

## Application Note

# The use of a double-channel nebulizer, MultiNeb®, for on-line chemical vapor generation

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## 1. Introduction

Chemical vapor generation (CVG) techniques are routinely used with ICP OES for the determination of trace levels of environmentally sensitive elements including arsenic, selenium, and other elements using the hydride generation technique, and mercury using the cold vapor technique. The major advantage using chemical vapor generation is the improvement of the analytical figures of merit. However, laboratories wishing to employ this technique must use a dedicated instrument to hydride determination or shut down an instrument to change over to hydride determination system. Once the instrument has been converted, no other determinations can be performed until it is changed back again. For laboratories that routinely analyze both volatile and non-volatile forming elements there is a significant time penalty in switching between the two sample introduction systems.

The new MultiNeb® is an innovative nebulizer for plasma-based techniques that allows to carry out on-line chemical vapor generation or conventional nebulization. It eliminates the need to switch between different sample introduction systems, saving analysis time and thus keeping your lab as productive as possible. In addition, the new MultiNeb® is less expensive and fragile than other commercial volatile generation devices such as multimode sample introduction system (MSIS).

## 2. Experimental

### On-line chemical vapor generation

The MultiNeb® used in this study consists of two independent liquid inlets and a common gas inlet in a single nebulizer body of polytetrafluoroethylene (Figure 1).

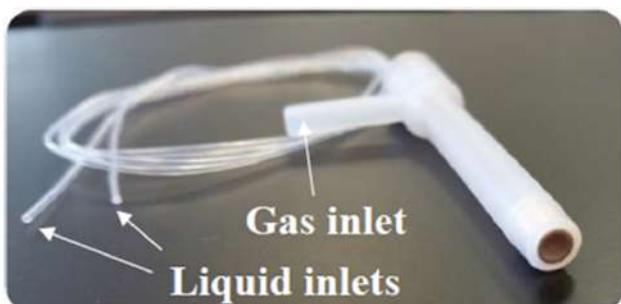


Figure 1. MultiNeb® nebulizer

The on-line CVG system is composed by the MultiNeb® nebulizer associated with a conventional cyclonic spray chamber with a volume of 50 mL (Agilent, Melbourne, Australia). No special modifications are required in the cyclonic spray chamber or other components of the standard liquid sample introduction system. The MultiNeb®-spray chamber combination is known as the “MultiNeb®-based system”.

For on-line CVG using the MultiNeb®-based system, calibration standards or samples with 1 M of HCl (i.e., channel 1) are sequentially aspirated through one liquid inlet, while an aqueous solution of borohydride (i.e., channel 2) is continuously introduced through the other one. Liquids interact inside the nebulizer generating the conditions for on-line CVG. Both volatile species and the tertiary aerosol are simultaneously transported to the spectrometer. When the analysis is performed without on-line CVG, deionized water is used instead of NaBH<sub>4</sub> reagent solution (Figure 2).

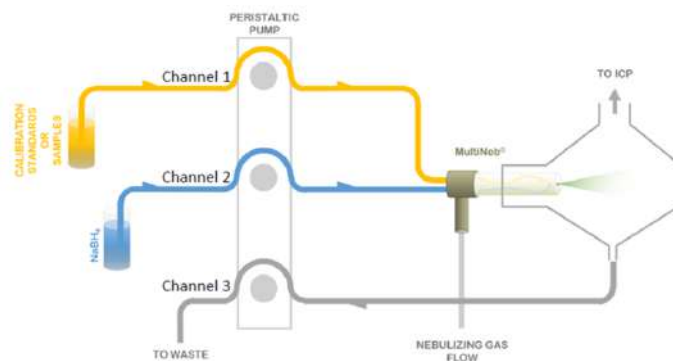


Figure 2. Scheme of the proposed on-line CVG using the MultiNeb® multiple nebulizer.

The multimode sample introduction system (MSIS) is used as a reference system for comparison with the MultiNeb®-based system. For on-line CVG using the MSIS, the sample is pumped through the nebulizer (OneNeb® Series 2) and into the bottom of the MSIS system. A flow of reductant is introduced through the top of the MSIS. The sample and reductant are mixed inside the MSIS system at the convergence of the vertically opposed tubes. The volatile species formed by the reactions are stripped from the mix and carried into the plasma by the nebulizer gas flow (Figure 3).

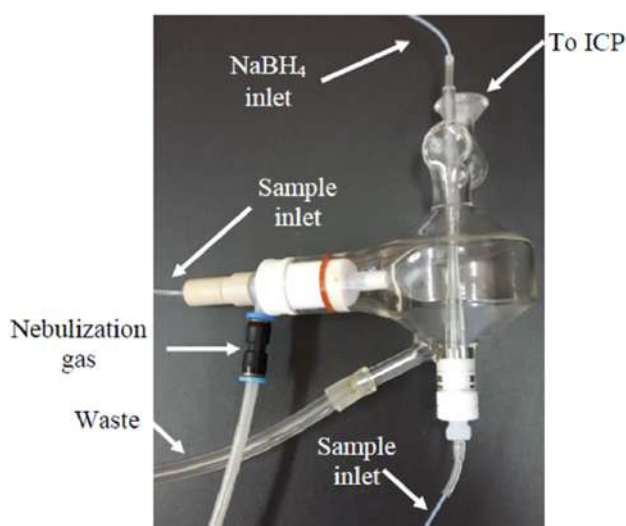


Figure 3. Photograph of the Agilent MSIS for on-line CVG.

## Reagents and solutions

Aqueous calibration standards are prepared by appropriate dilution of a 1000 mg L<sup>-1</sup> multi-elemental stock solution (ICP Multi Element Standard Solution IV, CetriPUR, Merck, Darmstadt, Germany) and 1000 mg L<sup>-1</sup> mono-element standard solutions of As, Ge, Hg, Se, Sb, and Te (High-Purity mono-element standard solutions, Charleston, UK) in distilled deionized water (18 MΩ cm resistivity). All aqueous solutions are acidified by adding up to 1 M of HCl 30% (w/w) high-purity acid (Merck p.a., Darmstadt, Germany). An aqueous calibration blank containing the same amount of HCl is also prepared.

A 1.5 % w v<sup>-1</sup> sodium borohydride (Scharlau, Barcelona, Spain) solution in 0.1% w v<sup>-1</sup> sodium hydroxide (Scharlau) is used prior to analysis.

## Instrumentation

All measurements are made using an axial view inductively coupled plasma optical emission spectrometer Agilent 720 ES (Agilent). The operating conditions are shown in Table 1.

Plasma parameters	MultiNeb <sup>®</sup> -based system	MSIS
Plasma power (kW)	1.2	1.2
Plasma gas flow rate (L min <sup>-1</sup> )	15	15
Auxiliary gas flow rate (L min <sup>-1</sup> )	1.5	1.5
Total nebulizer gas flow rate (L min <sup>-1</sup> )	0.65	0.65
Total liquid flow rate (mL min <sup>-1</sup> )	2.0	2.0
Reductant liquid flow rate (mL min <sup>-1</sup> )	1.0	1.0
Standard/sample liquid flow rate (mL min <sup>-1</sup> )	1.0	1.0
Replicates	5	5
Replicate read time (s)	1.0	1.0
Nebulizer	MultiNeb	OneNeb
Spray chamber	cyclonic	MSIS

**Table 1.** Operating conditions of the ICP OES

Several atomic and ionic emission lines corresponding to different elements contained in the samples are selected in order to cover a wide range of total excitation energy or energy sum “Esum” (i.e., excitation energy for atomic emission lines and the sum of ionization energy and excitation energy for ionic emission lines). Table 2 shows the elements and emission lines tested, with the corresponding Esum value.

Emission line (nm)	Excitation energy (eV)	Ionization energy (eV)	Esum (eV)
Sr I (407.771)	3,04	-	3,04
Ga I (417.206)	3,07	-	3,07
Al I (396.153)	3,14	-	3,14
Ag I (328.068)	3,78	-	3,78
Mg I (285.213)	4,34	-	4,34
Hg I (253.652)	4,89	-	4,89
Co II (228.616)	5,42	-	5,42
Bi I (223.061)	5,60	-	5,60
Te I (214.281)	5,79	-	5,79
Ge I (209.426)	5,92	-	5,92
Sb I (206.836)	5,99	-	5,99
Se I (196.026)	6,32	-	6,32
As I (188.979)	6,57	-	6,57
In II (230.606)	5,37	5,79	11,16
Ba II (233.527)	6,00	5,21	11,21
Cr II (267.716)	4,64	6,77	11,41
Mn II (257.610)	4,81	7,44	12,25
Tl II (190.801)	6,50	6,11	12,61
Fe II (238.204)	5,20	7,87	13,07
Ni II (231.604)	6,39	7,64	14,03
Cd II (226.502)	5,47	8,99	14,46
Pb II (220.353)	7,37	7,42	14,79

**Table 2.** Emission lines and energy values.

### 3. Results and discussion

#### Evaluation of the analytical figures of merit

##### Sensitivity and limit of detection

The analytical figures of merit (i.e., sensitivity and LOD) using on-line CVG are evaluated for both systems and compared. LOD values are calculated following the 3σ-blank criteria, being σ-blank the standard deviation of 10 blank measurements. Table 3 summarizes the analytical figures of merit obtained with both methods using on-line CVG. The relative sensitivity is defined as the ratio between the

value of sensitivity obtained with the MultiNeb®-based system, and the value of sensitivity obtained with the MSIS (i.e., a relative sensitivity value of 1 means no difference between the two on-line CVG systems).

In a similar way, the relative LOD is defined as the ratio between the value of LOD obtained with the MSIS and the value of LOD obtained with the MultiNeb®-based system. As noted, the MultiNeb®-based system provides values of relative sensitivity and LOD higher than 1 for most of the emission lines evaluated. The exception is the value of relative sensitivity of Tl II (190.801) emission line, which is slightly lower than 1.

Emission line (nm)	MSIS		MultiNeb®-based system		Relative Sensitivity <sup>b,c</sup>	Relative LOD <sup>d</sup>
	Sensitivity (cps g μg <sup>-1</sup> ) <sup>a</sup>	LOD (μg kg <sup>-1</sup> )	Sensitivity (cps g μg <sup>-1</sup> ) <sup>a</sup>	LOD (μg kg <sup>-1</sup> )		
Ag I (328.068)	7114±283	9	26875±5391	3	3.8±0.8	3
Al I (396.153)	12771±551	19	23903±1903	10	1.87±0.17	2
As I 188.979	8084±222	6	16590±302	3	2.05±0.07	2
Ba II (233.527)	253183±10384	1.7	720905±17177	0.5	2.85±0.14	3
Bi I (223.061)	19276±371	3	33489±778	1.7	1.74±0.05	1.7
Cd II (226.502)	29631±818	3	44817±1211	1.3	1.51±0.06	2
Co II (228.616)	5118±184	22	12051±367	8	2.35±0.11	3
Cr II (267.716)	12510±396	7	34036±935	3	2.72±0.11	2
Fe II (238.204)	14034±430	10	33271±1097	4	2.37±0.11	2
Ga I (417.206)	5601±319	48	6656±261	41	1.19±0.08	1.2
Ge I (209.426)	3513±59	7	5394±318	4	1.54±0.09	1.8
Hg I (253.652)	55049±4440	0.5	62225±3110	0.4	1.13±0.11	1.3
In II (230.606)	2666±131	53	3690±82	39	1.38±0.07	1.4
Mg I (285.213)	42130±2270	3	185698±6690	0.6	4.4±0.3	4
Mn II (257.610)	52538±2384	3	150736±3770	0.8	2.87±0.15	4
Ni II (231.604)	3307±111	32	6634±150	10	2.01±0.08	3
Pb II (220.353)	1443±45	62	2589±80	22	1.79±0.08	3
Sb I (206.836)	6741±385	7	12738±623	3	1.89±0.14	2
Se I (196.026)	1448±161	35	12087±1456	3	8.3±1.4	11
Sr I (407.771)	769894±63212	0.4	3114952±91282	0.11	4.0±0.4	4
Te I (214.281)	623±25	54	2641±379	15	4.2±0.6	4
Tl II (190.801)	741±65	83	655±142	64	0.9±0.2	1.3
Zn II (206.200)	16033±414	5	18852±465	3	1.18±0.04	1.7

**Table 3.** Analytical figures of merit obtained using on-line CVG with both the MSIS and the MultiNeb®-based system.

<sup>a</sup> Slope ± standard deviation. The number of calibration standards is six.

<sup>c</sup> Uncertainty expressed as combined standard uncertainty.

<sup>b</sup> Sensitivity (MultiNeb®-based system) / Sensitivity (MSIS).

<sup>d</sup> LOD (MSIS) / LOD (MultiNeb®-based system).

Table 4. compares the analytical figures of merit for volatile forming elements using on-line CVG with the MultiNeb®-based system to those obtained without on-line CVG.

As observed, on-line CVG methodology improves sensitivity and LOD values compared to conventional nebulization.

The results show that the use of on-line CVG provides relative sensitivity and LOD values greater than 1 for all emission lines evaluated, evidencing that the generation of volatile species leads to enhanced sensitivity in ICP OES. This improvement depends on the analyte evaluated and the sensitivity values range from 3 to 44 times higher than those found without on-line CVG. This fact leads to decrease the LOD values, ranging the relative LOD values from 2 to 50.

For all volatile forming elements studied, mercury offered the most successful results in the analysis by on-line CVG using the MultiNeb®-based system, obtaining a sensitivity of  $62225 \pm 3110$  cps  $\mu\text{g}^{-1}$  and a LOD of  $0.4 \mu\text{g kg}^{-1}$ . Conversely, the highest LOD value is obtained for tellurium (i.e.,  $15 \mu\text{g kg}^{-1}$ ).

It should be borne in mind that the on-line CVG conditions for either the MultiNeb®-based system or the MSIS are not optimized. Thus, these preliminary results can improve when the optimum conditions are established.

Emission line (nm)	MultiNeb®-based system				Relative Sensitivity <sup>b,c</sup>	Relative LOD <sup>d</sup>
	Without on-line CVG		With on-line CVG			
	Sensitivity (cps $\mu\text{g}^{-1}$ ) <sup>a</sup>	LOD ( $\mu\text{g kg}^{-1}$ )	Sensitivity (cps $\mu\text{g}^{-1}$ ) <sup>a</sup>	LOD ( $\mu\text{g kg}^{-1}$ )		
As I (188.979)	615±38	77	16590±302	3	27.0±1.7	29
Bi I (223.061)	1542±25	40	33489±778	1.7	21.7±0.6	24
Ge I (209.426)	717±29	36	5394±318	4	7.5±0.5	9
Hg I (253.652)	1419±30	20	62225±3110	0.4	44±2	50
Sb I (206.836)	1063±9	38	12738±623	3	12±0.6	14
Se I (196.026)	494±3	90	12087±1456	3	24±3	30
Te I (214.281)	849±19	36	2641±379	15	3.1±0.5	2

**Table 4.** Analytical figures of merit obtained with and without on-line CVG using the MultiNeb®-based system

<sup>a</sup> Slope  $\pm$  standard deviation. The number of calibration standards is six.

<sup>b</sup> Sensitivity (with on-line CVG) / Sensitivity (without on-line CVG).

<sup>c</sup> Uncertainty expressed as combined standard uncertainty.

<sup>d</sup> LOD (without on-line CVG) / LOD (with on-line CVG).

## Precision

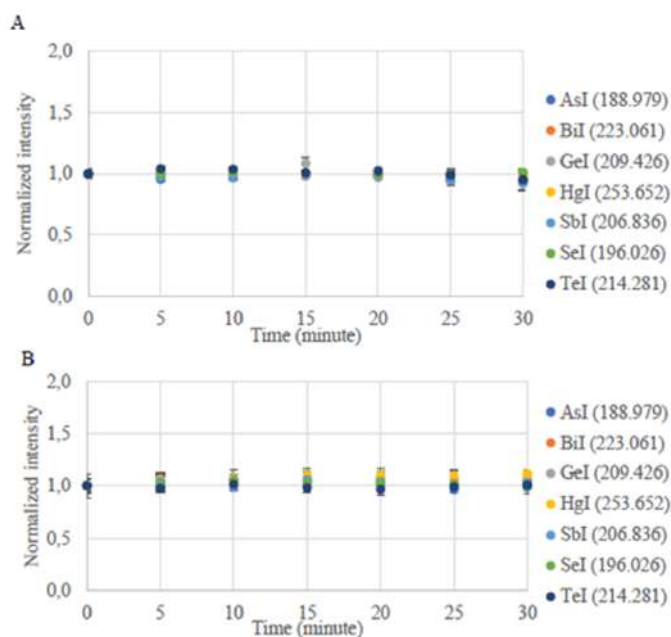
Stability of both on-line CVG systems are evaluated by the long-term precision analysis. The results of the long-term stability tests are shown in Figure 4.

Figure 4A shows the resulting normalized signal of the volatile forming elements evaluated for 30 minutes using on-line CVG with the MultiNeb®-based system and Figure 4B shows the results obtained by the MSIS. The normalized signal is defined as the ratio between the signal value obtained at a given time and the signal value obtained at time zero (initial value). A normalized value of 1 implies no difference between the two measurements (i.e., no signal drift). In both cases, data are acquired every five minutes over the 30 minutes. Comparison of Figure 4A and 4B shows that the signal stability for the MultiNeb®-based system is slightly better as compared to the MSIS system.

For all volatile forming elements studied, mercury offered the most successful results in the analysis by on-line CVG using the MultiNeb®-based system, obtaining a sensitivity of  $62225 \pm 3110$  cps  $\mu\text{g}^{-1}$  and a LOD of  $0.4 \mu\text{g kg}^{-1}$ . Conversely, the highest LOD value is obtained for tellurium (i.e.,  $15 \mu\text{g kg}^{-1}$ ).

## 4. Conclusions

The on-line chemical vapor generation methodology proposed in this work using the new MultiNeb® offers a simple and robust alternative for generation of volatile species without requiring any special device. The results obtained in this study demonstrate the high flexibility and the better performance of the MultiNeb® compared to the MSIS.



**Figure 4.** Evolution of the emission signal of all volatile forming elements evaluated for 30 minutes using on-line CVG (a) MultiNeb®-based system and (b) MSIS. Error bars are the standard deviation of 5 replicates.

# Ingeniatrics



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