

Analytical evaluation of a dual micronebulizer sample introduction system for inductively coupled plasma spectrometry

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The analytical performance of a dual nebulization system is evaluated for sample nebulization at lower solution uptake rates in inductively coupled plasma optical emission spectrometry (ICP-OES). The system is essentially a modified cyclonic spray chamber that allows the simultaneous operation of two micronebulizers. This work is focused on the optimization and evaluation of the main analytical figures of merit of this sample introduction system. The usefulness of this dual micro-nebulizer in practical ICP-OES studies is demonstrated by using a tandem calibration technique and by operating this system for hydride generation studies. Results showed that this system presents similar figures of merit to a conventional spray chamber but that the non-spectroscopic interferences, usually present at lower solution uptakes rates, can be compensated for by using the tandem calibration technique with this system. Additionally, the two micronebulizers coupled to the modified cyclonic spray chamber can be used for efficient volatile hydride generation from sub-mL amounts of samples. Interference effects by transition metals have been shown to be corrected by the addition of thiourea. The analytical applicability of the dual system was checked by analyzing two standard reference materials: NIST 1577b, Bovine Liver and NIST 1566a Oyster Tissue. The accuracy achieved when using different calibration techniques and hydride generation are within the certified values when applying the significance *t*-test at the 95% confidence level.

Introduction

The most common form of sample introduction in inductively coupled plasma (ICP) spectrometry is liquid sample introduction. This way of presenting the sample to the plasma offers the following analytical benefits: simple sample handling, sample dilution, and easy calibration for quantification purposes. In addition, excellent signal stability and reproducibility of the measurements can be achieved. Usually, the introduction of liquid samples into plasmas involves the use of a nebulizer to transform the sample into an aerosol, followed by a spray chamber that is employed to modify the characteristics of the aerosol generated by the nebulizer, by adapting them to plasma requirements (fine and stable aerosol, and low solvent plasma load).

It has been reported that conventional nebulizer–spray chamber sample introduction systems are not convenient for the analysis of limited, expensive, or hazardous liquid samples because they suffer from low transport efficiency, memory effects, contribute significantly to matrix effects and generate significant amounts of waste.¹ A recent trend in plasma spectrometry is the design of nebulizer–spray chambers that

work at lower solution uptake rates. The principles and description of these devices can be found in the literature.² In brief, these devices consist of: pneumatic micronebulizers coupled to a low inner volume spray chamber, micronebulizers coupled to a desolvation system and direct injection nebulizers. Specifically, the use of micronebulizers coupled to a low inner volume spray chamber looks attractive because their use imposes a simple trajectory towards the plasma, which is beneficial from the point of view of memory effects and interferences. Compared with conventional cyclonic spray chambers, repeatability, sensitivity and limits of detection are slightly improved, low wash out times can be obtained, analyte transport efficiency are close to 100%, there is a low liquid solvent loading and reduced signal noise caused by completely desolvated droplets.

On the other hand, the use of two sample introduction devices is becoming familiar these days. The dual systems mainly consist of the following devices operating in parallel: nebulizer–spray chamber arrangement with a solid sample introduction system,³ two nebulizer–spray chamber arrangements^{4–6} and two tandem spray chambers.^{7,8}

Dual sample introduction systems are very attractive for inductively coupled plasma spectrometry because they can be used for calibration purposes in laser ablation^{9,10} and electrothermal vaporization,³ for tandem calibration techniques^{4,5} and to increase the sensitivity, improve the reproducibility and reduce oxide formation in double focusing sector field ICP-MS.⁷ Finally, dual sample introduction devices can be

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used for fundamental studies: for example, these systems can be used to study matrix effects in dry and wet conditions of the plasma^{11–14} and to demonstrate the charge-transfer mechanism.^{6,15}

In this work, a dual micronebulization system was investigated. It consists of a modified cyclonic spray chamber which allows the operation in parallel of two concentric micronebulizers. Optimization of the instrumental plasma parameters of this system and an evaluation of the main analytical figures of merit, plasma robustness, sensitivity and short and long-term precision, were carried out.

Finally, the usefulness of the dual sample introduction system is explored by analyzing two certified materials, bovine liver and oyster tissue, using the tandem calibration mode and hydride generation techniques, respectively, at low sample uptake rates.

Experimental

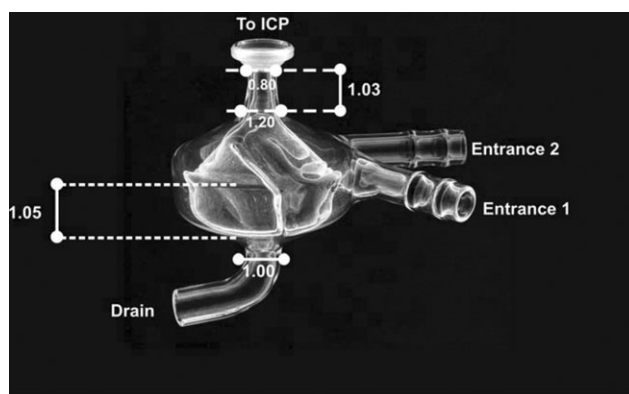
Instrument

A PerkinElmer Model ICP Optima 3000 radially viewed Ar emission spectrometer and a standard demountable-type quartz plasma torch were used throughout. The id of the alumina injector was 2.0 mm. A Gilson minipulse peristaltic pump was used to feed both nebulizers. A Spetec Perimax 12 pump was used to flow away the waste. Two high efficiency nebulizers, HEN (HEN-170-AA, Meinhard Glass Products, Analytical Reference Materials International Corp, CO, USA) and a glass cyclonic spray chamber (Glass Expansion, Pty, Australia) were used. Test solution is delivered to the nebulizers by using narrow-bore Tygon tubing (0.015 inch id, Elkay Products, Inc., Boston Turnpike, Shrewsbury) to reduce peristalsis-related noise. All functions of the plasma were computer-controlled. Table 1 presents the optimized plasma

Table 1 Instrumental conditions

Operating parameter	Nebulizer system	
	Dual ^a	HEN-Cy ^b
RF power/W	1500	1500
Outer gas flow rate/L min ⁻¹	12	12
Intermediate gas flow rate/L min ⁻¹	0.5	0.5
Nebulizer gas flow rate/L min ⁻¹	0.4 ^c	0.8
Viewing height above load coil/mm	5	5
Sample uptake rate/μL min ⁻¹	60 ^d	60
Working wavelengths/nm	As(i) 188.9, Ba(ii) 455.4, Cd(ii) 226.5, Mg(i) 285.2, Mg(ii) 280.2, Mn(ii) 257.6, Sb(i) 206.8, Se(i) 196, Sr(ii) 407.7, Zn(i) 213.8 and Zn(ii) 206.2	

^a Dual: Two high efficiency nebulizers (HEN) coupled to a modified cyclonic spray chamber. ^b HEN-Cy: High efficiency nebulizer coupled to a conventional cyclonic spray chamber. ^c Nebulizer gas flow rate for each HEN of the dual system. ^d Sample uptake rate for each HEN of the dual system.



(b)

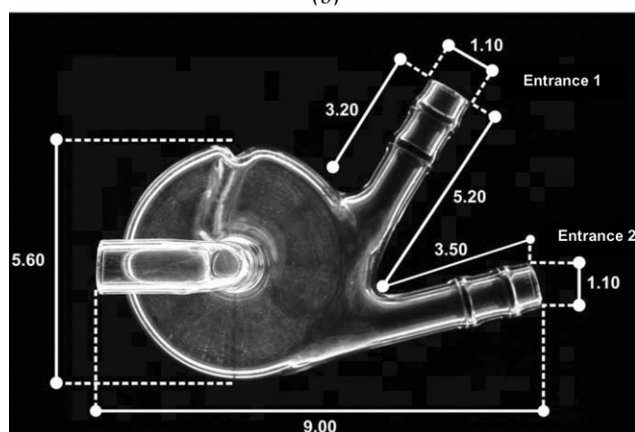


Fig. 1 Schematic diagram of the modified cyclonic spray chamber used for dual micro-nebulization. The figure shows some critical dimensions in cm: (a) side view and (b) bottom view.

operating parameters and the working wavelengths. They were selected based on their sensitivity and freedom from spectral interferences.

A microwave oven, CEM Model MARS5 (CEM Corporation, Matthews, NC, USA) was used to digest the samples.

Configuration of the dual introduction system

Fig. 1 shows a schematic sketch having some critical dimensions of the sample introduction system used in this work. It is based on a modified cyclonic spray chamber in which two high efficiency nebulizers (HEN) were coupled. The inner volume of the spray chamber was 50 cm³ and was made of conventional Pyrex glass. Two peristaltic pumps were used: one to deliver the solution to both nebulizers and the second to remove the waste.

Reagents

ICP multi-element standard solution IV (1000 mg L⁻¹) of Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl and Zn was from Merck (Darmstadt, Germany). All chemicals used were of analytical-reagent grade. Distilled, deionized water (Milli-Q, 18 MΩ cm) was used for solution preparation. Ultra-high-purity commercial acids (Merck, Darmstadt, Germany) were used to prepare all reagents, standards and samples. A 0.5% (m/v) sodium tetrahydroborate solution was prepared daily by dissolution of

NaBH₄ powder (Riedel de Haën) in 0.05% (m/v) NaOH (ACS reagent).

Microwave digestion procedure

The accuracy of the dual nebulization method was evaluated by the analysis of two standard reference materials, NIST 1577b Bovine Liver (Gaithersburg MD, USA) and NIST 1566a Oyster tissue (Gaithersburg MD, USA). The certified standards were dissolved using a microwave oven procedure according to the CEM application note for these types of materials: The Teflon digestion vessels were cleaned with 10 mL of concentrated nitric acid and then thoroughly rinsed with twice-deionized water. After weighing 0.5000 g of the dry sample directly into the Teflon digestion vessel, concentrated nitric acid (5 mL for Bovine Liver and 3 mL for Oyster Tissue) and deionized water (2 mL) were added to each vessel. A blank was also prepared in the same way. The digestion program involved a one-stage heating cycle, as follows: 10 min at 350 psi and at 210 °C. The power was kept constant at 600 W. After cooling, the digested solutions were transferred into 25 and 10 mL (for Bovine Liver and Oyster Tissue, respectively) volumetric flasks and diluted to volume with twice-deionized water. The final concentration of nitric acid was 10% v/v for Bovine Liver and a concentration of 10% v/v hydrochloric acid was used for Oyster Tissue.

Results and discussion

Optimization of the dual micro-nebulization system

Usually, 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. Generally, a robust ICP is achieved by applying high rf power and by increasing the residence time of the aerosol in the plasma. The intensity ratio Mg II 280.270/Mg I 285.213 nm^{16,17} is commonly used to estimate plasma robustness, with higher ratios (> 8 in radially viewed instruments) indicating a more robust plasma. In order to optimize the instrumental conditions for the new modified cyclonic spray chamber, the plasma robustness was taken as the instrumental response. Results were compared with those obtained with conventional cyclonic spray chambers with an inner volume of 47 cm³. The Mg II/Mg I ratios were corrected for the spectral response of the Echelle spectrometer and detector system by assuming a constant background continuum over the wavelength region from 280 to 285 nm.¹⁷ The correction factor for our system was 0.486. Table 1 shows the optimum operating conditions found.

Analytical figures of merit

Nebulizer position has been proved^{18,19} to affect the magnitude of the signal when cyclonic chambers are used. A change in this variable modified the gap between the nebulizer tip and the walls of the spray chamber and, consequently, the droplet impact processes. In this work, three different nebulizer positions (25, 30 and 35 mm) were studied, covering a total length of 1 cm. These positions were taken from the nebulizer tip up

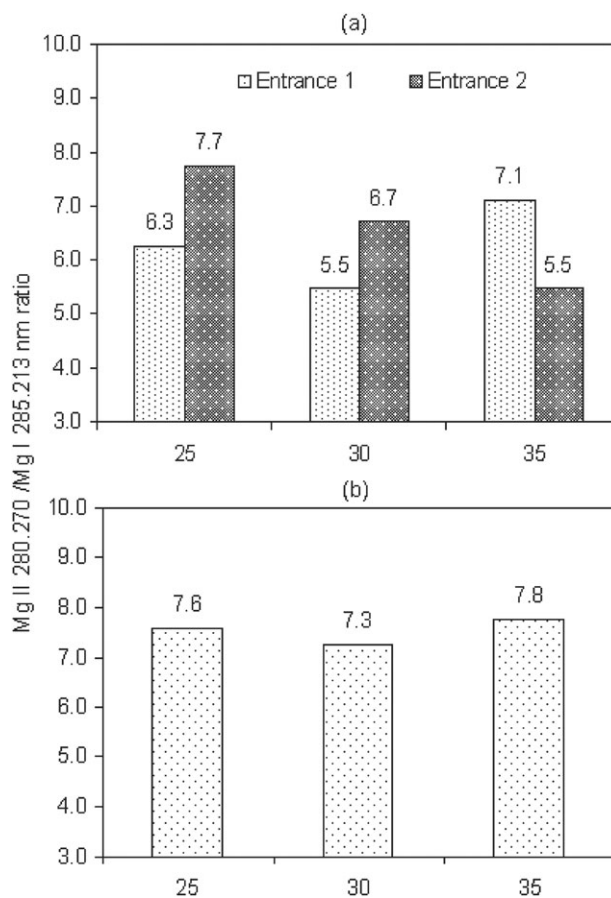


Fig. 2 Effect of the nebulizer position on the Mg II 280.270/Mg I 285.213 ratio: (a) dual system, (b) HEN-Cy system. RF power was 1500 W.

to the point where the nebulizer is introduced. The effect of the nebulizer position on the plasma robustness (Mg II/Mg I ratio) is shown in Fig. 2. The robustness reached from each of the two entrances when the dual system (two HENs coupled to a modified cyclonic spray chamber, CyM) was used is shown in Fig. 2(a) (refer to Fig. 1 for a reminder of the chamber's entrances). It can be seen that optimum robustness (7.1) is observed from the 1st entrance at a distance of 35 mm: however, for the 2nd entrance, the optimum (7.7) was achieved at 25 mm. These results are compared with those obtained when a commercial cyclonic spray chamber (Cy) is used (Fig. 2(b)). Hence, the optimum robustness is obtained at 35 mm. Therefore, it can be said that the robustness has a dependence on the nebulizer layout into the cyclonic spray chamber.

Signal to background ratio (SBR), detection limits (LOD), and short- and long-term stabilities were obtained in order to evaluate the performance of the dual system. For this, water was run through entrance 1 and the multi-element solution (5 mg L⁻¹) through entrance 2 (preliminary studies showed that better signals were obtained when this arrangement was used). The results are shown in Table 2. It can be seen that sensitivity is improved when the dual system is used, when compared with those obtained for the HEN-Cy system for most analytes studied. In order to explain the improvement achieved, the

Table 2 Sensitivity, detection limits, short and long-term stability for the dual and HEN–Cy systems

Element and wavelength/nm	SBR		Detection limits/ng mL ⁻¹		Precision (%RSD)		Long-term stability (% RSD)	
	Dual ^a	HEN–Cy ^b	Dual ^a	HEN–Cy ^b	Dual ^a	HEN–Cy ^b	Dual ^a	HEN–Cy ^b
Ba 455.403	4060	1080	1.1	2.6	3.7	0.6	2.8	0.5
Cd 226.502	4231	3633	1.1	1.1	3.6	1.1	2.6	0.8
Mg 280.270	1316	549	0.6	1.9	3.2	0.6	1.8	0.6
Mn 257.610	1757	1722	0.4	0.6	3.4	0.3	2.5	0.4
Sr 407.771	4293	1942	0.4	1.0	3.2	0.4	2.5	0.6
Zn 206.200	2492	1213	3.8	5.4	3.2	0.5	1.6	0.5
Zn 213.856	1014	572	2.8	3.9	3.3	1.2	2.3	0.4

^a Dual: Two high efficiency nebulizers (HEN) coupled to a modified cyclonic spray chamber. Sample uptake and nebulization gas flow rate were 60 $\mu\text{L min}^{-1}$ and 0.4 L min^{-1} , respectively, for each HEN. ^b HEN–Cy: High efficiency nebulizer coupled to a conventional cyclonic spray chambers. Sample uptake and nebulization gas flow rate were 60 $\mu\text{L min}^{-1}$ and 0.8 L min^{-1} , respectively.

mass analyte transport rate was determined by an indirect method²⁰ and the result was similar for both systems (3.8 $\mu\text{g min}^{-1}$). It was observed that the background obtained for the dual system was much lower than those obtained for the HEN–Cy system. Consequently, the SBR becomes higher when using the dual system. This may be the cause of the sensitivity improvement. The limits of detection were calculated according to the $3s_B$ criterion, where s_B is the standard deviation of twenty replicate readings of the background. The limits of detection obtained from the dual system were similar to or slightly better than those obtained with the HEN–Cy. The short term stability was expressed as the relative standard deviation (RSD) of fluctuations in the emission signal around a mean value from a series of 20 replicates. The HEN–Cy system's RSD values were more precise. The reduction in precision when using the dual system can be attributed to a turbulent effect within the spray chamber which is produced when the aerosols are mixed.

Measurement of the long term reproducibility quantifies the drift of the spectrometer. This property is important because the occurrence of drift necessitates periodic calibration, which is usually time-consuming. Long-term stability (5 $\mu\text{g mL}^{-1}$ solution over a period of 150 min) is shown in Table 2. Similar to the precision, the HEN–Cy system shows more stability than the dual system.

Dual micronebulizer system for tandem calibration methodology (TCM)

A variety of calibration methods are used for the analysis of liquid samples. Those samples which possess a matrix that interferes with the analyte are generally limited to the method of standard additions, matrix-matching, internal standards or even indirect calibration by the use of a certified reference material. A calibration method based on the simultaneous introduction of samples and standard into the plasma by two independent nebulizers is described. In order to evaluate the independence of sample and standards from the flow rates, a parameter known as the relative transport efficiency (f_r) was calculated, according to Hamier *et al.*⁴ This factor has been calculated from individual values for each element and the average value was taken to calculate the true sample concentration.

The system consists of a dual micronebulizer in which the sample solution is aspirated through one nebulizer while

standards are aspirated through the other. The aerosols from both nebulizers merge into a modified cyclonic chamber, where they are mixed together and pass to the ICP torch. This calibration mode can be considered a variation on the standard addition method, the main difference being that in this system, the addition of the standard is not performed in the sample itself but from a different nebulizer system.

The advantages in the development of this alternative sample introduction device grafted onto the ICP in place of a classical nebulizer are the reduced matrix effects, reduced sample preparation, and increase in the sensitivity of the analytes being analyzed.

To investigate the analytical applicability of the new dual system, the standard reference material NIST 1577b, Bovine Liver, was analyzed using different calibration techniques, *i.e.*, the tandem calibration technique,^{4,5} standard addition and external calibration (matrix-matching). For the tandem calibration technique, the SRM sample solution and the aqueous standard solutions of different concentrations were pumped through entrances 1 and 2, respectively, of the dual micronebulizer (Fig. 1).

Analytical results for the reference material, obtained from the three different calibration modes, together with certified values are presented in Table 3. For all elements determined, precision expressed as the relative standard deviations (RSD) was found to be better for TCM (3%), followed by the standard addition method (4%) and external calibration (matrix-matching) (7%). The results show that the accuracies achieved when using the different calibration techniques are comparable. The significance *t*-test²¹ was applied and no significant difference was found at the 95% confidence level between the results reported.

From an operational perspective, it would be best if a method could be developed which uses simple aqueous standards rather than a complex, matrix matched set of standards that may vary from one sample type to another.

Dual micronebulizer system for hydride generation

The new dual system was used to generate the volatile hydrides of As, Sb and Se. Operation of the dual system consisted of pumping NaBH₄ solution with a peristaltic pump to generate an aerosol of NaBH₄ through entrance 1 (Fig. 1) and the acidified sample solution was delivered with the same pump through entrance 2. Sample and NaBH₄ aerosols were

Table 3 Analysis of SRM Bovine liver (NIST 1577b) by different calibration modes

Element and wavelength/nm	Concentration ^a /μg g ⁻¹			Certified values ^c
	TCM ^b	Standard addition	External calibration (matrix matching)	
Ca 396	115.1 ± 1.7	117.2 ± 4.4	117.9 ± 1.4	116.0 ± 4.0
Cu 324	161.8 ± 2.5	161.8 ± 0.2	149.3 ± 10.4	160.0 ± 8.0
Fe 259	185.6 ± 0.9	185.2 ± 0.9	179.4 ± 6.9	184.0 ± 15.0
Mg 280	602.2 ± 6.4	606.2 ± 11.8	610.9 ± 28.3	601.0 ± 28.0
Mn 257	10.2 ± 0.2	10.2 ± 0.2	10.0 ± 0.7	10.5 ± 1.7
Zn 206	126.5 ± 3.9	126.3 ± 0.6	127.5 ± 5.3	127.0 ± 16.0

^a Mean ± standard deviation for three digest solutions. ^b TCM: Tandem calibration methodology. ^c Uncertainly expressed as 95% tolerance limits.

generated and a reaction occurred into the modified cyclonic spray chamber to concurrently produce the volatile hydrides. A multi-element standard solution of As, Sb and Se (2 μg mL⁻¹ each) was used for this study.

In order to test the applicability of the dual system for hydride generation to ICP-OES, an optimization of the As, Sb, and Se emission signal intensities as a function of the HCl concentration, nebulization gas flow and sample uptake rate was carried out.

Instrumental parameters were optimized using the robustness criteria with the unit working as a liquid sample introduction system, as described above. These conditions were fixed in order to check the performance of the system as a hydride generator. Then, the optimization of conditions related to the chemical reaction of the production of the hydrides (*i.e.* NaBH₄ and HCl concentrations) was carried out. The criterion used in this process was to get maximum sensitivity since a good robustness does not necessarily indicate maximum signal intensity during the hydride generation of the analytes under study.

Increased sensitivity is observed for all the analytes as the acid and NaBH₄ concentrations increased to 10% (v/v) and 0.5% (m/v), respectively.

It has been reported²² that the magnitude of the rate constant of the reaction that describes the complete process of hydride release, *i.e.*, analyte reduction to the hydride and liberation of hydride to the gaseous phase from the reaction mixture, is affected by the purge gas flow rate and by the design of the hydride generator employed. The nebulizer gas flow is relevant to this new dual system, because it determines the contact time of the reactants for efficient production of element hydrides. A flow rate of 0.6 L min⁻¹ and a sample uptake rate of 240 μL min⁻¹ were chosen as optimum. The robustness was further monitored once that the chemical and instrumental conditions were optimized for the hydride generation mode. An acceptable robustness of *ca.* 8 was obtained.

Under these optimum conditions, sensitivity, detection limit, and short and long-term stabilities were determined for the three volatile elements As, Sb and Se using the dual system. Results are shown in Table 4. The precision achieved by the use of the dual design for all hydride forming elements represents a significant improvement in comparison with those reported by Wolnik *et al.*,²³ which is the only article that used a dual system with the same objective as the one used in this work. Detection limits are comparable for As, but Sb and Se detection limits are one order of magnitude lower than those

Table 4 Sensitivity, detection limit and precision for the direct hydride generation with the dual system^a. The rf power was 1500 W and solution uptake was 240 μL min⁻¹

Element and wavelength/nm	SBR	Detection limit ^b /ng mL ⁻¹	Precision (%RSD)
As 188.979	71	5.3	1.8
Sb 206.833	249	2.9	0.8
Se 196.026	76	4.9	1.7

^a Two high efficiency nebulizers (HEN) coupled to a modified cyclonic spray chamber. ^b Based on 3 s of the blank solution.

reached in this work. The LODs achieved here are poorer than those reported in other studies^{22,24,25,30–35} using hydride systems designs different to the one used here. In this respect, it should be considered that this system uses a sample uptake rate of 240 μL min⁻¹ (0.24 mL min⁻¹), which is significantly lower than the ones used in their work. This device is useful for handling samples with limited volume. Therefore, there is a compromise between low LODs and sample volume availability.

Measurements of the long term reproducibility quantify the drift of the spectrometer. The average RSD values are 3.7, 2.8 and 2.4 for As, Sb and Se, respectively.

Interferences from transition metals using the dual system in hydride generation

It is well known that interferences from transition metals are the most severe and therefore must extensively studied. The performance of the system was evaluated by studying the effect of transition metal ions Co²⁺, Fe³⁺, Ni²⁺ and Cu²⁺ (200 μg mL⁻¹) on the intensities of As, Sb and Se (2 μg mL⁻¹) under the operating optimum conditions already shown. A variation in the analytical signal by more than ±5% in the presence of foreign ions was regarded as an interference. Results are shown in Fig. 3. It was observed that the interference from all transition ions became severe for Se, to a lesser extent As, followed by Sb. The same interferences have been reported by others authors.^{22,24–30}

Several pieces of evidence concerning the mechanism of action of masking agents demonstrated that a route through which some additives can control the interference effects is the competitive adsorption of the masking agent and hydride on the surface of finely dispersed particles formed by the interfering species.³⁶

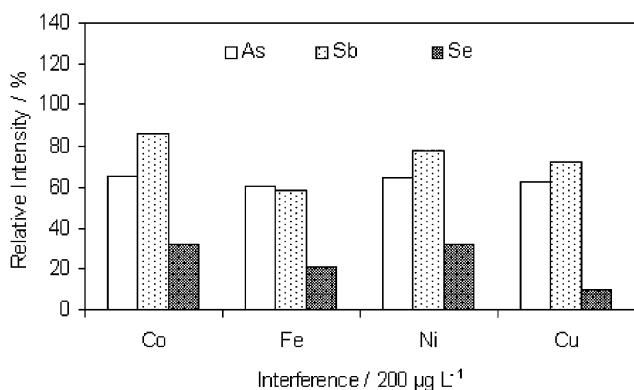


Fig. 3 Effect of some transition metals on the emission intensity signal of As, Sb and Se. The concentration of borohydride and HCl were 0.5% and 10%, respectively. The borohydride solution and sample uptake rates were 240 $\mu\text{L min}^{-1}$.

The predominant reaction of the interference from transition metals is probably the reduction of the interfering metal ion by tetrahydroborate, which results in the formation of metal particles or metal borides.^{37,38} The finely dispersed precipitate may adsorb and decompose the hydrides. The interference can be minimized in different ways. A decrease in the NaBH_4 concentration and an increase in the concentration of HCl have been used.

Chelating agents have also been used to mask the interference from transition metals. Among them, thiourea is one of the chelating agents most used to mask this type of interference. The effect is to prevent the reduction of the interfering metals. It, unlike most other complexing agents, forms highly soluble complexes in strongly acidic solutions³⁹ (normally desirable in this case). It should therefore be particularly well suited for the masking of copper²⁹ and for other transition metals, as shown in the results given in the present research work.

The effect of a masking agent such as thiourea on the relative emission signals of As, Sb and Se is shown in Fig. 4. Results shown in Fig. 4(a) represent the net effect of the thiourea on the analyte emission intensities without the interference ions. This study was carried out in order to check if thiourea had any influence on the analyte emission signals.

It can be seen from these results that Se was the only analyte affected by the presence of the masking agent. The depletion of the Se signal in the presence of thiourea was previously reported by Lund *et al.*²⁹ and recently by Rojas *et al.*³¹ Fig. 4(b) shows the effect of thiourea 0.5% (m/v) on the analytes' emission signals ($2 \mu\text{g mL}^{-1}$) in presence of the interferences studied. The effectiveness of thiourea as a masking agent is observed and is in agreement with the literature.^{28,29,31}

Analysis of the standard reference material

To check the analytical accuracy of the dual system for the hydride generation to ICP-OES, the standard reference material NIST 1566a "Oyster Tissue" was analyzed for the elements As and Se. Antimony has not been included since its value is not certified on NIST 1566a. The results are shown in

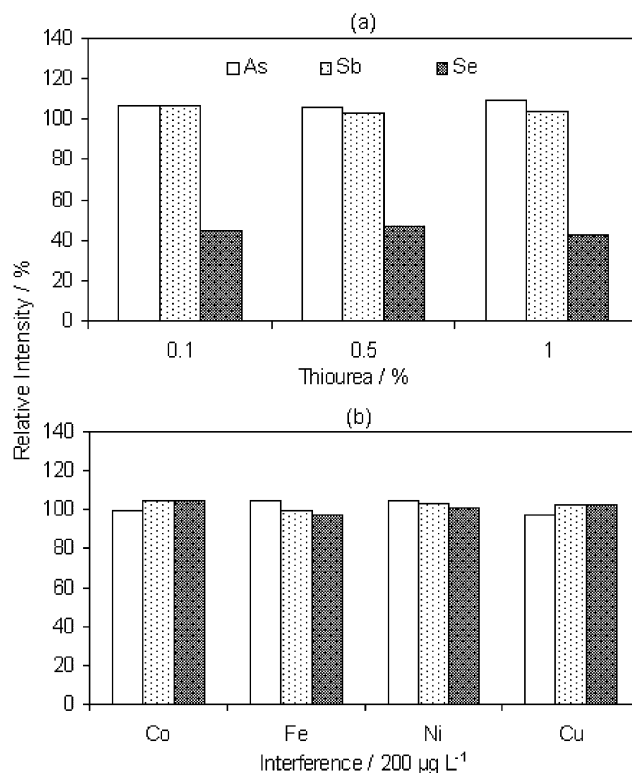


Fig. 4 Effect of thiourea on the emission intensity signals of As, Sb and Se, (a) without and (b) with interference. The concentrations of borohydride and HCl were 0.5% and 10%, respectively. The borohydride solution and sample uptake rates were 240 $\mu\text{L min}^{-1}$.

Table 5 Analysis of Oyster Tissue (NIST 1566a)

Element and wavelength/nm	Concentration/ $\mu\text{g g}^{-1}$	
	Found ^a	Certified ^b
As 188.979	14.7 \pm 0.6	14.0 \pm 1.2
Se 196.026	2.5 \pm 0.3	2.21 \pm 0.24

^a Mean \pm standard deviation for three digest solutions. ^b Uncertainty expressed as 95% tolerance limits.

Table 5. The certified values for As and Se given in the NIST standard are in good agreement with the concentrations found (95% confidence level).

Conclusions

A simple and low-cost cyclonic spray chamber has been designed to operate with two micro-nebulizers. The full versatility of this system has been exploited by checking its capability in carrying out standard additions on line (TCM) and also its potential benefits in ICP-OES for hydride generation. Signal to noise ratios and detection limits are improved compared with conventional cyclonic spray chambers. However, precision was slightly poorer than with the conventional system. The long-term stability obtained indicates that the system is stable for at least two and a half hours of continuous operation.

Tandem calibration methodology was usable with the dual micro-nebulization system developed here. The accuracy of this operation mode was proved by analyzing NIST 1577b, Bovine Liver. In addition, the dual system allowed efficient hydride generation for the elements at lower sample and reagent uptake rates with a precision lower than 2%. Thiourea was effective in correcting the interferences caused by the transition metals.

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