Design and evaluation of a new fully microwave-assisted liquid sample introduction device for inductively coupled plasma atomic emission spectrometry

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A new fully microwave-assisted liquid sample introduction system (MASIS) is presented and evaluated in Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The device employs a single TM_{010} microwave cavity for the simultaneous aerosol generation and desolvation. The different experimental requirements of both physical processes demand a careful system design and a judicious selection of the experimental conditions. The behavior of the MASIS depends on the: (*i*) microwave power; (*ii*) nebulizer nozzle inner diameter; (*iii*) sample uptake rate; and, (*iv*) matrix nature (*i.e.* acids, salts) and concentration. Thus, optimum operating conditions are obtained when increasing the microwave power, the matrix concentration and the sample uptake rate as well as when decreasing the nebulizer nozzle inner diameter. The analytical figures of merit afforded by the MASIS in ICP-AES are compared to those obtained with: (1) a pneumatic concentric nebulizer coupled to a cyclonic spray chamber (CS); (2) a microwave thermal nebulizer (MWTN) coupled to a cyclonic spray chamber; and (3) a pneumatic nebulizer coupled to a microwave desolvation system (MWDS). MASIS provides limits of detection up to 50 times lower than those obtained with the CS and up to 8 times lower than those with the MWTN and MWDS. No significant difference in the signal precision between the different devices tested is observed (*i.e.* 2–5%). Regarding the wash-out times, both MASIS and MWDS show the highest values of this parameter (*i.e.* 70 s) due to their higher inner volume. Wash-out time values for both MWTN and CS are lower than 30 s.

Introduction

Analytical figures of merit in Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) strongly depend on the sample introduction system employed.[1] Liquid samples are usually introduced in ICP-based techniques by means of a pneumatic concentric nebulizer attached to a spray chamber.[1] The main drawbacks of these conventional systems are typically related to its low sensitivity, consequence of the low sample transport efficiency afforded, and the tendency to get clogged when using high salt-content solutions.

To improve the analytical behavior of the conventional liquid sample introduction systems, more efficient nebulizers, sometimes based on different physical principles, have been developed.[1,2] Among them, one should mention the ultrasonic,[3,4] hydraulic[5] or thermal nebulizers.[6–8] In thermal nebulization, the sample is forced to pass through an electrically heated capillary.[6–8] Microwave radiation (MW) has also been employed as a promising alternative energy source in thermal nebulization.[9,10] Using these devices, the aerosol is generated as a consequence of the interaction between the sample vaporized inside the capillary and the remaining liquid. The aerosols generated by thermal nebulizers are finer than those produced by the conventional pneumatic ones, thus giving rise to higher plasma analyte transport rates (W_{tot}).[6] Unfortunately, with W_{tot}, the plasma solvent transport rate (S_{tot}) also increases. As a consequence, the plasma energy available for analyte atomization and excitation may decrease, thus reducing the expected sensitivity enhancement.[11,12] In order to avoid the negative influence of the amount of solvent reaching the plasma, the use of these so-called "high efficient" nebulizers usually demand a desolvation system.[13–15] In those systems, the aerosol generated by the nebulizer (primary aerosol) is firstly heated using either conductive (*e.g.*, using a heating tape)[16] or radiative (*e.g.*, infrared or microwave radiation) devices.[17–20] This way, the solvent is partially evaporated thus reducing the aerosol droplet size. After that, the vapor generated is removed from the aerosol stream by means of a condensation unit, membranes, *etc*.[14,21–23] As a result of this two step process, W_{tot} is increased whereas S_{tot} is simultaneously reduced. The use of these devices, irrespective of the specific nebulizer and/or the desolvation system, afford limits of detection (LOD) that are, on average, one order of magnitude lower than those obtained with a conventional sample introduction system.[17–24]

During the last five years a microwave-based thermal nebulizer (MWTN) and a microwave-based desolvation system (MWDS)[20,24] have been separately developed and extensively evaluated by our research group in ICP-AES and ICP-MS. The MWTN consists of a PTFE capillary placed inside of a TM_{010} MW cavity. As a consequence of the interaction between the liquid stream and the microwave radiation, the aerosol is generated at the exit of the nebulizer nozzle. When operating

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with the MWDS, the aerosol generated by a pneumatic concentric nebulizer is introduced into a spray chamber placed inside the same MW cavity employed with the MWTN. Once the solvent is evaporated, the vapor is removed from the aerosol stream by means of two Liebig condensers. The appropriate design of the MW system (*i.e.*, magnetron, transmission system and cavity) allows a precise control of the sample-radiation interaction process. When comparing to a conventional sample introduction system, both the MWTN and the MWDS significantly improve the analytical figures of merit in ICP-based techniques. Thus, the LOD improvement factor achieved in ICP-AES is, on average, 7 and 10 times for the MWTN and the MWDS, respectively.[20] When operating with the MWDS in ICP-MS, the LOD improvement was only of 3–4 times due to the lack of an efficient solvent removal step (*i.e.* high background signal). Finally, the use of the MWDS minimizes interferences due to diluted organic solutions making it possible to calibrate using pure aqueous standards.[24]

From the previous experience with the MWTN and the MWDS, it seems reasonable to design a unique sample introduction device in which only one microwave cavity would be used to first generate and next evaporate a liquid aerosol before introducing it into the ICP. Ideally, this new device would combine the advantages of both MWTN and MWDS. The aim of this work is, therefore, to design and characterize a new fully microwave-assisted sample introduction system (MASIS) for ICP-based techniques coupling a thermal nebulizer and an aerosol heating unit using the same microwave cavity. The developed prototype has been evaluated in ICP-AES and its behavior compared with the MWTN, the MWDS and a conventional sample introduction system. As far as we know this is the first time that a single energy source has been used to generate aerosols and then to evaporate the solvent contained in the droplets.

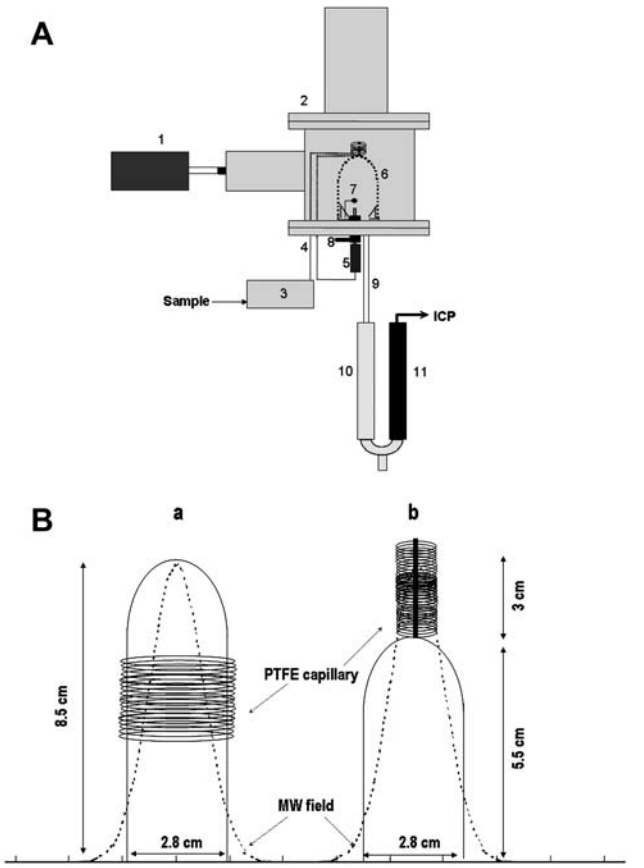

Fig. 1 (**A**) Experimental setup of the new microwave assisted sample introduction system (MASIS): (1) Magnetron; (2) TM_{010} cavity; (3) HPLC pump; (4) PTFE capillary; (5) nebulizer nozzle; (6) spray chamber; (7) aerosol impact bead; (8) carrier gas flow inlet; (9) aerosol and spray chamber drains exit; (10) Liebig condenser; (11) Peltier condenser. (**B**) Scheme of the different spray chamber-PTFE capillary configurations tested.

Experimental

MASIS design

Fig. 1 shows a scheme of the MASIS prototype developed. It consists of (1) a magnetron (model GMP 03 K/SM, Sairem S.A., Neyron, France) to produce microwave radiation with a frequency of 2.45 GHz which is transmitted into a (2) TM_{010} cavity. The liquid sample is introduced into the microwave cavity by means of (3) an HPLC pump (Chrom Tech, Inc., Apple Valley, Minnesota, USA) using a (4) PTFE capillary. Once inside the MW cavity, the liquid sample is heated and, hence, the aerosol is generated. The (5) nebulizer PEEK nozzle is coupled to a (6) single pass spray chamber provided with (7) an impact bead and placed inside the same microwave cavity. An aerosol carrier gas flow (8) is introduced into the spray chamber by means of a T-joint placed at the nebulizer entrance and is controlled by means of a rotameter (Cole-Palmer Ins. Co., Chicago, Illinois, USA). The aerosol emerging from the spray chamber (9) sequentially passes through a (10) Liebig (33 cm × 1.3 cm id) and a (11) home-made Peltier (30 cm length × 0.8 cm id) condensers where the solvent evaporated inside the spray chamber is partially removed from the aerosol stream. Liebig and Peltier condensers' temperatures are kept at 10 °C and −15 °C, respectively. The MASIS is coupled to the ICP by means of a silicone tube (40 cm length × 1.0 cm id).

The main component of the MASIS is the microwave cavity, the same TM_{010} previously designed and reported for both the MWDS and the MWTN.[10,20] The only difference lies in two additional holes at the base of the cavity to introduce the PTFE capillary. The dimensions of the holes were calculated to avoid microwave leakages. It is important to remark that in this type of cavities, the microwave energy distribution pattern fits a Gaussian curve, its maximum being located along the center of the cavity. Therefore, for an efficient aerosol generation and heating, both the PTFE capillary and the spray chamber must be placed in this position. To accomplish this requirement, several configurations were evaluated. Firstly, the nebulizer capillary was coiled around the spray chamber (Fig.1.B.a). Nonetheless, when using this configuration, the liquid vein was not properly vaporized since most of the sample was located outside the MW field, thus generating a very unstable aerosol. It is important to note that, using the current microwave cavity, it is not advisable to modify the diameter of the spray chamber (*i.e.*, 2.8 cm). This parameter was calculated to ensure that the spray chamber walls were not irradiated by the microwave field, thus reducing the

turbulences generated by the evaporation of the liquid aerosol impacting on it. The other possibility was to reduce the spray chamber height in order to locate the sample capillary on its top (Fig. 1.B.b). To this end, spray chambers of heights ranging from 8.5 to 4.5 cm in steps of 1 cm were evaluated. Compromise conditions are required to get a reproducible sample heating efficiency and minimize the aerosol impact losses against the inner walls of the spray chamber. The liquid sample heating efficiency was monitored through the pump pressure. When the heating efficiency increases, the volume of sample evaporated inside the capillary increases and, hence, a higher pump pressure is required to keep the flow constant. It was experimentally observed that MW heating efficiency improved on decreasing the spray chamber height. Nonetheless, this improvement was at the expense of an enhancement of the aerosol losses against the upper walls of the spray chamber. Taking into account these considerations, a spray chamber height of 5.5 cm (*i.e.* 36 cm^3 inner volume) was selected as a compromise. Previous studies with the MWTN have pointed out that aerosol generation is also improved by modifying the PTFE capillary dimensions (*i.e.* length and internal diameter).[8] Nonetheless, the capillary length and internal diameter were not modified throughout this work. Though the nebulization process is improved by increasing the PTFE capillary length, no space was available above the spray chamber to place capillaries longer than 1 m. As regards the capillary internal diameter, 0.5 mm was selected for a better control of the MW power reflected inside the cavity.

Previous studies have shown[10] that MWTN requires of sample uptakes rates (Q_l) above 0.6–1.0 $mL \cdot min^{-1}$ to generate a reproducible aerosol. However, the best analytical behavior of the MWDS has been observed when operating at lower Q_l values.[18,20] To simultaneously fulfil the requirements of both the MWTN and MWDS, an impact bead made up of quartz was placed inside the spray chamber.[25] The use of an impact surface simultaneously reduces the aerosol mass, size and velocity. As a consequence, solvent vaporization is improved and turbulences reduced due to the lower amount of liquid vaporized.[18,19] This vapour reduction also has a beneficial effect on the analyte transport rate since analyte losses due to nucleation are significantly reduced in the vapour removal step.

Table 1 ICP-AES operating conditions

Perkin-Elmer Optima 3000 ICP-AES	
Plasma forward power/W	1450
Argon flow rate/L min^{-1}	
Plasma	16
Auxiliary	0.7
Nebulizer	0.6^a–0.5^b
Sample uptake rate/μL min^{-1}	Variable
Observation height/mm ALC	12^a–10^b
Integration time/ms	100
Readings/replicates	10/3

[a] MWDS and CS. [b] MWTN and MASIS.

Table 2 Wavelength and line type for the elements tested

Element	Wavelenght/nm (line type)
Li	670.781 (I)
Sr	460.673 (I)
Ca	422.673 (I)
Al	396.152 (I)
Cr	357.869 (I)
Ag	328.068 (I)
Cu	324.754 (I)
Ar	420.068 (I)
Al	309.271 (I)
Mg	285.213 (I)
Ni	232.003 (I)
Cd	361.061 (I)
Ba	455.403 (II)
Sr	421.552 (II)
Sr	407.771 (II)
Ba	233.527 (II)
Mg	280.270 (II)
Mn	257.610 (II)
Cr	267.710 (II)
Fe	238.204 (II)
Ca	317.933 (II)
Co	238.892 (II)
Co	228.616 (II)
Ni	231.064 (II)
Cd	214.438 (II)
Pb	220.353 (II)
Zn	202.548 (II)
Cu	224.700 (II)

Sample introduction systems

For the sake of comparison, the MWTN and the MWDS were used to evaluate the independent contribution of the microwave nebulization and desolvation on the analytical figures of merit obtained with MASIS. Details of both devices are found elsewhere.[10,20,24] MWTN was coupled to a home-made thermostated cyclonic spray chamber (inner volume 33 cm^3). The temperature was kept constant at −5 °C using a thermostated bath (Haake F3-K, Haake Mess-Technik GmBH U Co, Karlsruhe, Germany). As previously described for MASIS, an aerosol carrier gas flow was introduced at the spray chamber entrance and it was controlled by means of the same rotameter. For comparison purposes, the MWDS used the same spray chamber, condensation devices and conditions employed with the MASIS. Finally, a conventional sample introduction system (CS) consisting of a pneumatic concentric nebulizer (Model TR-30-K2, Meinhard, Santa Ana, California, USA) coupled to the thermostated cyclonic spray chamber just described was used. In the CS, the sample was delivered to the nebulizer by means of a peristaltic pump (Model Minipulse 3, Gilson, Villiers-Le-Bel, France) whereas the nebulizer gas flow rate was controlled as with the MWTN.

ICP instrumentation

ICP-AES measurements were made using a PerkinElmer Optima 3000 ICP-AES system (PerkinElmer, Shelton, CT, USA). Table 1 shows the operating conditions used with this instrument and the different sample introduction systems evaluated. Table 2 shows the analytical lines of the different elements evaluated in the present work

Reagents

All chemicals employed were of analytical grade. Test solutions containing 10 μg mL^{-1} of each analyte were prepared by diluting

appropriate aliquots of 1000 μg mL^{-1} multielemental reference solutions (Merck ICP IV, Darmstadt, Germany) in diluted $HN0_3$, HCl and NaCl solutions.

Results

MASIS characterization

The development of a liquid sample introduction device combining a microwave-based nebulizer and an aerosol heating unit in the same microwave cavity is a challenge due to: (i) the above mentioned design considerations; and (ii) the different optimum conditions required for each individual component. Thus, in order to get the better analytical behavior in ICP-AES, a judicious selection of the experimental conditions is required.

Influence of the MW power. Previous results reported in the literature have shown that for both the MWTN and MWDS systems, the best analytical response is obtained when operating at high MW powers.[10,20] Due to this, the MW power used with the MASIS was fixed at the maximum available value, *i.e.*, 290 W. In fact, it was observed that when operating at lower microwave powers, no reproducible aerosols were generated. It is interesting to note that the MW radiation power reflected in the cavity was of 40 W on average. This slightly high value is similar to that obtained with the MWTN and it can be justified taking into account that the present TM_{010} cavity was initially designed for aerosol heating (*i.e.* liquid droplets in a gas stream), and not for the current purposes (*i.e.*, aerosol generation and desolvation).[10]

Influence of the matrix nature and concentration. Three matrices ($HN0_3$, HCl and NaCl) at two different concentrations (0.34 and 0.84 M) were tested. Fig. 2 shows the influence of the matrix nature and concentration on the Mn net emission intensity obtained with the MASIS. Similar results were obtained for all the analytes studied (see Table 2). From the data shown in this figure it can be derived that, irrespective of the matrix considered, the emission signal increases when increasing the matrix concentration. Among the different matrices tested, HNO_3 and HCl provide higher signals (*i.e.* up to 1.4 times) than NaCl regardless of the matrix concentration employed. At this point it is important to remark that no clogging problems were observed when running with concentrated NaCl solutions. These results are similar to those previously reported with the MWTN.[10]

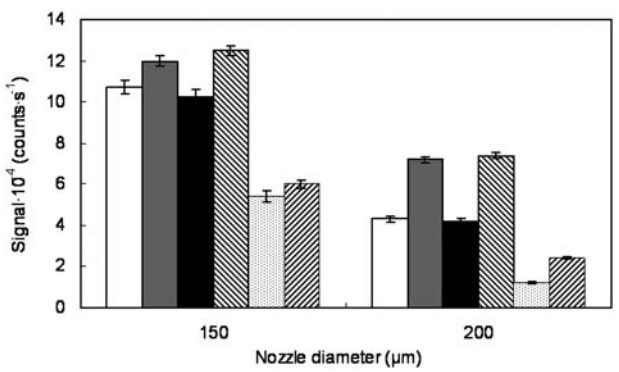

Fig. 2 Influence of the nozzle inner diameter on the Mn emission intensity obtained for MASIS when running with different matrices: (□) 0.34 M $HN0_3$; (▩) 0.84 M $HN0_3$; (■) 0.34 M HCl; (▧) 0.84 M HCl; (▤) 0.34 M NaCl; (▨) 0.84 M NaCl. Q_l: 1.8 mL min^{-1}.

When operating with both the MWTN and the MWDS, it has been observed that the sample properties play a very important role since they strongly affect the heating process.[9,18,24] Among them, the solution dielectric loss (*i.e.*, tanδ) is a key parameter since it determines the MW sample heating efficiency.[26] For inorganic matrices, tanδ mainly depends on the ion concentration and type (*i.e.* on the solution conductivity). Thus, the higher the liquid sample conductivity, the higher the heating process efficiency. This means a more efficient aerosol generation and desolvation process that results in an increase in the analyte transport rate to the plasma, W_{tot}. As a consequence, the emission signal also increases when the matrix concentration (*i.e.* higher ionic concentration) is increased and when operating with acid solutions (*i.e.*, $(H^+)_{ionic\ mobility} > (Na^+)_{ionic\ mobility}$). In fact, the HPLC pump pressure increases when the matrix concentration is increased. For a given matrix concentration, the pump pressure is higher for the acid solutions than for the NaCl one.

Unfortunately, it was not possible to measure W_{tot} due to the difficulty to operate with the MASIS at the high concentrated solutions required to perform these experiments (usually above 300 μg·mL^{-1}). To understand this fact it must be taken into account that a given fraction of the aerosol generated by the nebulizer impacts against the inner walls of the spray chamber and the impact bead. Before draining, the resulting liquid is heated and can be evaporated by the action of the microwave field. The analytes and matrix components contained in these droplets are deposited on the base of the spray chamber thus absorbing MW radiation. As a consequence, both the PTFE spray chamber adapter and the PEEK nebulizer nozzle melt after some minutes working. A carefully re-design of both nebulizer nozzle and spray chamber configuration could mitigate this issue.

Finally, it is important to indicate that the lowest matrix concentration used in the above study (*i.e.*, 0.34 M) is, irrespective of the matrix considered, the minimum value required to get a reproducible aerosol generation. This value is about 8 times higher than that observed with the MWTN.[10] It can be explained by considering that, for a given MW power, the energy available for the nebulization process is lower with the MASIS than with the MWTN due to the higher amount of sample present inside the MW cavity. To counterbalance this lower amount of energy, higher matrix concentrations are required.

Influence of the nebulizer inner nozzle diameter. Fig. 2 also shows the influence of the inner nozzle diameter (d_n) on the Mn net emission signal for different matrix solutions. As it can be observed in this figure, for all the matrices tested, the signal raises up when d_n is reduced. For a given set of experimental conditions, a reduction in d_n causes the system pressure to increase,[6,8] thus increasing the amount of energy available for the aerosol generation process and giving rise to finer aerosols. As a result, W_{tot} would increase as well as the emission signal.[9,10] Finally, the data in Fig. 2 show that the influence of d_n on the emission signal is more significant for diluted matrix solutions than for concentrated ones. Thus, for 0.34 M HNO_3, when reducing d_n from 200 to 150 μm, the Mn signal was enhanced by 147%, whereas for 0.84 M HNO_3, this signal improvement was just of 66%. This fact

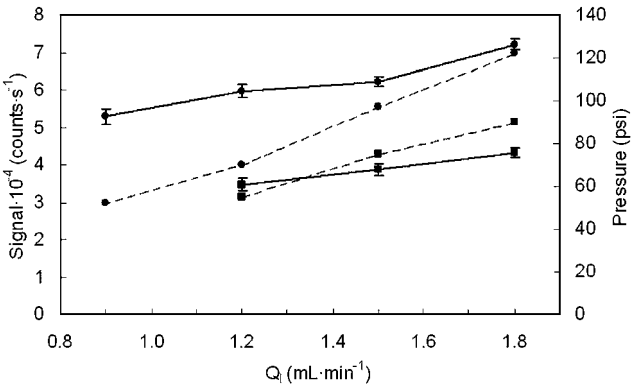

Fig. 3 Influence of the sample uptake rate on the Mn emission signal (straight lines) and HPLC pump pressure (dotted lines) obtained for different $HN0_3$ solutions. (●) 0.84 M; (■) 0.34 M. d_n 200 μm.

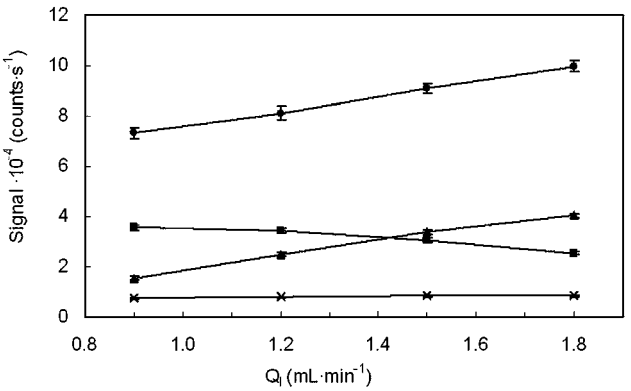

Fig. 4 Influence of the sample uptake rate on the Mn emission intensity obtained with the different sample introduction systems tested: (●) MASIS; (▲) MWTN; (■) MWDS; (×) CS. 0.34 M $HN0_3$. MWTN and MASIS: d_n 150 μm.

can be explained by taking into account that the concentrated solutions are more efficiently heated and, as a consequence, the nebulization process is less dependent on the nebulizer dimensions.

Influence of the sample uptake rate. Fig. 3 shows the influence of Q_l on the Mn emission signal (continuous lines) and on the HPLC pump pressure (dotted lines). As regards the emission signal, it increases when Q_l is increased. Thus, for 0.84 M $HN0_3$, the Mn signal obtained at 1.8 mL·min^{-1} is 36% higher than that at 0.9 mL·min^{-1}. Similar behavior was obtained for HCl and NaCl solutions and it can be explained taking into account that when Q_l is increased, the amount of analyte reaching the plasma also increases, due to (i) the increased amount of analyte nebulized; and, (ii) the increased solution volume evaporated inside the capillary which increases the system pressure (dotted lines in Fig. 3) and gives rise to finer aerosols.[8–10]

Finally, it is also worth mentioning that when operating with the MASIS, the minimum Q_l achievable to obtain a reproducible aerosol simultaneously depends on the matrix properties and on d_n. Thus, the nebulization of 0.34 M $HN0_3$ at 0.9 mL·min^{-1} using a 200 μm inner nozzle diameter is very unstable. The opposite situation is obtained when working with 0.84 M $HN0_3$ or when using a 150 μm nebulizer nozzle. Under these conditions, the matrix is efficiently heated and the interaction between liquid and solvent vapor streams is improved.

Evaluation of the MASIS in ICP-AES

Emission signal. Fig. 4 shows the influence of Q_l on the Mn net intensity obtained using all the sample introduction systems tested (*i.e.*, MASIS, MWDS, MWTN and CS). The results in Fig. 4 point out that the relative behavior among the different sample introduction systems depends on Q_l. Thus, as expected, for MASIS, MWTN and CS, the highest emission signals are obtained at the highest Q_l evaluated.[9,10] As regards MWDS, the signal decreases when Q_l increases.[18,19] Among the different sample introduction systems tested, the highest emission signals are provided by MASIS followed by MWTN/MWDS and CS. The relative behavior of MWTN and MWDS depends on Q_l. Thus, up to a Q_l of 1.4 mL min^{-1}, the MWDS provides higher signals than the MWTN. However, the opposite behavior was observed for higher Q_l values.

The higher emission signal obtained with all the microwave-assisted sample introduction systems in comparison with the CS can be explained taking into account the highest amount of analyte loaded into the plasma with the former devices, since: (1) microwave based nebulizers generate the finest aerosols; and, (ii) the high efficient aerosol microwave heating.[20] MASIS should combine the benefits of both microwave-based nebulizer and desolvation system. Nonetheless, the overall contribution of both processes on the signal seems to depend on the Q_l employed. Thus, at low Q_l, the coarser aerosols generated by the nebulizer[10] are efficiently desolvated and transported into the plasma, since the low amount of solution inside the device reduces the extent of the aerosol losses phenomena.[18,20] On the opposite case, when operating at high Q_l, the nebulization process is improved but the desolvation efficiency decreases.

Signal precision. Table 3 shows the relative standard deviation values (RSD) of the net emission intensity values obtained with the MASIS for all the experimental conditions studied. These are the minimum and maximum RSD values of the emission signals obtained for all the lines measured (Table 2). RSD values obtained with MASIS depend on the experimental conditions used. Thus, low RSD values, under 5%, are obtained using

Table 3 Relative standard deviations of the emission signals obtained for all the experimental conditions tested with MASIS

Matrix	Concentration (M)	Q_l (mL·min^{-1})	d_n (μm)	RSD (%)
HNO_3	0.84	1.8	200	1–5
HNO_3	0.84	0.9	200	4–10
HNO_3	0.84	1.8	150	2–5
HNO_3	0.34	1.8	200	1–8
HNO_3	0.34	1.2	200	2–6
HNO_3	0.34	1.8	150	2–6
HCl	0.84	1.8	200	1–5
HCl	0.34	1.8	200	2–8
NaCl	0.84	1.8	200	2–6
NaCl	0.34	1.8	200	4–10

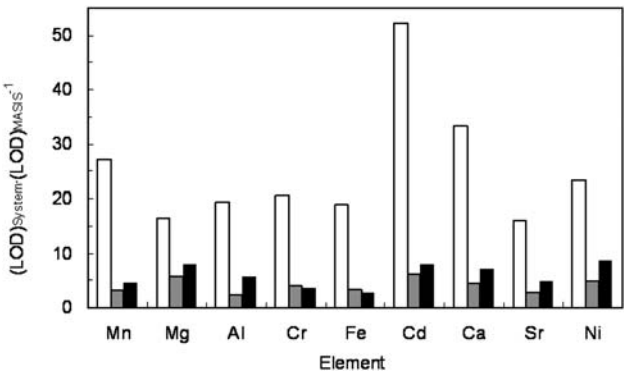

Fig. 5 Comparison of the limits of detection obtained with MASIS and the different sample introduction systems tested in the present work: (□) CS; (▩) MWTN; (■) MWDS. 0.84 M $HN0_3$. Q_l 1.8 mL·min^{-1}. MWTN and MASIS: d_n 150 μm.

conditions that improve the aerosol generation (*i.e.* high matrix concentration and Q_l and narrow d_n). This behavior has also been observed with the MWTN.[10] Among the four systems tested, the lowest RSD values (about 3%) are shown by CS and MWDS.

Limits of detection. Fig. 5 shows the LOD obtained with the CS, MWTN and MWDS referred to those afforded by the MASIS. Thus, values above unity mean lower LOD for MASIS than for the system considered. For all the systems, optimum experimental conditions (*i.e.*, those providing the maximum analyte emission signal) were employed. Results in Fig. 5 indicate that MASIS is the system that provides the lowest LOD irrespective of the analyte considered. Thus, MASIS afford LOD up to 50 times lower than the CS and up to 8 times lower than those obtained with the MWTN or MWDS. These results are the expected since MASIS is the system that gives rise to the highest sensitivity and no significant differences in terms of background intensity and RSD of blank solution are observed between all of them.

The LOD obtained with MASIS have also been compared with the values previously reported in the literature when operating with three different high efficient nebulizers (*i.e.*, thermospray, hydraulic high pressure and ultrasonic)[27,28] and an infrared-assisted desolvation system (*i.e*, Mistral).[18] Fig. 6 gathers all this information. As it can be observed in this figure, the LOD obtained with MASIS are of the same order of magnitude than those typically reported for all these high efficiency sample introduction systems. Finally, it is also worth to mention that MASIS also affords lower LOD than some commercial desolvation systems such as the so-called Apex-E (Elemental Scientific Inc.)[29] or Marin-5 (Cetac).[30] Thus, compared to a CS, MASIS LOD improvement is, on average, 20 times whereas for the Apex-E and Marin-5 is 5 and 8 times, respectively.

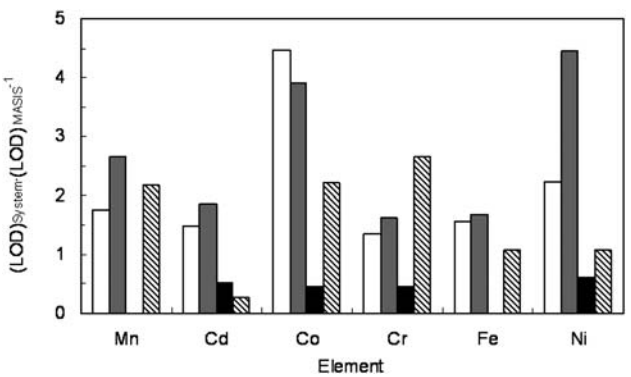

Fig. 6 Comparison of the limits of detection obtained with MASIS and some high efficiency sample introduction systems reported in the literature: (□) thermospray; (▩) hydraulic higher pressure nebulizer; (■) ultrasonic nebulizer; (▨) MISTRAL. MASIS: 0.84 M $HN0_3$, Q_l 1.8 mL·min^{-1}. TN and HHPN (from ref. 27): water; Q_l 1.2 mL·min^{-1}. USN (from ref. 28): water, Q_l 1.3 mL·min^{-1}. MISTRAL (from ref. 18): 0.1 M HNO_3; Q_l 0.4 mL·min^{-1}.

Stabilization time. Stabilization time is defined as the time required to achieve a constant signal after modifying the experimental conditions (*i.e.* sample uptake rate, microwave power, *etc*).[20] The stabilization time for the CS is lower than 10 s since any change in the experimental conditions is immediately reflected on the nebulization and aerosol transport to the plasma. This time rises up when increasing the complexity of the sample introduction device. This is that it would be expected when operating with the microwave-based sample introduction systems due to the heating mechanism itself and to the contribution of the different system components. Thus, when working with MASIS, signal stabilizes around 3–10 min since MW power is switched on, depending on the experimental conditions. After that, stabilization times between 2 to 4 min are required when modifying the experimental conditions. Similar values were obtained for MWDS. Using the MWTN, stabilization times were always lower than 2 min regardless of the experimental conditions tested. The higher stabilization times obtained with MASIS and MWDS when compared to MWTN could be attributed to the complexity of the desolvation step (heating/solvent removal) and their higher internal volume (*i.e.* 135 *vs.* 33 cm^3).[17,31]

Wash-out time. Wash out time can be defined as the time required for reaching 1% of the stable signal after blank introduction,[1] and it depends on the experimental conditions and the system design (*i.e.* inner volume) used. Thus, when operating with MASIS at 1.8 mL min^{-1} and using a 1 mg Mn L^{-1}, the wash out time is around 70 s. This value increases up to 180 s when working at 0.9 mL min^{-1}. The MWDS affords similar values. However, for MWTN and CS, wash out times never reached 60 s. Thus, for instance, operating at 1.8 mL min^{-1}, the wash-out times obtained with these systems were about 20 s. The higher inner volume of MASIS and MWDS compared to MWTN and CS implies that more time is required to rinse out their walls.

It is important to point out that wash-out times for MASIS and MWDS also depend on the analyte concentration employed. Thus, operating at 1.8 ml min^{-1} with a 10 mg L^{-1} analyte solution, the wash-out time increases up to 5 min. Visual inspection of the spray chamber after nebulization of 200 mg Mn·L^{-1} solution reveals that the analyte is significantly accumulated in the spray chamber walls due to aerosol losses against the impact bead rendering wash-out difficult. In order to assess this issue, it would be advisable to operate independently the microwave based nebulizer and the desolvation system. Thus, switching off the desolvation component would allow rinsing out efficiently

spray chamber walls. In fact, a commercial IR based desolvation system recommends this procedure to wash-out the spray chamber.[25] Nonetheless, current MASIS prototype cannot operate in this way.

Conclusions

The new MASIS has demonstrated to be a high efficient sample introduction device for ICP-AES combining simultaneously the benefits of both microwave-based nebulization and desolvation systems. Analytical figures of merit for this fully microwave-based system depend on the MW power, matrix nature and concentration, nebulizer nozzle dimensions and sample uptake rate. MASIS improves up to 50 times the LOD obtained with a conventional sample introduction system. In addition, no clogging problems are observed with this device when operating with high salt content solutions (*i.e.* up to 0.84 M NaCl).

It must be remarked that the MASIS is a highly versatile sample introduction system since, depending on the matrix characteristics and analysis requirements, its configuration can be easily modified working either as a microwave based nebulizer, as a desolvation system or as a simultaneous nebulization/desolvation device.

It is expected that the current analytical figures of merit showed by the MASIS in ICP-AES can be easily improved by the appropriate re-design of the MW cavity. In addition, attending to the results shown in this work, it can be easily derived that the MASIS would be very useful for the elemental analysis of a wide variety of samples both in ICP-AES and ICP-MS. Experiments on these topics are currently being carried out in our laboratories.

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