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Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Evaluation of dual sample introduction systems by comparison of cyclonic spray chambers with different entrance angles for ICP-OES

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ARTICLE INFO

Article history:

Received 5 May 2009

Received in revised form 27 May 2009

Accepted 28 May 2009

Available online xxxx

Keywords:

Dual introduction system

Cyclonic chamber

Hydride elements

Non-hydride elements

ICP-OES

ABSTRACT

The operating characteristics of a number of locally constructed inductively coupled plasma (ICP) dual sample introduction designs used for the determination of volatile and non volatile elements have been compared. Four cyclonic spray chamber arrangements with entrance angles of 0, 45, 90, and 180° were tested. The operating characteristics studied included instrumental conditions, chemical conditions for the hydride generation reaction and analytical figures of merit. Analytical performance of the nebulization systems was characterized by determination of the signal to background ratio (SBR), the limits of detection (LODs), and the precision (RSDs). In general, the results suggest that the dual system with 45° configuration was found to be the best indicator of the analytical performance of the dual pneumatic nebulizer-cyclonic chamber arrangement studied, giving the best SBR, precision (1.0–3.5%) and in most cases the lowest detection limits (0.3–24.6 ng L⁻¹) for both, the hydride and non-hydride forming elements. Long-term reproducibility from the 45 degree-dual system was superior to those of different angles configuration (ranging from 4.2 to 5.1% for the non- and hydride forming elements respectively). The applicability of the dual system was proven by analyzing NIST 1573 Tomato Leaves with satisfactory results.

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1. Introduction

There has been a tremendous activity in the area of sample introduction since ICP has been commercially available. Some of the considerations in selecting an introduction system include dissolved solid content, suspended solid presence, presence of HF or caustic, detection limit requirements, precision requirements, sample load requirements, sample size limitations, and operating budget. The concentric nebulizer and all glass introduction systems may not work at all for your application. The analyst is left with the task of choosing the best introduction components after taking into account the appropriate considerations.

The basic designs that have remained over the years are the Scott double-pass and the Cyclonic spray chambers. The Cyclonic design [1–4] is relatively new but it is very efficient and merits some attention. An evaluation of the capabilities of a cyclonic spray chamber has been made by several investigators [1,5–8]. The cyclonic spray chamber operates by centrifugal force. Droplets are discriminated according to their size by means of a vortex produced by the tangential flow of the sample aerosol and argon gas inside the chamber. Smaller droplets are

carried with the gas stream into the ICP, while the larger droplets impinge on the walls and fall out through the drain. It is generally accepted that a cyclonic spray chamber has a higher sampling efficiency, which, for clean samples, translates into higher sensitivity and lower detection limits. However, the droplet size distribution appears to be different from a double-pass design, and for certain types of samples, can give slightly inferior precision.

Normally, introduction of analytes/samples by hydride generation and pneumatic nebulization is performed separately by using different sample introduction systems. The feasibility of simultaneous determination of both hydride and non-hydride-forming elements using the same introduction system has been reported [9–19]. The main reason for using dual mode sample introduction is to decrease the limit of detection for the hydride forming elements that often exist in very low concentrations, and additionally save time by analyzing other elements of interest simultaneously.

It has been reported [20] that the gas and the liquid flow rates are the most critical variables that affect the aerosol characteristics when pneumatic nebulization is used. The higher the gas flow rate and the lower the liquid flow rate, the finer the aerosols. Moreover, Kahen et al. [21] reported that droplet size and velocity distributions are the most important factors that determine the quality of an aerosol and a study on the tertiary aerosol revealed the ICP spray chamber is not only a droplet size filter but a velocity filter as well; it's a momentum

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Table 1
Instrumental conditions.

Operating parameters	Dual Neb-Cy systems' configuration			
	0°	45°	90°	180°
RF power/W	1500	1500	1500	1500
Viewing height above load coil/mm	5	8	5	5
Nebulizer gas flow rate/L min ⁻¹	0.6 ^a and 0.2 ^b	0.8 ^a and 0.4 ^b	0.8 ^a and 0.3 ^b	0.7 ^a and 0.4 ^b
Sample uptake rate/mL min ⁻¹	0.9 ^c	0.9 ^c	0.9 ^c	0.9 ^c
Nebulizer tip position (entrance 2)/mm	25	25	35	25
Nebulizer tip position (entrance 1)/mm	35	35	30	25
Working wavelengths/nm	As (I) 193.696, Be (I) 234.861, Ca (II) 393.366, 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.

separator. Based on this, the angle between the two entrances of a cyclonic chamber combined with a dual nebulizer arrangement may also have an effect on the aerosol characteristics. The performance characteristics of several dual nebulizer-cyclonic spray chamber configurations, in which the angle between the two entrances on the dual spray chamber has been varied: 0, 45, 90 and 180° are evaluated in terms of aerosol transport efficiency and ICP-OES analytical figures of merit. Up to our knowledge, a comparison study of this parameter on this type of arrangement has not been reported. These dual systems are used for the determination of hydride and non-hydride forming elements. Instrumental operating parameters and chemical conditions have also been optimized for each system. The applicability of

the new systems was checked by analyzing Tomato Leaves reference material.

2. Experimental

2.1. Instrumentation

2.1.1. Configuration of the dual introduction system

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. Fig. 1 presents the different dual configuration systems used in this work. They consist of two conventional concentric pneumatic nebulizers connected to different modified cyclonic chambers (Cys). They were homemade from conventional pyrex glass in a local glass blowing technical laboratory. Four different concentric nebulizers-cyclonic spray chamber arrangements were used. The angles between the two entrances of the configurations under study were: 0, 45, 90 and 180°. The dual system operates in a continuous mode in which acidified sample solution is pumped through entrance 2 and the borohydride solutions through entrance 1 (Fig. 1).

Sample and NaBH₄ aerosols were generated and a reaction occurred into the cyclonic spray chamber to produce the volatile hydrides. Two peristaltic pumps were used: one delivers the acidified sample and the sodium tetrahydroborate solutions and the second removes the waste. 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. Also, nebulizer position has been proven [18] to affect the magnitude of the signal when cyclonic chambers are used. A change in this variable modifies the gap between the nebulizer tip and the walls of the spray chamber and, consequently, the droplet impact processes. So, the distance between the nebulizer tip up to the point where the nebulizer is introduced was also studied for both entrances, based on previous studies [18,22,23]. The results showed

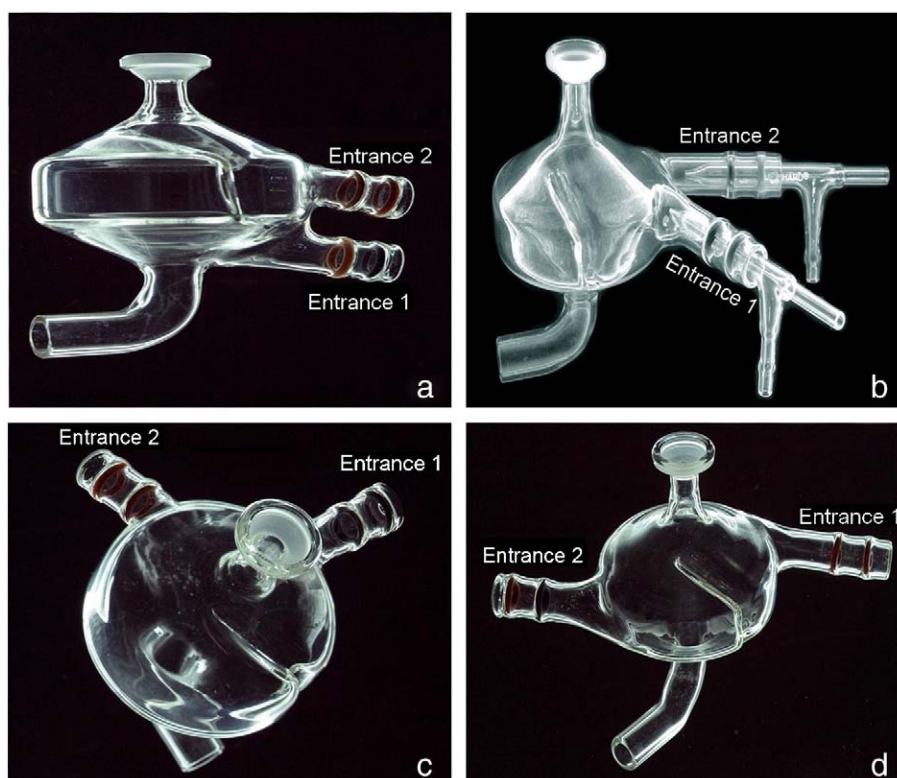


Fig. 1. Schematic diagram of the cyclonic spray chambers with different entrance angles: (a) 0°; (b) 45°; (c) 90°; (d) 180°.

that better signals are reached at the distances reported in Table 1 for each configuration.

2.2. Reagents

ICP multi-element solutions (100 mg L^{-1}) of As, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Se, Sb, Sr, V, and Zn, were from VHG labs, Inc. All chemicals used were of analytical reagent grade. Deionized water ($18 \text{ M}\Omega \text{ cm}$) was used for solution preparation. Ultrahigh-purity commercial acids (Merck) 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).

2.3. Microwave digestion procedure

The certified standard reference material (0.25 g) was digested with HNO_3 (5 mL), in Teflon vessels (XP1500Plus, 50 mL), allowing samples to be predigested by standing open for a minimum of 15 min before sealing vessels and proceeding to the following one stage heating program: power 800 W (100%); ramp time: 15 min; pressure: 800 psi; temperature 200°C ; hold time 15 min. The MW digestion procedure was slightly modified (avoiding the use of HF) from the one supplied by the CEM manufacturer. Once the samples were digested, they were allowed to reach room temperature and pressure. Then, the optimum amount of 10, 15, 15 and 10% (v/v) HCL for the 0, 45, 90 and

180° chamber configurations respectively, was added and solutions made up to 25 mL with deionized water.

2.4. Applicability

The operational application of the developed introduction device was carried out analyzing Tomato Leaves standard reference materials 1573, supplied by NIST. On the other hand, spike and recovery studies (at 0.5 and $1.0 \mu\text{g L}^{-1}$ of each analyte) were performed on the SRM for those elements which are not certified in the standard and as well for those that originally were below the quantification limits. Those elements detectable and certified in the reference material were directly analyzed. The values reported are the average recoveries for three replicate samples.

3. Results and discussion

3.1. Optimization of the instrumental parameters

The optimization of the chemical and instrumental conditions for each dual system was carried out using a multi-element standard solution containing $2 \mu\text{g mL}^{-1}$ of 18 elements. Plasma temperature and electron number density have been used to check the conditions where the signal from fixed concentration of analyte is not significantly affected by changes in the matrix composition (robustness definition). However, monitoring the plasma through these two parameters is neither easy nor a costless indicator to check robust

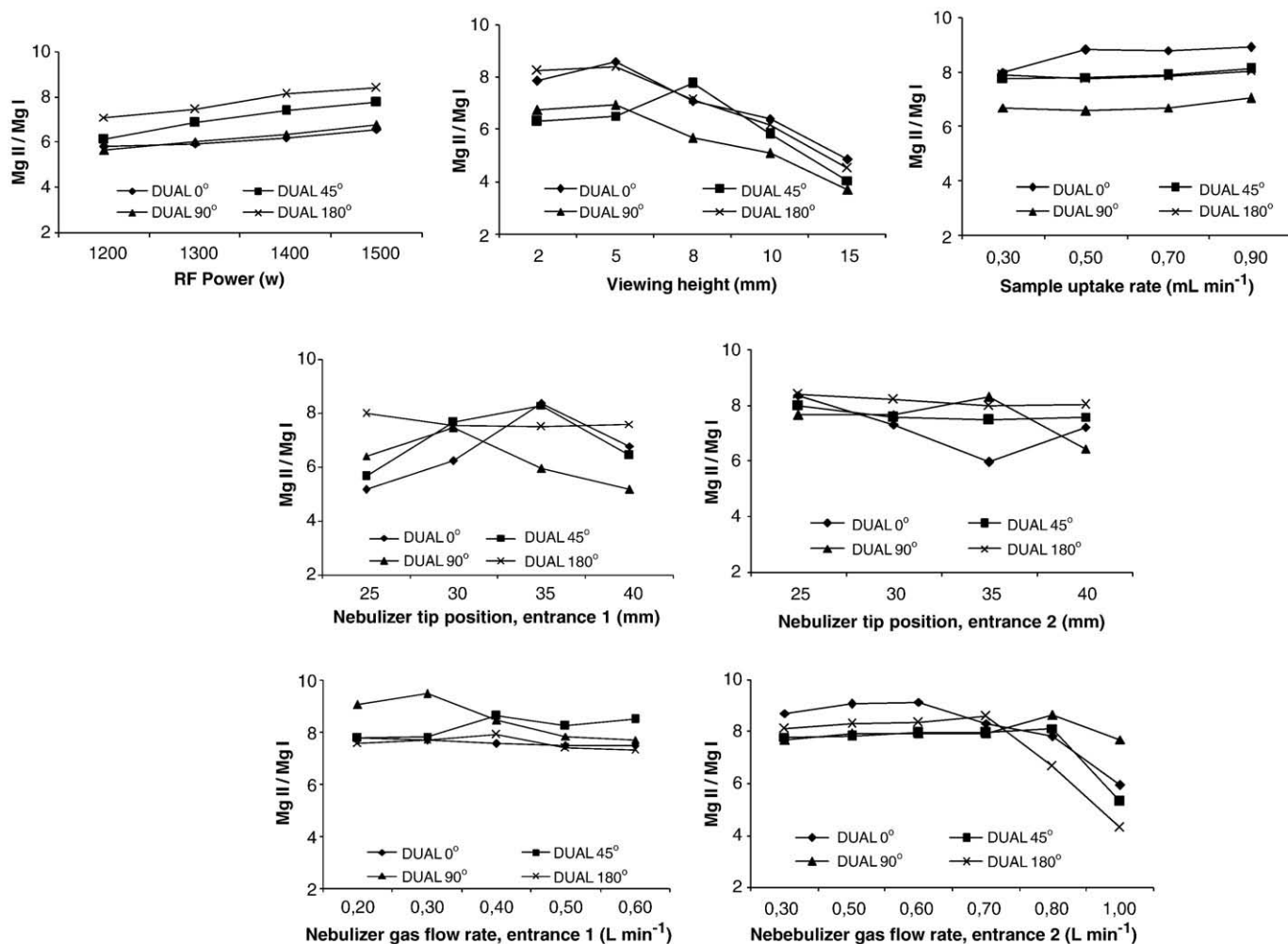


Fig. 2. Optimization of the instrumental conditions for each configuration.

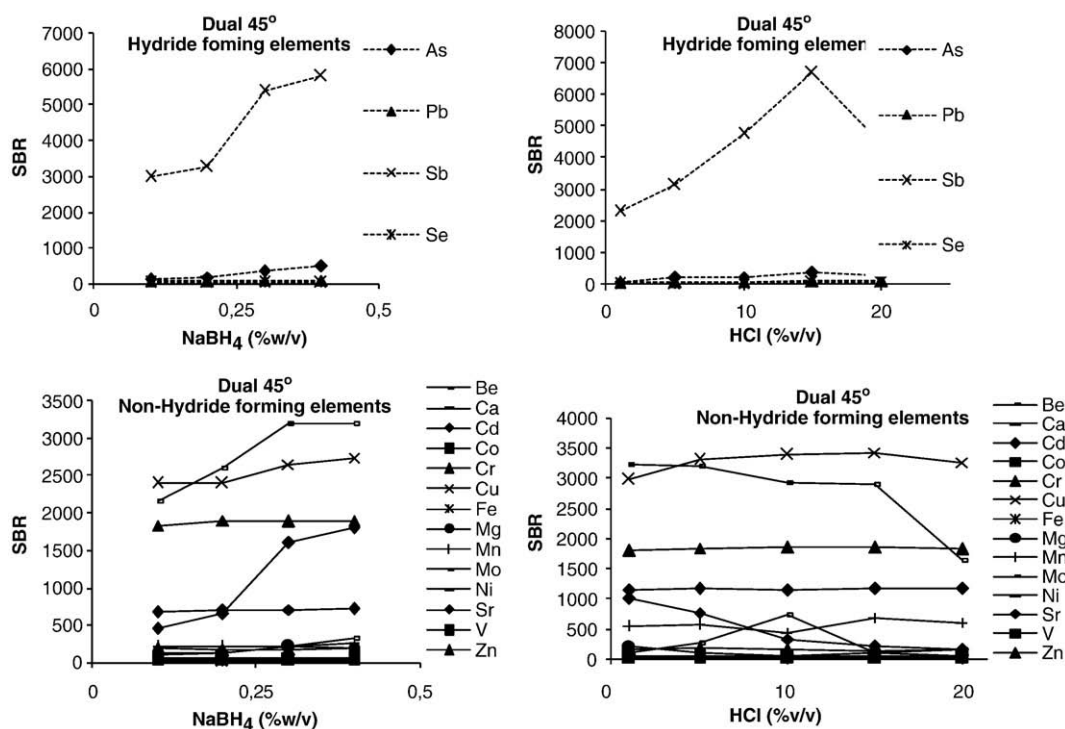


Fig. 3. Optimization of the chemical conditions for the 45° angle configuration.

conditions, as it has been indicated by Tognoni et al. [24]. The use of MgII/MgI intensity ratio is the most common method proposed for the same purpose [25–27]. The success gained by this diagnostic tool is demonstrated by enormous examples found in the literature. The parameters investigated were RF power, nebulizers' gas flow rate for the two entrances, sample uptake rate, observation height and nebulizers' tip position (for entrances 1 and 2). Fig. 2 shows these results and in Table 1, the optimum operating conditions reached for each configuration are summarized.

3.2. Chemical conditions

The criterion used in this process was to get maximum SBR since a good robustness does not necessarily indicate maximum signal intensity during the hydride generation of the analytes under study. However, it

was taken as a compromise to get maximum SBR between the hydride and non-hydride forming elements because the SBR magnitude between the two groups of the elements was wide. Hydrochloric acid and sodium borohydride concentrations were varied between 1 and 20% v/v and from 0.1 to 0.4% (m/v) respectively. For simplicity, only the results for the 45° unit are shown in Fig. 3. The rest of the configurations show similar behavior. In general, the sensitivity for the hydride and non-hydride forming elements increases for each configuration: 0, 45, 90 and 180°, at the following concentrations: 10, 15, 15 and 10% (v/v) HCl and 0.4, 0.4, 0.3, and 0.4% (m/v) NaBH₄ respectively.

3.3. Analytical performance of the system

It has been shown that simple experiments [28] can be used to determine the various figures of merit of ICP spectrometers. These are

Table 2 Sensitivity, precision and detection limits.

Element	Dual 0°			Dual 45°			Dual 90°			Dual 180°		
	SBR	Precision, % RSD	Detection limit, µg L ⁻¹	SBR	Precision, % RSD	Detection limit, µg L ⁻¹	SBR	Precision, %RSD	Detection limit, µg L ⁻¹	SBR	Precision, %RSD	Detection limit, µg L ⁻¹
As	136	2.6	21.6	306	2.7	2.2	126	6.4	10.3	55	4.7	34.9
Be	1934	6.7	0.04	3305	2.7	0.4	3017	6.5	0.4	6794	6.9	0.3
Ca	1.1	8.1	399.6	6	2.9	24.6	3	6.4	533	2.0	10.3	299.9
Cd	1120	7.7	1.8	149	1.1	1.3	1805	5.5	1.1	1747	9.2	1.1
Co	27	12.4	20.7	116	1.0	4.4	50	6.6	12.7	58	12.7	7.4
Cr	336	9.0	3.7	328	1.4	5.9	363	5.5	5.0	395	13.6	4.8
Cu	249	8.1	6.9	72	3.5	3.3	37	5.6	9.3	4546	10.8	0.4
Fe	26	13.7	29.1	66	1.3	3.6	47	5.3	13.9	43	10.2	13.9
Mg	38	5.4	17.1	150	2.8	1.3	101	4.2	19.6	55	8.2	9.1
Mn	10684	8.4	0.1	1045	2.2	0.7	515	5.3	2.6	805	8.2	1.9
Mo	259	9.1	18.8	143	1.5	12.8	173	5.5	8.9	200	12.1	11.6
Ni	46	10.3	13.6	105	1.7	8.4	125	4.3	8.6	165	10.1	6.9
Pb	22	10.2	43.4	41	2.4	23.1	46	4.9	42.3	45	15.0	39.8
Sb	126	2.7	3.7	153	2.0	3.8	322	2.1	7.1	193	2.6	2.8
Se	39	3.9	20.4	66	1.6	9.3	9	4.0	117.4	28	5.4	41.8
Sr	137	8.2	3.7	599	1.7	0.3	361	5.8	6.5	221	11.0	2.2
V	43	8.5	11.7	64	2.4	3.8	158	5.4	4.6	113	10.3	5.9
Zn	741	5.9	0.9	589	1.9	1.6	223	5.1	6.7	243	10.3	4.4

Table 3
Analysis of standard reference material “Tomato Leaves” (NIST 1573).

Element	Concentration ($\mu\text{g g}^{-1}$)	
	Found	Certified
As	nd ^b	0.27 (0.05) ^a
Cr	4.39 (0.09)	4.5 (0.5) ^a
Pb	nd ^b	6.3 (0.3) ^a
Cu	11.9 (0.7)	11 (1) ^a
Zn	59.2 (2.9)	62 (6) ^a
Fe	676 (36)	690 (25) ^a
Mg	7289 (385)	7000 (0.5)
Mn	236 (10)	238 (7) ^a
Sr	44.7 (0.6)	44.9 (0.3) ^a

() Values in parenthesis correspond to the standard deviations.

^a Certified values.

^b Not detected.

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 plasma robustness is the capability of the ICP system to accept a change in the concentration of major elements, acids, and other elements without any significant variation in the line intensity of the analytes. It is expressed as the ratio of Mg (II)/Mg (I) and it was found to have experimental ratio values of 8.3, 8.8, 9.5 and 9.4 for the dual 0, 45, 90 and 180° introduction systems respectively and all compared well with that reported by Mermet and Poussel [29] of an optimum value of ≥ 10 .

Table 2 shows the comparison of the four dual mode systems. The study was conducted using the optimized parameters given in Table 1. The precision was expressed as the relative standard deviation (RSD) of the fluctuations in the emission signal of each analyte around the mean value from a series of ten replicates. The detection limit was calculated following the approach of Mermet and Poussel [29] and it is related with the SBR of the analyte at a given concentration and the RSD of the background. In general, the results suggest that the dual system with a 45° configuration gave the best SBR, precision and in most cases the lowest detection limits for both, the hydride and non-hydride forming elements. However, an improvement of the SBR for the non-hydride forming elements was obtained with the configurations of 0 and 180° angles.

Measurement of the long-term reproducibility quantifies the drift of the spectrometer. It is important because the occurrence of drift necessitates periodic recalibration, which is time-consuming. Long-term reproducibility may be used as an indication of the validity of analytical measurement over long periods of time between calibrations. The emission intensity signals given by the hydride and non-hydride forming elements were taken over a period of 160 min. The average RSD values for the hydride forming elements were: 11.2% (0°); 5.1% (45°); 9.1% (90°) and 5.7% (180°) for each configuration indicated in parentheses and for the non-hydride forming elements were: 8.1% (0°); 4.2% (45°); 8.8% (90°) and 11.7% (180°).

3.4. Applicability

The certified reference material Tomato Leaves was analyzed with the 45° angle configuration to verify the applicability of the optimized sample introduction system. The results obtained and the corresponding certified values are shown in Table 3. The values are the mean of three individual samples. As it can be seen from Table 3, the results are in very good agreement with the certified values. Arsenic and lead could not be quantified directly, because their concentrations were below the quantification limits ($Q_L = 0.7 \mu\text{g/g}$ As and $Q_L = 8 \mu\text{g/g}$ Pb). For most of the elements determined the *t*-test (based on the 95% confidence level) shows no statistically significant difference between the mean values found and the certified or information values. The

recovery at $500 \mu\text{g L}^{-1}$ and at $1000 \mu\text{g L}^{-1}$ gave acceptable results of 86–98% and 92–101% respectively for the rest of the elements (As, Be, Cd, Co, Mo, Ni, Pb, Sb, Se and V).

4. Conclusions

It can be concluded that the 45° angle configuration device gives superior performance over the other aforementioned nebulizer-cyclonic chamber arrangements. This unit gave the best SBR, precision and in most cases the lowest detection limits for both, the hydride and non-hydride forming elements when compared with other different angle configurations studied in this work. It shows that it is an effective unit for the recovery of many analytes. These may indicate that the configuration of the system has high sample transport efficiency, being adequate for direct hydride generation and nebulization. Good recoveries were obtained for the determined elements. In addition, the fact that the device can be constructed locally in a glassblowing laboratory adds some advantage regarding cost.

Acknowledgments

The authors gratefully acknowledge Instituto Venezolano de Investigaciones Científicas, IVIC, FONACIT through Group Project No. 1998003690, and Jose Sanchez from the glassblowing department at INTEVEP, and Jorge Rivas and Enrique Gonzalez from the photography department at IVIC.

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