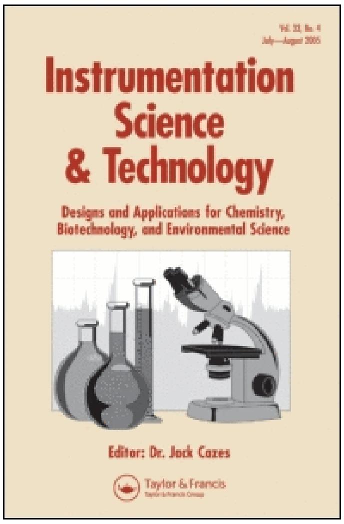

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[a] Laboratorio de Química Analítica, Centro de Química, Instituto Venezolano de Investigaciones Científicas, IVIC, Caracas, Venezuela [b] Centro de Química Analítica, Escuela de Química, Universidad Central de Venezuela, Caracas, Venezuela

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Performance of a Dual Sample Introduction System with Conventional Concentric Nebulizers for Simultaneous Determination of Hydride and Non-Hydride Forming Elements by ICP-OES

Zully Benzo,[1] Domingo Maldonado,[1] José Chirinos,[2] Eunice Marcano,[1] Clara Gómez,[1] Manuelita Quintal,[1] and Janeth Salas[1]

[1]Laboratorio de Química Analítica, Centro de Química, Instituto Venezolano de Investigaciones Científicas, IVIC, Caracas, Venezuela
[2]Centro de Química Analítica, Escuela de Química, Universidad Central de Venezuela, Caracas, Venezuela

Abstract: A dual sample introduction system that combines the benefits of nebulization and vapour generation in a single device is described. It consists of two commercial conventional concentric nebulizers coupled to a modified cyclonic chamber. The effect(s) of the solvent load produced by the amount of liquid carried for the system by the two nebulizer assemblies is investigated. Better sensitivities, similar precision and DL's (with the exception of hydride forming elements) were obtained compared with those obtained with the system working in single mode. Long term stability was less than 7% with the dual mode, being 2% and 6% for the non-hydride and hydride forming elements, respectively, in the single mode operation. DL's obtained are of the same order of magnitude as those reported by several authors, with the exception of Se whose conditions were in compromise with the optimal reached for the rest of the elements. Accuracy of the dual system was proved by analyzing NIST 1648, urban particulate matter, with satisfactory results.

Keywords: Dual-mode introduction system, Hydride generation, ICP-OES

Address correspondence to Zully Benzo, Laboratorio de Química Analítica, Centro de Química, Instituto Venezolano de Investigaciones Científicas, IVIC, Apdo. Postal 20632, Caracas 1020-A, Venezuela. E-mail: zbenzo@ivic.ve

INTRODUCTION

Normally, introduction of analytes/samples by chemical vapor and pneumatic nebulization are performed separately by using different sample introduction systems. New approaches to generating the hydride based on a modified nebulizer-spray chamber arrangement have been recently reported.[1–9]

In these systems, the sample and reducing agent are integrated into to 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 several analytical benefits in ICP-OES.[3–5,7,9–15] Dual introduction systems are very attractive for inductively coupled plasma spectrometry. Analytical methods suitable for determination of hydride and non-hydride forming elements, simultaneously, from the solution using dual sample introduction systems have also been described.[1,10–20] Nebulizing solutions while generating volatile species has been investigated for the determination of hydride and non-hydride forming elements, simultaneously, from the solution. Wolnik et al.[1] described a Tandem nebulization system in which a Meinhard concentric glass nebulizer is mounted in a Teflon spray chamber, joined to a cross-flow nebulizer and fitted to a spray chamber connected to the ICP torch. Better detection limits for the volatile elements in food were obtained while no significant improvement was obtained for the non-hydride-forming elements. Huang et al.[2] developed a nebulizer-hydride generator system for simultaneous determination of hydride-forming and non hydride-forming elements. Better detection limits were obtained for the volatile elements, whereas those of the other elements were unchanged, compared with conventional nebulization. Fengzhou et al.[6] developed an integrated nebulizer-hydride generator system in which the spray chamber for pneumatic nebulization was modified for use in hydride generation. After modification, the spray chamber functioned as a phase separator and generated an aerosol with smaller-diameter droplets. Improvements in detection limits for the hydride forming elements and mercury were obtained, and were essentially unchanged for the non-hydride forming elements. Rojas et al.[15] used a modified V-groove with one additional channel to introduce the hydride solution. Better detection limits were obtained when compared with those obtained when using cross-flow and ultrasonic nebulizers for the hydride-forming element. However, precision and detection limits for nebulization of non-hydride elements were slightly higher than for conventional nebulization systems. Asfaw and Wibotoe[16] developed a method for the simultaneous determination of Se and other non-hydride-forming elements in various beverages using a commercial multi-mode sample introduction system, MSIS. The sensitivity for Se increased more than ten times when dual-mode sample introduction was used and the sensitivity for the non-hydride generated elements was not affected significantly when the mode was changed from single to dual. Zoltan et al.[17] described a nebulizer system for the simultaneous determination of hydride and non hydride elements, which consists of a modified cross-flow nebulizer in which two introduction channels (for HCl and $NaBH_4$), perpendicular to the sample introduction channel, were incorporated. This system was coupled with a conventional Scott double-pass spray chamber. Detection limit for the hydride forming elements Sb and Sn, and for V and Zn were better when compared with other systems based on similar principles.

Later on, Asfaw and Wibotoe,[18] using the multi mode sample introduction system MSIS for determining hydride and non hydride forming elements by ICP-MS, found that the sensitivity for the hydride forming elements increased significantly using the dual mode sample introduction compared with pneumatic nebulization. No significant change in sensitivity was observed for the other elements. Gómez et al.[19] used a dual introduction system for the determination of hydride forming elements and other elements. It consisted of a crossflow nebulizer and concentric Meinhard pneumatic nebulizer connected to the conventional double-pass spray chamber of the instrument using a T-shaped adaptor. Main analytical figures of merit for the nebulization of hydride forming elements were better than those that do not form volatile hydrides, when compared with conventional nebulization systems. Maldonado et al.[20] evaluated the analytical performance of a dual nebulization system for sample nebulization at lower solution uptake rates in ICP-OES, focusing on the operation of two high effficiency micronebulizers (HEN) coupled to a modified cyclonic spray chamber for the analysis of sub-mL amounts of samples. The system allowed efficient hydride generation for the elements at low sample uptake rate. Detection limits and sensitivity were improved and precision was poorer that with similar systems. Matusiewicz et al.[21] used a slurry sampling method for the simultaneous determination of hydride forming (As, Bi, Ge, Sb, Se, Sn) and Hg and non-hydride forming (Ca, Fe, Mg, Mn, Zn) elements, without total sample digestion using a commercial dual-mode sample introduction system (MSIS) coupled with microwave induced plasma optical emission spectrometry (MIP-OES). The method required small amounts of reagents and reduced contamination and losses.

In cyclone chambers, the aerosol enters through a tangential inlet on the periphery of the vessel to follow a downward spiral motion. It acts as an impact wall chamber, initially removing the majority of large droplets, whereupon the centrifugal forces act on the droplets that are left. At the bottom of the chamber, the aerosol changes direction and moves toward the top of the vessel in an even tighter spiral, that is concentric with the original path. The droplets that are thrown against the wall leave by the drain tube at the base, and the fine droplets pass though the outlet tube. Cyclone spray chambers are not commonly used, but they are very efficient and merit more attention than they have thus far received.

This work is part of an on-going project involved in the developed of dual-nebulizer-spray chamber systems in which hydrides and non-hydride forming elements may be determined simultaneously. The ideal dual nebulizer prototype, which includes two entrances through which reductant and analyte solution are fed, should lead to an improvement of the figures of merit. Based on this, a similar system using a dual micro-nebulization system was investigated for a tandem calibration technique and for hydride generation studies by the authors.[20] New interest emerges to investigate the response of the system but using two commercially conventional concentric nebulizers coupled to a modified cyclonic chamber. This arrangement should give information about the effect(s) of the solvent load due to the amount of liquid carried for the system by the two nebulizers.

Therefore, the present work explores the performance of a dual nebulizer system for the simultaneous determination of hydride and non-hydride forming elements. It consists of two concentric Meinhard nebulizers operating in parallel, connected to a modified cyclonic spray chamber of the ICP-OES. Instrumental operating parameters, chemical conditions, and an evaluation of the analytical figures of merit are given.

EXPERIMENTAL

Instrumentation

A radially viewed Ar ICP-OES instrument (Perkin-Elmer, Model Optima 3000) was used throughout this work. The operating conditions and the working wavelengths are listed in Table 1. Figure 1 presents the dual nebulizer system used. It consists of two concentric conventional Meinhard pneumatic nebulizers connected to a modified cyclonic chamber. The dual system operates in a continuous mode in which acidified sample and borohydride solutions are continually pumped for hydride generation using the two concentric nebulizers. The chemical vapor is generated when the small droplets of sample and reductor react. The dual configuration allows the aerosols used for hydride generation to be optimized by changing the solution uptake rate and gas flow of both nebulizers, independently.

Table 1. Instrumental conditions

Operating parameters		
RF power/W	1500	
Outer gas flow rate/L min^{-1}	15	
Auxiliary gas flow rate/L min^{-1}	0.5	
Nebulizer gas flow rate/L min^{-1}	0.8[a] and 0.4[b]	
Viewing height above load coil/mm	8	
Sample uptake rate/mL min^{-1}	0.9[c]	
Working wavelengths/nm	As(I) 193.696,	Be(I) 234.861
	Cd(II) 226.502	Co(II)238.892
	Cr(II) 205.560	Cu(I) 324.752
	Fe(II) 239.562	Mg(II) 280.271
	Mn(II) 257.610	Mo(II) 202.031
	Ni(II) 231.604	Pb(II) 220.353
	Sb(I) 217.582	Se(I) 196.026
	Sr(II) 407.771	V(II) 292.402
	Zn(II) 213.857	

[a] Nebulizer gas flow rate for concentric Meinhard (entrance 2) of the dual system.

[b] Nebulizer gas flow rate for concentric Meinhard (entrance 1) of the dual system.

[c] Sample uptake rate for each concentric nebulizer of the dual system.

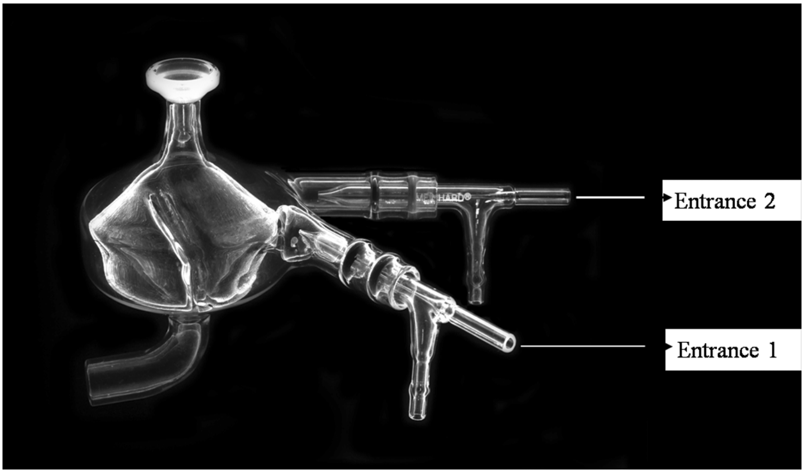

Figure 1. Schematic diagram of the modified cyclonic spray chamber with dual nebulization.

Reagents

ICP multi-element solutions (100 mg L^{-1}) of As, Be, Ca, Cd, Co, Cs, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Se, Sb, Sr, Ti, Tl, V, Zn, and Ba were from VHG labs, Inc. All chemicals used were of analytical reagent grade. Deionized water (18 MΩ cm) was used for solution preparation. Ultra-high-purity commercial acids (Riedel de Haën) were used to prepare all reagents, standards, and samples. A 0.5% (m/v) sodium tetrahydroborate solution was prepared daily by dissolution of $NaBH_4$ powder (Riedel de Haën) in 0.05% (m/v) NaOH (ACS reagent).

Configuration of the Dual Introduction System

Figure 1 shows a schematic diagram of the sample introduction system used in this work. It is based on a modified cyclonic chamber in which two concentric Meinhard nebulizers were coupled. It was made of conventional pyrex glass; two peristaltic pumps were used: one delivers the acidified sample and the sodium tetrahydroborate solutions and the second removes the waste.

Microwave Digestion Procedure

Validation of the method described in this work was performed using the urban particulate standard reference material 1648 supplied by NIST. The certified standard was dissolved using a microwave oven procedure according to a CEM application note for this type of material.

RESULTS AND DISCUSSION

Optimization of the Dual-Mode Sample Introduction

Optimization of the Instrumental Parameters

In order to optimize the chemical and instrumental conditions for the dual system, a multielement standard solution containing 2 μg mL^{-1} of 11 elements was used. The As, Sb, Se, and Be signal-to-background ratio (SBR) as a function of the $NaBH_4$ and HCl concentrations was used for the optimization of the hydride generation.

The efficiency of the energy transfer in the plasma is measured by plasma robustness in ICP-OES. Under robust conditions, no significant variation in the analyte signal intensities is observed when the matrix or reagent composition changes. Instrumental parameters were optimized using the robustness criteria. It is defined as the MgII/MgI ratio which was taken as the response for the instrumental optimization. The conditions investigated were RF power, nebulizer gas flow, sample uptake rate, and observation height. Table 1 shows the optimum operating conditions found.

Optimization of Hydride Generation

To evaluate the efficiency of hydride generation with the system developed in this work, the As, Sb, and Se SBR ratio was studied as a function of the sodium borohydride and hydrochloric acid concentrations. Operation of the dual system consisted of pumping $NaBH_4$ solution with a peristaltic pump to generate an aerosol through Entrance 1 (Fig. 1) and the acidified sample solution was pumped through Entrance 2. Both aerosols were generated and a reaction occurred in the modified cyclonic chamber to produce the volatile hydrides. The criterion used in this process was to get maximum SBR, since a good robustness does not necessary indicate maximum signal intensity during the hydride generation of the analytes under study. The results are the means of three measurements. Increased sensitivity is observed for all the analytes as the acid and $NaBH_4$ concentrations increased to 15% (v/v) and 0.4% (m/v), respectively.

Analytical Figures of Merit

Sophisticated and complex diagnostics have been suggested in the literature for the analytical evaluation of ICP spectrometers. However, they cannot be easily conducted on commercially available ICP-OES systems and, therefore, are not extensively used. There is, thus, a demand for simple, fast experiments to obtain a fair estimation of the analytical figures of merit of ICP-OES systems. It has been shown that simple experiments[22] can be used to determine the various figures of merit of ICP spectrometers. These are selectivity, repeatability, long-term stability, robustness, and limit of detection, parameters which serve as diagnosis of resolution, RSD of the signal, stability, MgII/MgI, and the SBR of the Ni(II) 231 nm (and the RSD of the background), respectively.

The selectivity is related to the practical resolution of the dispersive system. It diagnoses the resolution and is measured with the Ba(II) 230 nm line profile. The experimental selectivity with the system reported here gave a value of 6 pm. The best value reported in the literature[23] is $\leq$5 pm for the Varian Liberty 220.

The robustness is the capability of the ICP system to accept a change in the concentration of major elements, acids, and other elements without

Table 2. Figures of merit

	SBR		Precision (% RSD)		Detection limit (μg mL^{-1})	
Analyte	Dual*	Single**	Dual*	Single**	Dual*	Single**
As	306.1	1.10	0.65	2.53	2.2	104.6
Be	3304.5	1930.9	0.40	0.39	0.4	0.3
Cd	115.8	144.8	0.68	0.34	1.3	2.0
Co	115.8	30.5	0.70	0.34	4.4	5.2
Cr	149.4	59.6	0.88	0.46	5.9	4.3
Cu	72.4	41.8	0.82	0.33	3.3	3.0
Fe	65.8	12.3	0.86	0.31	3.6	13.5
Mg	149.7	26.0	0.80	0.41	1.3	1.7
Mn	1045.3	275.9	0.75	0.33	0.7	1.1
Mo	143.4	117.9	0.89	0.47	12.8	14.2
Ni	104.7	65.0	0.88	0.37	8.4	10.4
Pb	41.3	28.9	0.91	0.98	23.1	35.9
Se	66.1	3.6	0.76	5.52	9.3	256.2
Sb	152.7	1.3	0.33	1.54	3.8	184.9
Sr	598.7	141.8	0.49	0.27	0.3	0.3
V	63.7	75.3	0.45	0.41	3.8	3.1
Zn	588.6	149.8	0.39	0.30	1.6	1.5

*Dual system operation.

**Single system operation.

any significant variation in the line intensity of the analytes. It is expressed as the ratio of Mg(II)/Mg(I) and a robustness of 8.8 was found experimentally for the dual system, and 8.2 for the single system and was comparable to that reported by Mermet et al.[23] of an optimum value of $\leq$10.

The signal-to-background ratio (SBR) is a measurement of the sensitivity of determination. Table 2 also shows the sensitivity reached for the dual system and compared with those obtained with the same system but working in the single mode. In general, better sensitivities are obtained with the dual system.

Precision (Table 2), expressed as the relative standard deviation (RSD) of the fluctuations in the emission signal around the mean value from a series of replicates, resulted in an RSD of less than 1% for all elements; it is well compared with the values obtained for the single mode.

Detection limit measurements are used as a measure of overall instrument performance, since they are dependent upon the type of plasma and nebulization system, the efficiency of the spectrometer in transporting light, spectrometer stability, radio frequency power, gas flow rates, torch height, sample consumption rate, spectral lines utilized, resolution, integration time, and matrix. Therefore, detection limits (DL) represent a statistically valid means of assessing performance. The DL has been calculated following the approach of Boumans (24).

Table 2 shows the detection limit of the elements indicated. They were calculated with a multielement standard of 2 ppm. For comparison purposes, the detection limits obtained with the dual system was compared with those obtained with the same system but working in a single mode (Entrance 1 closed). It is clear, that detection limits for those hydride forming elements, such as As, Se, and Sb, are very high due to the non-generation of their respective hydrides as a consequence of the absence of the hydride reaction. Others are similar. Table 3 shows the DLs, obtained for different hydride generating system designs and where simultaneous determination of hydride-forming and non-hydride forming elements has been reported. We can say that the DLs obtained for the dual system investigated are of the same order of magnitude as those

Table 3. Comparison of the detection limit

	DL μg mL^{-1}							
Analyte	This work	Dual [ref 22]	HEN-C_y [ref 22]	DHG [ref 22]	[ref 15]	[ref 16]	[ref 1]	[ref 19]
As	2.2			5.3*	7	0.4*	3	
Be	0.4						<1*	
Cd	1.3	1.1	1.1			3	9*	
Co	4.4				0.3		3*	
Cr	5.9					6*	3*	
Cu	3.3					11	5	
Fe	3.6						6*	
Mg	1.3	0.6	1.9		0.2	3	1*	
Mn	0.7	0.4	0.6		0.04	2	<1	
Mo	12.8						5	
Ni	8.4				0.5	6*	6	
Pb	23.1				2.5			
Sb	3.8			2.9*	6	2.0	0.7	0.52*
Se	9.3			4.9		0.1	0.5	
Sr	0.3	0.4	1.0				4*	
V	3.8							3.2
Zn	1.6	2.8	3.9			3*	7	4.7

*Different λ.

Dual: Two high efficiency nebulizers (HEN) coupled to a modified cyclonic spray chamber.

HEN-C_y: High efficiency nebulizer coupled to a conventional cyclonic spray chamber.

DHG: Direct Hydride generation coupled to a modified cyclonic spray chamber.

reported by several authors for the non-hydride and hydride forming elements, with the exception of Se. Selenium optimum conditions for generating the hydride differ markedly from those optimum conditions found for the rest of elements. Acid optimum concentration for Se was 20% (v/v) and 0.2% (m/v) $NaBH_4$, which differ from the chosen conditions: 15% v/v acid and 0.4% w/v $NaBH_4$.

Measurements of long-term reproducibility quantify the degree of drift of the spectrometer, and may thus be used as an indication of the validity of analytical measurements over long periods of time between calibrations. Long term stability was less than 7% for all elements analyzed during 3 hours with the dual mode system, being 2% and 6% for the non-hydride and hydride forming elements, respectively, in the single mode operation.

Validation of the Method by Analysis of Reference Material

To prove the analytical applicability of the nebulizer system, the standard reference material, NIST 1648, urban particulate matter, was analyzed for the elements As, Cd, Cr, Cu, Ni, V, Pb, Zn, and for those noncertified elements Mg, Si, Sb, Co, and Mn. The results are given in Table 4 together with the certified values. The values are based on measurements of three replicate samples. The certified values are in good agreement with the concentrations found (95% confidence level).

Table 4. Analysis of standard reference material "urban particulate matter"

	Concentration $\mu g.g^{-1}$	
Elements	Found	Certified
As	113.6 (1.3)	115 (10)
Cd	72.1 (1.2)	75 (7)
Cr	369.3 (7.3)	403 (12)
Pb	6288.1 (91.1)	6550 (80)
Ni	78.2 (0.6)	82 (3)
V	121.8 (3.3)	140 (3)
Cu	583.9 (4.5)	609 (27)
Zn	4572.6 (82.7)	4760 (14)
Fe	36946.4 (1080.5)	39100 (1)
Mg	7887.2 (220.7)	8000*
Sb	38.4 (0.8)	45*
Co	17.9 (0.9)	18*
Mn	829.4 (6.5)	860*

*Noncertified values.

( ) Values in parenthesis correspond to the standard deviations.

CONCLUSIONS

The system investigated here provides a convenient means of determining elements, either by nebulization or hydride generation (for those elements capable of forming volatile species), or simultaneously in the same device without suffering losses in time and productivity. In general, good signal-to-background ratio was obtained. Except for a few elements, detection limits are very good compared with other dual designs used for the same purposes.

Determination of long-term stability indicates that the system is stable for at least 3 h continuous operation. Ongoing work in our laboratory will result in further elaboration of the use of this type of device.

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REFERENCES

1. Wolnik, K.A.; Fricke, F.L.; Hahn, M.H.; Caruso, J.A. Sample introduction system for simultaneous determination of volatile elemental hydrides and other elements in foods by inductively coupled argon plasma emission spectrometry. Anal. Chem. **1981**, *53*, 1030–1035.
2. Huang, B.; Zhang, Z.; Zeng, X. A new nebulizer-hydride generator system for simultaneous multielement inductively coupled plasma-atomic emission spectrometry. Spectrochim. Acta B **1987**, *42*, 129–137.
3. Watling, R.J.; Collier, A.R. Continuous hydride generation in inductively coupled plasma atomic emission spectrometry using a dual platinum grid nebuliser system. Analyst **1988**, *113*, 345–346.
4. Hwang, J.D.; Guenther, G.D.; Diomiguardi, J.P. Hydride generator system for a 1-kw inductively coupled plasma. Anal. Chem. **1989**, *61*, 285–288.
5. Schramel, P.; Li-Qiang, X. Determination of arsenic, antimony, bismuth, selenium and tin in biological and environmental samples by continuous flow hydride generation ICP-AES without gas-liquid separator. Fresenius J. Anal. Chem. **1991**, *340*, 41–47.
6. Fengzhou, Q.; Guoying, G.; Chun, X. A compact, versatile, integrated nebulizer-hydride generator system for simultaneous determination of volatile elemental hydrides and other elements by ICP-AES. Appl. Spectrosc. **1991**, *45*, 287–292.
7. Ding, W.W.; Sturgeon, R.E. Minimization of transition metal interferences with hydride generation techniques. Anal. Chem. **1997**, *69*, 527–553.

8. Tao, G.H.; Sturgeon, R.E. Sample nebulization for minimization of transition metal interferences with selenium hydride generation ICP-AES. Spectrochim. Acta B **1999**, *54*, 481–489.
9. Moor, C.; Lam, J.W.H.; Sturgeon, R.E. A novel introduction system for hydride generation-inductively coupled plasma mass spectrometry: Determination of selenium in biological materials. Anal. Atom. Spectrom. **2000**, 143–149.
10. Hutton, R.C.; Preston, B. A simple versatile hydride-generation configuration for inductively coupled plasmas. Analyst **1983**, *108*, 1409–1411.
11. Huang, B.; Zeng, X.; Zhang, Z.; Liu, J. Recent studies on inductively coupled plasma sample introduction-I. Hydride generation. Spectrochim. Acta **1988**, *43B*, 381–389.
12. Fengzhou, Q.; Guoying, G.; Chun, X. A compact, versatile, integrated nebulizer-hydride generator system for simultaneous determination of volatile elemental hydrides and other elements by ICP-AES. Appl. Spectrosc. **1991**, *45*, 287–292.
13. Pohl, P.; Zyrnicki, W. Simultaneous determination of As, Bi, Se and Sn and non-hydride forming elements by HG-ICP-AES without liquid phase separation. Chem. Anal. **2000**, *45*, 699–708.
14. McLaughlin, R.L.J.; Brindle, I.D. A new sample introduction system for atomic spectrometry combining vapour generation and nebulization capacities. J. Anal. Atom. Spectrom. **2002**, *17*, 1540–1548.
15. Rojas, I.; Murillo, M.; Carrión, N.; Chirinos, J. Investigation of the direct hydride generation nebulizer for the determination of arsenic, antimony and selenium in inductively coupled plasma optical emission spectrometry. Anal. Bioanal. Chem. **2003**, *376*, 110–117.
16. Asfaw, A.; Wibetoe, G. Simultaneous determination of hydride (Se) and non-hydride-forming (Ca, Mg, K, P, S, and Zn) elements in various beverages (beer, coffee and milk), with minimum sample preparation, by ICP-AES and use of a dual-mode sample-introduction system. Anal. Bioanal. Chem. **2005**, *382*, 173–179.
17. Zoltan, T.; Benzo, Z.; Murillo, M.; Marcano, E.; Gómez, C.; Salas, J.; Quintal, M. Performance of a new nebulizer system for simultaneous determination of Sb, Sn (hydride generation), V and Zn by ICP-OES. Anal. Bioanal. Chem. **2005**, *382*, 1419–1430.
18. Asfaw, A.; Wibetoe, G. Dual mode sample introduction for multi-element determination by ICP-MS: The optimization and use of a method based on simultaneous introduction of vapor formed by $NaBH_4$ reaction and aerosol from the nebulizer. J. Anal. Atom. Spectrom. **2006**, *21*, 1027–1035.
19. Gómez, L.R.; Márquez, G.D.; Chirinos, J.R. Dual nebulizer simple introduction system for simultaneous determination of volatile elemental hydrides and other elements. Anal. Bioanal. Chem. **2006**, *386*, 188–195.
20. Maldonado, D.; Chirinos, J.; Benzo, Z.; Gómez, C.; Marcano, E. Analytical Evaluation of a dual micronebulizer sample introduction system for inductively coupled plasma spectrometry. J. Anal. Atom. Spectrom. **2006**, *21*, 743–749.

21. Matusiewicz, H.; Slachcinski, M. Simultaneous determination of hydride forming (As, Bi, Ge, Sb, Se, Sn) and Hg and non-hydride forming (Ca, Fe, Mg, Mn, Zn) elements in sonicate slurries of analytical samples by microwave induced plasma optical emission spectrometry with dual-mode sample introduction system. Microchem. J. **2007**, *86*, 102–111.
22. Poussel, E.; Mermet, J.M.; Samuel, O. Simple experiments for the control, the evaluation and the diagnosis of inductively coupled plasma sequential systems. Spectrochim. Acta **1993**, *48B*, 743–755.
23. Mermet, J.M.; Poussel, E. ICP Emission Spectrometers: 1995 analytical figures of merit. Appl. Spectrosc. **1995**, *49*, 12A–18A.
24. Boumans, P.W.J. Detection limits and spectral interferences in atomic emission spectrometry. Anal. Chem. **1994**, *66*, 459A–467A.

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