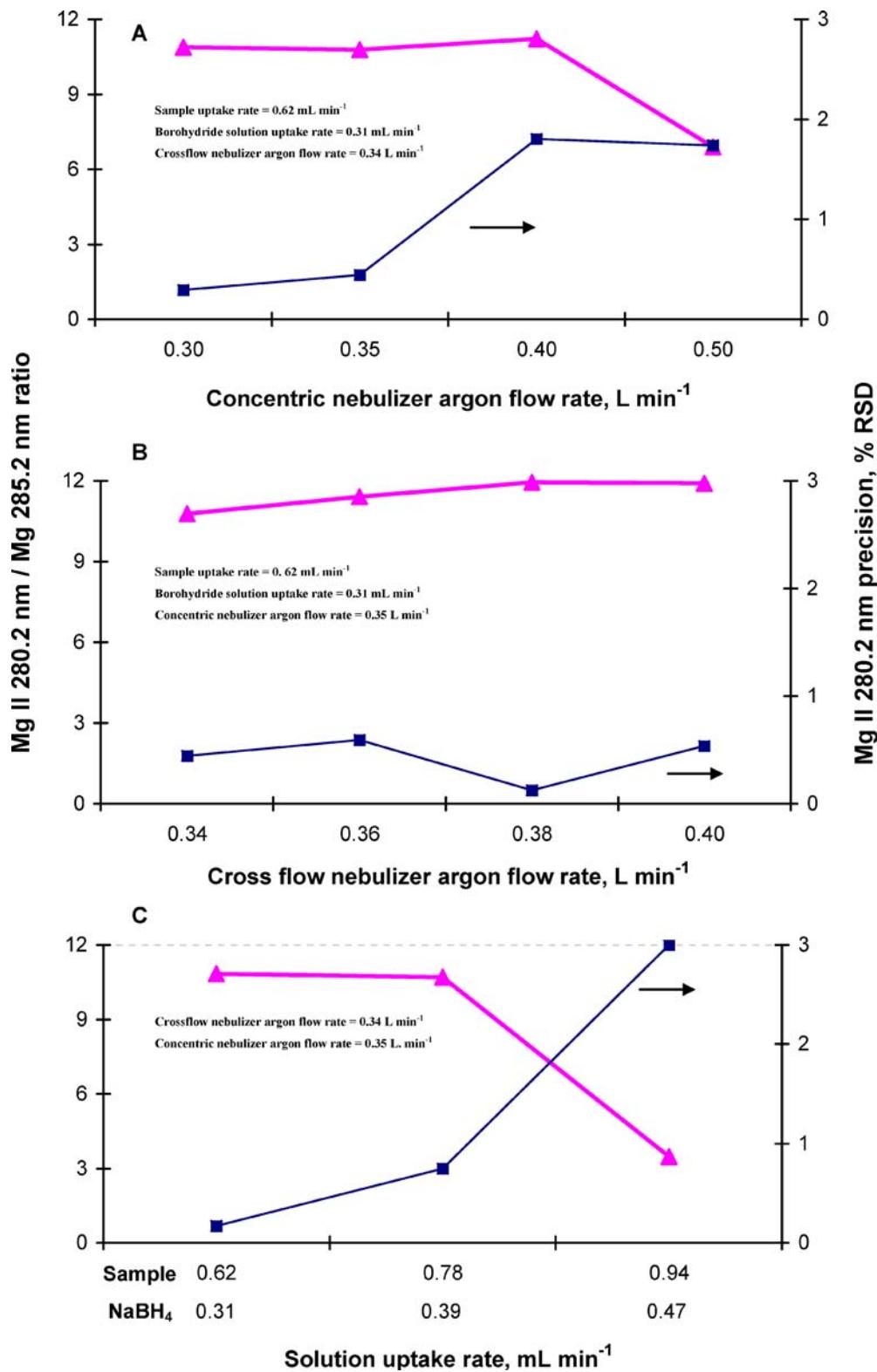
Typical figures of merit (sensitivity, detection limit and short-term precision) were used to compare the analytical performance of the dual nebulizer system to those of the conventional crossflow-Scott-type spray chamber arrangement and the ultrasonic nebulizer; the signal-to-background ratio was used to express the sensitivity. The limit of detection (LOD) was defined as the concentration of analyte that produces a signal equal to three times the

standard deviation of the background fluctuations. Short-term precision was expressed as the relative standard deviation (RSD) of the fluctuations in the emission signal about a mean value from a series of ten replicates.

Table 3 presents the signal-to-background ratios (SBRs), detection limits and short-term precisions for As, Sb, Hg,

and Se measured in the radially viewed mode using the dual system, the crossflow and the ultrasonic nebulizers. Hg was included in the volatile hydride group even though this element produces atomic vapor in presence of borohydride solution. The SBRs are reported for a concentration of  $1 \mu\text{g mL}^{-1}$ . In general, the SBRs obtained

**Fig. 2a–c** Mg(II) 280.2 / Mg(I) 285.2 ratios (*triangles*) and relative standard deviations for the Mg(II) 280.2 nm emission signal (*squares*) obtained using the dual nebulization system, as a function of (a) the concentric nebulizer argon flow rate, (b) the crossflow nebulizer argon flow rate, (c) the sample solution uptake rate. The plasma RF power and the auxiliary gas flow rate were 1350 W and  $0.5 \text{ L min}^{-1}$ , respectively



**Table 2** Operating conditions of the plasma with conventional and dual nebulization system

Operating Parameters	Conventional nebulization	Dual nebulization system
RF Power (W)	1350	1350
Intermediate gas flow rate ( $\text{L min}^{-1}$ )	1.5	0.5
Crossflow nebulizer gas flow rate ( $\text{L min}^{-1}$ )	0.6	0.35
Sample solution uptake ( $\text{mL min}^{-1}$ )	1.90	0.60
Concentric nebulizer gas flow rate ( $\text{L min}^{-1}$ )	–	0.35
Borohydride solution uptake ( $\text{mL min}^{-1}$ )	–	0.30

for As, Hg, Sb and Se using the dual system are from 2 to 50 times higher than the values obtained with the crossflow nebulizer and the ultrasonic nebulizer. As and Hg are the elements that exhibit significantly increased sensitivity in the dual system. In contrast, the SBRs of these elements when the sodium borohydride solution was not used were lower than the values obtained using conventional nebulization.

The dual nebulization system generates volatile hydrides, while also permitting elements that do not form volatile hydrides to be nebulized; however, the SBRs obtained for this latter group of elements are slightly lower than those obtained with the crossflow nebulizer and the ultrasonic nebulizer. These changes in sensitivity occur because, in dual mode nebulization, the crossflow nebulizer operates at lower gas flow rates and the trajectory of the sample aerosol into the ICP discharge is significantly modified when compared to the other modes of nebulization.

The limits of detection achieved by the dual nebulizer system yield the same conclusions as for the signal-to-background ratios. The best results for volatile hydride-forming elements were obtained with the dual nebulization system. Short-term precision values for As, Hg, Se and Sb obtained in dual nebulization mode are a little higher (RSDs are close to 1%) than those obtained using the other nebulization systems. It is important to note that no

significant memory effects were found in the case of Hg and Se when compared to the ultrasonic nebulizer.

The long-term reproducibility of the dual system quantifies the degree of drift of the spectrometer using the hydride. This figure of merit is very important in ICP-OES, because the presence of drift implies time-consuming and periodic recalibration [22, 23]. The long-term reproducibility may be illustrated by plotting the signal intensity as a function of time. Figure 3 presents the emission intensities for some volatile hydride-forming elements (Sb 206.8 nm, Se 196.0) and nonvolatile hydride-forming elements (Mg 285.2 nm, Zn 202.5) over a period of 2 h after a warm-up time of 30 min. These emission signals were mean-centered. The figure shows the typical drift of the ICP-OES. However, average RSD values of 4.7, 4.2, 1.1 and 1.8 for Sb, Se, Mg and Zn, respectively, were obtained. This result indicates that a higher drift was produced by the generation of volatile hydrides.

#### Interferences from transition metals using the dual nebulizer system

Hydride generation is not free from nonspectral interferences. Strong oxidants, interference from transition and noble metals and other species, including ions of other volatile hydride-forming elements, can produce deleterious

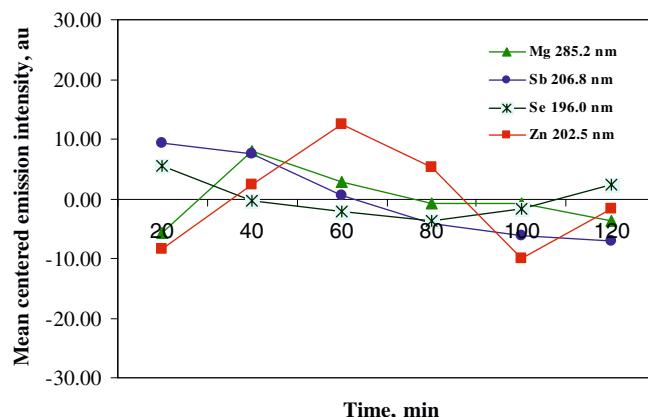
**Table 3** Relative detection limits, sensitivities and precisions for the dual system, the crossflow and the ultrasonic nebulizers

Nebulizer elements	Signal-to-background ratio			Detection limit ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>			Precision (%RSD) <sup>b</sup>		
	Dual system	Crossflow	Ultrasonic	Dual system	Crossflow	Ultrasonic	Dual system	Crossflow	Ultrasonic
<b>Volatile hydride forming</b>									
As(I) 189.0	67.35 (1.57) <sup>c</sup>	2.64	3.95	3 (160) <sup>c</sup>	26	70	1.25(0.41) <sup>c</sup>	0.45	1.85
Sb(I) 206.8	9.22 (0.16) <sup>c</sup>	4.05	10.19	19 (2730) <sup>c</sup>	517	2	1.17(0.41) <sup>c</sup>	0.31	0.12
Se(I) 196.1	12.40 (0.83) <sup>c</sup>	1.57	6.20	10 (60) <sup>c</sup>	28	116	0.81(0.29) <sup>c</sup>	0.29	4.79
Hg(I) 184.9	544.4 (9.89) <sup>c</sup>	11.11	8.13	0.1 (14) <sup>c</sup>	5	81	0.50(0.92) <sup>c</sup>	0.40	4.38
<b>Other elements</b>									
Ba(II) 455.4	9.26	12.78	224.6	41	9	0.9	2.52	0.77	1.42
Cu(I) 324.7	1.81	2.00	52.34	70	53	1.6	0.84	0.71	0.54
Mg(I) 285.2	6.43	8.50	174.1	3	10	0.6	1.57	0.57	0.68
Mg(II) 280.2	86.69	114.0	730.6	49	1	0.1	2.10	0.83	0.33
Mn(II) 257.6	37.90	52.69	855.6	3	1	0.2	0.79	0.36	1.11
Zn(II) 202.5	47.69	59.49	442.3	1	1	0.5	0.32	0.21	1.46

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

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

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



**Fig. 3** Long-term stability when using the dual nebulization system for hydride generation. The plasma was generated with 1350 W; the borohydride solution and sample uptake rates were  $0.31 \text{ mL min}^{-1}$  and  $0.62 \text{ mL min}^{-1}$ , respectively

effects on hydride generation. It is well-known that the interferences from transition metals are the most severe and must therefore be studied extensively [10–12, 15, 16, 24–28]. A number of works overcome these nonspectral interferences by using selective reactions. For example, the use of reduction agents/masking agents—such as potassium iodide, thiourea, L-cysteine and EDTA—has been commonly employed to reduce interferences from transition metals [10–12, 15, 16, 24–28]. With this type of idea in mind, some experiments were conducted to evaluate the effects of Cu on the determination of As, Sb and Se using the dual nebulizer system. This transition metal was selected because it generates a significant negative effect on hydride generation [15].

Figure 4 presents the relative emission intensities (with and without the presence of Cu) for As, Sb and Se obtained using the dual nebulization system. Solutions containing  $1 \mu\text{g mL}^{-1}$  of As, Sb and Se in the presence of  $100 \mu\text{g mL}^{-1}$  Cu were analyzed. In short, the emission signal of Se is significantly affected by the presence of

**Table 4** Trace element concentrations in oyster tissue (NIST 1566a), obtained using the dual nebulization system

Element and wavelength (nm)	Concentration ( $\mu\text{g g}^{-1}$ )	
	Found <sup>a</sup>	Certified <sup>b</sup>
As 189.04	$11.7 \pm 0.6$	$14.0 \pm 1.2$
Se 196.09	$2.1 \pm 0.6$	$2.21 \pm 0.24$
Cu 259.90	$63.2 \pm 0.6$	$66.3 \pm 4.3$
Mn 257.60	$10.9 \pm 0.2$	$12.3 \pm 1.5$

<sup>a</sup>Mean  $\pm$  standard deviation of five digest solutions

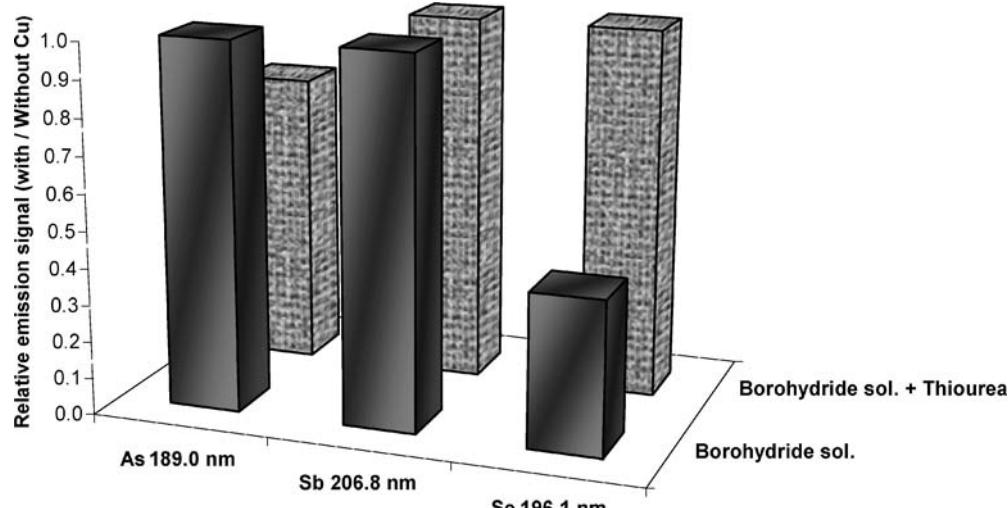
<sup>b</sup>Uncertainty expressed as 95% tolerance limits

Cu (it causes a >65% reduction in the signal). On the other hand, As and Sb are not significantly affected by Cu. The depletion of the Se signal in the presence of Cu has also been described in other reports that have studied the effects of transition metals. The effects of reductants/masking agents like thiourea on the relative emission signals of As, Sb and Se in the presence of  $100 \mu\text{g mL}^{-1}$  of Cu are also shown in Fig. 4. It is clear that the original emission intensity of Se can be recovered in the presence of thiourea, without significantly affecting the emission signals of As and Sb. Thiourea is an efficient reductant/masking agent for hydride generation in the presence of a high concentration of transition metals such as Cu. Again, these results are in agreement with the literature [15, 27, 28].

#### Analysis of the standard reference material

To investigate the analytical viability of the dual nebulization system as a sample introduction system, the standard reference material NIST 1566a was analyzed. SRM 1566a consists of oyster tissue with known amounts of trace element concentrations. Results are shown in Table 4 for the determination of As, Se, Cu and Zn. The dual system provides results comparable with the certified values at the 95% confidence level.

**Fig. 4** Effect of copper on the emission intensities of As, Sb and Se with and without the use of thiourea. The plasma was obtained with 1350 W in the dual nebulization system; the borohydride solution and sample uptake rates were  $0.31 \text{ mL min}^{-1}$  and  $0.62 \text{ mL min}^{-1}$ , respectively. The concentrations of Cu and thiourea in the solution were  $100 \mu\text{g mL}^{-1}$  and  $1000 \mu\text{g mL}^{-1}$



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## Conclusions

Volatile hydride generation using a dual nebulization system was successfully coupled to a radially viewed ICP–OES spectrometer without using any special device. The values of Mg(II) 280.270 nm/Mg(I) 285.213 nm ratios indicate that a robust plasma can be obtained for hydride generation. This dual nebulization system provides better signal-to background ratios, detection limits and precisions for the determination of As, Hg, Sb and Se than crossflow and ultrasonic nebulizers. In contrast, analytical figures of merit for the nebulization of elements that do not form volatile hydrides were lower than found for conventional nebulization systems, mainly due to the fact that both pneumatic nebulizers operate far from their optimal gas flow conditions. Studies of matrix effects produced by transition metals showed that the emission signal of selenium was significantly depleted by the presence of Cu. In this case, the introduction of a reductant or masking agent like thiourea is recommended in order to avoid any loss of sensitivity during hydride generation.

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## References

1. Montaser A, Minnich MG, McLean JA, Liu H (1998) Sample introduction in ICP–MS. In: Montaser A (ed) Analytical atomic spectrometry. Wiley-VCH, New York
2. D' Ulivo A (2004) Spectrochim Acta B 59:793–825
3. Sturgeon RE (2002) Appl Spectrosc 56:20–21
4. Wolnik K, Frickle F, Hahn M, Caruso, M (1981) Anal Chem 53:1030–1035
5. Huang B, Zhang Z, Zeng X (1987) Spectrochim Acta B 42:129–137
6. Watling RJ, Collier AR (1988) Analyst 113:345–346
7. Hwang JD, Guenther GD, Diomiguardi JP (1989) Anal Chem 61:285–288
8. Schramel P, Li-Qiang X (1991) Fresenius J Anal Chem 340:41–47
9. Fengzhou Q, Guoying G, Chun X (1991) Appl Spectrosc 45:287–292
10. Ding WW, Sturgeon RE (1997) Anal Chem 69:527–531
11. Tao GH, Sturgeon RE (1999) Spectrochim Acta B 54:481–489
12. Moor C, Lam JWH, Sturgeon RE (2000) J Anal Atom Spectrom 15:143–149
13. Roger L, Mc Laughlin J, Brindle ID (2002) J Anal Atom Spectrom 17:1540–1548
14. Carrion N, Murillo M, Montiel E, Diaz D (2003) Spectrochim Acta 58B:1375–1389
15. Rojas I, Murillo M, Carrion N, Chirinos J (2003) Anal Bioanal Chem 376:110–117
16. Zoltan T, Benzo Z, Murillo M, Marcano E, Gomez C, Salas J, Quintal M (2003) Anal Bioanal Chem 382:1419–1430
17. Moenke-Blankenburg L, Shumann L, Guenther D, Kuss H, Paul M (1992) J Anal Atom Spectrom 7:251–254
18. Huxter V, Hamier J, Salin ED, (2003) J Anal Atom Spectrom 18:71–75
19. Olofsson R, Rodushkin I, Alxelsson D (2000) J Anal Atom Spectrom 15:727–729
20. Chan G, Hieftje G (2004) Spectrochim Acta 5:163–183
21. Chan G, Chan W, Mao X, Russo R (2001) Spectrochim Acta 5:77–92
22. Mermet JM (1991) Anal Chim Acta 250:85–94
23. Mermet JM, Pousell E (1995) Appl Spectrosc 49:12A–18A
24. Campbell AD (1992) Pure Appl Chem 64:227–244
25. Kirkbright GF, Taddia M (1978) Anal Chim Acta 100:145–150
26. Overduin SD, Brindle ID (2001) J Anal Atom Spectrom 16:289–292
27. Bye R, Engvik L, Lund W (1983) Anal Chem 55:2457–2458
28. Risnes A, Lund W (1996) J Anal Atom Spectrom 11:943–948