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ORIGINAL PAPER

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Mixed-gas inductively coupled plasma atomic emission spectrometry using a direct injection high efficiency nebulizer

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Abstract Experimental studies and computer simulations were conducted to identify plasma operating conditions and to explore and contrast the excitation conditions of Ar, Ar-O_2, and Ar-He inductively coupled plasmas (ICPs) for the introduction of microliter volumes of sample solutions with a direct injection high efficiency nebulizer (DIHEN). The best MgII 280.270 nm/MgI 285.213 nm ratio (6.6) measured with Ar ICP atomic emission spectrometry for the DIHEN (RF power = 1500 W; nebulizer gas flow rate = 0.12 L min^{-1}) was less than the ratio (8.2) acquired on the same instrument for conventional nebulization (1500 W and 0.6 L min^{-1}). Addition of small amounts of O_2 or He (5%) to the outer gas flow improved excitation conditions in the ICP, that is, a more robust condition (a MgII/MgI ratio of up to 8.9) could be obtained by using the DIHEN with Ar-O_2 and Ar-He mixed-gas plasmas, thereby minimizing some potential spectroscopic and matrix interferences, in comparison to Ar ICPAES.

Keywords Direct injection high efficiency nebulizer · DIHEN · Mixed-gas inductively coupled plasmas · Atomic emission spectrometry · Matrix interferences · Computer simulation

Introduction

Argon inductively coupled plasmas (Ar ICPs) are commonly used as desolvation, vaporization, atomization, excitation, ionization sources in analytical atomic emission and mass spectrometry [1, 2]. Argon-supported ICP discharges provide low detection limits, wide concentration dynamic ranges, and minimal matrix effects. Mixed-gas plasmas are formed when N_2, O_2, air, H_2, or He are added to one or more gas flows of the ICP torch. Almost all commercial ICP instruments are sustained in Ar, rather than less expensive molecular gases such as air, N_2, and O_2, mainly because the Ar ICP is formed more easily at reasonable power levels (1–2 kW) and generally provides better detection limits for elements possessing spectral lines below 350 nm [3, 4]. However, mixed-gas plasmas offer a superior ability to decompose refractory particles, increased tolerance to higher solvent and analyte loads, and less structured background spectra above 350 nm, leading to improved analytical performance in certain applications [3, 5, 6, 7]. These characteristics allow for the analysis of a wider range of samples than are possible using Ar alone. For example, introduction of O_2 or He to the outer gas flow of the Ar ICP is effective in suppressing the background caused by organic solvents [8, 9] and in improving the evaporation efficiency of slurries [10, 11] when conventional nebulizer-spray chamber arrangements are used. However, except for two recent conference presentations [12, 13], no report is available on studies of mixed-gas plasmas for the direct injection of the sample.

The principal aim of this research is to explore the excitation conditions of the mixed-gas ICPs for the direct introduction of test solutions using the DIHEN. The DIHEN is a low consumption micronebulizer (1–100 μL min^{-1}) for ICP mass spectrometry (ICPMS) [14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25] that operates at very low nebulizer gas flow rates (ca 0.2 L min^{-1}) compared to conventional pneumatic nebulizer-spray chamber arrangements (ca 1.0 L min^{-1}). Initial studies describing the use of the DIHEN for ICP atomic emission spectrometry (ICPAES) were presented by Montaser and coworkers [12, 13] and Todolí and Mermet [26, 27]. The latter work, however, was limited to Ar ICPAES measurements at a maximum RF power of 1300 W. In contrast, our current and previous accounts [12, 13] consider the efficacy of the DIHEN for atomic emission studies of the Ar ICP and the mixed-gas plasmas operated at 1500 W. Such a study is significant because plasma-related matrix effects are usually more serious for direct liquid introduction [27] since the

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mass of sample (and solvent) presented to the plasma is greater and usually has larger droplets than the aerosol injected in conventional nebulization. It has been reported that only 45% of the aerosol produced by the DIHEN are composed of droplets less than 10 µm [19]. Because the DIHEN is delicate and relatively expensive, our study was initially guided by computer simulation of Ar, Ar-O_2, and Ar-He plasmas to locate a thermally safe region to place the DIHEN within the torch. To explore the excitation condition or robustness of the mixed-gas ICP versus the Ar ICP, the ratio of MgII/MgI was also measured for the DIHEN with the plasma under the end-on viewing condition and compared to results using conventional nebulization. Finally, the effects of acid concentration and easily ionized elements on the MgII/MgI ratios were examined for the DIHEN and contrasted to previous work [26, 27]and our findings for conventional nebulization using the Ar ICP and the Ar-O_2 plasma [12, 13].

Experimental

Computer code for the simulation of plasma temperature in the vicinity of the DIHEN nozzle

Version 2.0 of the High Frequency Induction (HiFI) plasma code [28] was used to calculate properties of Ar and mixed-gas plasmas as a function of the operating conditions listed in Table 1. The code predicts plasma temperature, gas velocity, power input, gas enthalpy, and magnetic flux density [5, 28, 29]. Only the result for plasma temperature was used in this work as an initial guide for locating a thermally safe region within the ICP torch to place the DIHEN, that is, to prevent excessive heating of the DIHEN nozzle due to the changes in the plasma operating conditions. The results of this code must be treated as estimates because the model assumes the following: (1) the plasma is in a state of local thermodynamic equilibrium (LTE), (2) a steady state and laminar flow prevails in the ICP torch, (3) the plasma is axially symmetric and optically thin, (4) viscous dissipation and displacement currents are negligible, and (5) flow, electromagnetic, temperature, and concentration fields are two-dimensional.

Instrumentation and operating conditions

The instrumentation and operating conditions are shown in Table 1. A free-running generator (Elan 5000 ICPMS generator), modified in our laboratory [30], was used for all ICPAES studies. The outer gas flow consisted of either Ar or Ar-O_2 and Ar-He mixtures. Argon was used in the intermediate and nebulizer gas flows.

To estimate the robustness of the ICP [31], the line intensity ratio MgII 280.270 nm/MgI 285.213 nm was measured using a 5 µg mL^{-1} solution of Mg prepared by diluting a 1000 µg mL^{-1} stock solution (Spex Certiprep Inc., Metuchen, NJ) in distilled, deionized water (18 MΩ cm). The effect of 2 M HNO_3 (Optima grade, Fisher Scientific, Pittsburgh, PA) and 0.1% and 1% NaCl (ACS grade, Fisher Scientific) on plasma robustness was also investigated.

Results and discussion

The plasma operating conditions for DIHEN-ICPAES

In general, ignition of the Ar plasma for the DIHEN-ICPAES measurement is straightforward and similar to conditions used for conventional nebulization, that is, the plasma is ignited at outer, intermediate, and nebulizer gas flows of 15, 1.2, and 0 L min^{-1}, respectively. The Ar ICPAES operating conditions under the end-on viewing mode are generally comparable to those used for Ar ICPMS [14, 15, 16, 17, 18, 19, 20, 21], that is, the RF power, nebulizer gas flow rate, and solution uptake rate

Table 1 Operating conditions for DIHEN-ICPAES instrument

Operating parameter	Description
RF generator	PE-Sciex Elan 5000 (Perkin-Elmer Corporation, Norwalk, CT)
RF power (W)	1500
Nominal frequency (MHz)	32[a]
RF generator type	Free-running (Elan 5000 generator modified in our laboratory) [30]
Outer gas flow rate (L min^{-1})	15 Ar, and mixtures (2.5, 5 and 10% v/v) of Ar-O_2 or Ar-He. Matheson gas proportioner (Model MFMR-0800-AA, with tubes E200/E300) was used to mix gases.
Nebulizer gas flow (L min^{-1})	0.15
Intermediate gas flow rate (L min^{-1})	0.5, 1.2 (for plasma ignition and operation)
Solution flow mode	Continuous
Nebulizer systems	DIHEN (Model 170-AA, J E Meinhard® Associates, Inc., Santa Ana, CA) and crossflow nebulizer-Scott spray chamber.
Spectrometer	Czerny-Turner monochromator (Model 2061, McPherson Instrument, Acton, MA) having 1.00 m of focal length and 1200 lines m^{-1}grating. The entrance and exit slits were 50 µm each.
Observation position	The plasma was viewed end-on. It was imaged (1:5) onto the entrance slit of the spectrometer using a 5.00 cm plano-convex lens having a focal distance of 25 cm. This arrangement was not optically optimal, but was necessary to protect the available lens-monochromator system from excessive heat generated by the ICP. Furthermore, no shear gas or a water-cooled cone interface was used to remove the cool fringe of the plasma prior to observation.
Detection System	Photomultiplier tube (Type FACT50, EMI Electronic Ltd., Middlesex, England) cooled to –28°C and operated at –800 V.

[a]Measured in this work. The manufacturer designed the generator as a 39±1 MHz power supply

are typically 1500 W, 0.15 L min^{-1}, and 80 μL min^{-1}, respectively, for the DIHEN positioned 2 mm below the top of the intermediate tube of the ICP torch. Under such conditions for the Ar ICP, no erosion of the DIHEN tip is observed. As discussed below under computer simulation, the DIHEN tip is well protected from excessive heating if an intermediate gas flow of 1.2 L min^{-1} is maintained for operation with an Ar ICP. For studies of some mixed-gas plasmas, the DIHEN tip had to be positioned 3 mm below the top of the intermediate tube in order to shield it from the hot zone of the ICP. This position was used throughout this work for a consistent comparison of Ar ICP and mixed gas plasmas. Visual observation of the well-known yttrium bullet revealed that the aerosol was confined to the axial channel of the plasma.

Robustness of the plasma generated in Ar ICP using DIHEN

In ICPAES, the efficiency of the energy transfer in the plasma is expressed by plasma robustness [31], as measured by the intensity ratio MgII 280.270 nm/MgI 285.213 nm. Higher ratios, indicative of greater plasma robustness [32, 33, 34, 35, 36, 37, 38, 39, 40], are achieved by applying high RF power and by increasing the residence time of the sample aerosol in the plasma. The use of axial viewing generally leads to lower values of MgII/MgI ratios because the whole axial channel is probed, and the observation cannot be optimized for ionic lines, as performed by radial viewing [41]. Under robust conditions, no significant variation in the ratios is observed due to changes in the matrix or reagent composition.

The previous DIHEN-Ar ICPAES studies were conducted at 1300 W, a non-robust plasma condition, and resulted in unsatisfactory MgII/MgI ratios (<6) [26, 27]. Furthermore, matrix effects were only significantly minimized at low solution uptake rates (30–40 μL min^{-1}) for lines possessing low sum values (E_{sum}) of ionization and excitation energies [26, 27]. In the present work, MgII/MgI ratios are measured at 1500 W. Plots of MgII/MgI ratios for Ar ICP are shown in Fig. 1 as a function of nebulizer gas flow rate, RF power, and solution uptake rate using the DIHEN. The ratios are the mean of three measurements on different days and the precision is within 5%. Fig. 1A and B illustrate that the highest MgII/MgI ratios (ca 6.5) for the DIHEN are obtained at very low nebulizer gas flow rates (0.15 L min^{-1}) and high power (1500 W). However, at nebulizer gas flow rates less than 0.15 L min^{-1}, the plasma became unstable. The ratio is not strongly affected by the solution uptake rate (Fig. 1C), although slightly higher ratios were obtained at uptake rates below 100 μL min^{-1}.

Table 2 presents a compilation of MgII/MgI data for a few spectrometers using aqueous solution introduction by the DIHEN and conventional nebulizer-spray chamber arrangements under the best operating conditions reported for each nebulizer. The best MgII/MgI ratio obtained for

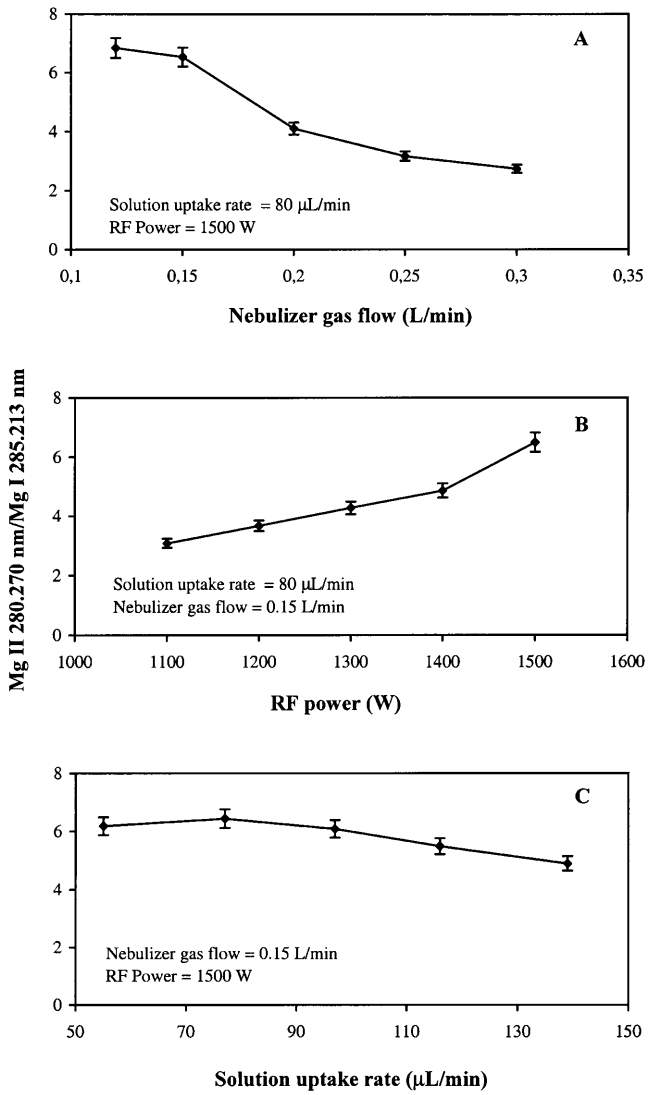

Fig. 1 Experimental ratio of Mg II/Mg I as a function of (**A**) nebulizer gas flow rate, (**B**) RF power and (**C**) solution uptake rate for the Ar ICP using the DIHEN

the DIHEN is 6.6 (at input RF power and nebulizer gas flow rate of 1500 W and 0.12 L min^{-1}, respectively), less than 8.2 acquired by our ICPAES instrument for conventional nebulization (at input RF power and nebulizer gas flow rate of 1500 W and 0.6 L min^{-1}, respectively). Also, the best ratio for the DIHEN is notably less than the values (7.3–11.9) reported for ICPAES instruments such as the Optima 3000XL [33, 37] (Perkin-Elmer Corporation) and Liberty Series II [38] (Varian Inc. Palo Alto, CA) operated with conventional nebulizer-spray chamber arrangements. Accordingly, the Ar ICP is less robust in the presence of the DIHEN compared to conventional nebulization.

The data in column six of Table 2 present the percentage decrease in the MgII/MgI ratio for changes in the plasma operating conditions towards the less robust state. For the DIHEN, the MgII/MgI ratio decreases by 24% when the RF power is reduced from 1500 to 1300 W. This

Table 2 Ratios of MgII 280.270 nm/MgI 285.213 nm for various axially viewed Ar ICPs using DIHEN and conventional nebulizer-spray chamber arrangements for aqueous solution introduction

Instrument	Nebulization	Input RF power (W)	Nebulizer gas flow rate (L min^{-1})	MgII/MgI	Decrease of MgII/MgI (%)[b]
This work	DIHEN	1500	0.12	6.6	24
		1300	0.12	5.0	
This work	Crossflow nebulizer-Scott type spray chamber	1500	0.60	8.2	11
		1300	0.60	7.3	
Optima [37]	Crossflow nebulizer-Scott type spray chamber	1500	0.60	9.7	6
		1350	0.60	9.1	
Liberty [38]	Concentric nebulizer-cyclonic spray chamber	1400	180[a]	11.9	4
		1200	180[a]	11.4	
Optima [33]	Modified conespray-Scott type spray chamber	1450	0.60	7.3	19
		950	0.95	5.9	

[a]Kpa; [b]Decrease of MgII/MgI=[(MgII/MgI at higher power–MgII/MgII at lower power)/(MgII/MgI at higher power)×100]

is in contrast to the 4–19% decline measured for conventional nebulization for various instrumental set-ups cited in Table 2. The 24% decrease in the MgII/MgI ratio for the DIHEN is still worse than the 19% decline reported for the Optima instrument [33] when the RF power (1450 W–950 W) and nebulizer gas flow rate (0.60–0.95 L min^{-1}) are changed significantly for conventional nebulization. These results collectively suggest that the Ar ICP is less robust for the direct introduction of aerosol, compared to conventional nebulization, even at 1500 W – the power level available for most ICPAES instruments. This finding is in line with the previous DIHEN-Ar ICPAES studies conducted at 1300 W [26, 27].

Since little improvement in the MgII/MgI ratio could be realized with a regular Ar ICP, that is, by increasing the power and decreasing the DIHEN gas flow rate, one may consider mixed-gas plasmas as a possible approach to enhance the robustness of the ICP. Based on prior experimental studies with conventional nebulization [3, 42, 43, 44, 45, 46] introduction of molecular gases to the outer gas flow reduces the diameter of the axial channel, thus enhancing the sample-plasma interaction and analytical measurements. The magnitude of these effects is related to the plasma gas composition and RF power. Furthermore, the position of the mixed-gas plasma shifts downward in the ICP torch [3, 42, 43], a process which may damage the DIHEN nozzle. To counteract this downward shift, the intermediate gas flow may be increased. In the following section, computer simulation was applied to consider the cited effects collectively, and to find safe operating conditions for the DIHEN nozzle based on predicted plasma temperatures.

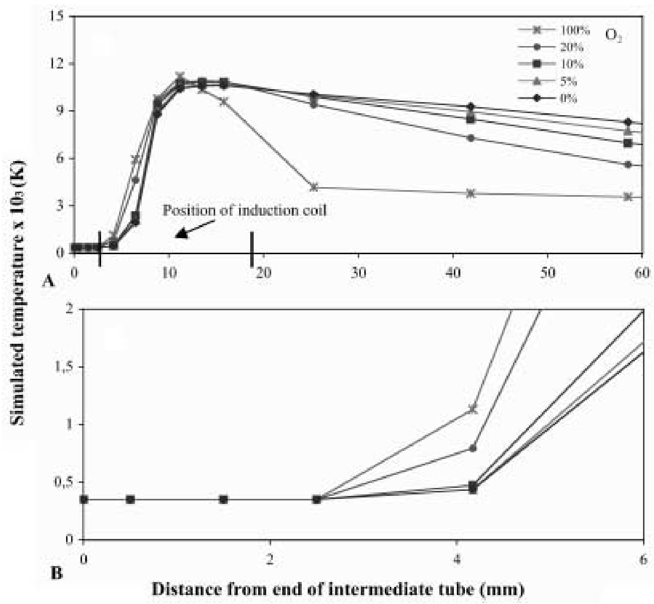

Fig. 2 Simulated plasma temperature (K) as a function of the distance from the end of the torch intermediate tube for Ar-O_2 ICPs. RF Power, nebulizer gas flow and intermediate gas flows are 1500 W, 0.15 L min^{-1} and 1.2 L min^{-1}, respectively

Simulation of the axial temperature profiles, as a function of gas composition, using Ar-O_2 and Ar-He mixtures in the plasma gas flow

Fig. 2 shows simulated axial temperature distributions of Ar and Ar-O_2 ICPs above the intermediate tube of the torch for the introduction of 0, 5, 10, 20, and 100% O_2 in the outer gas flow. In all cases, the predicted axial channel temperatures rise steeply within the load coil region (3–17 mm), reach a peak near the top turn of the induction coil, and then decline gradually at distances of 20–60 mm. At distances over 20 mm (Fig. 2A), the temperature declines as the O_2 composition in the outer gas is increased, resulting in a more dense plasma that is smaller than the Ar ICP. Close to the intermediate tube of the torch, however, the axial temperature rises as the O_2 content is increased, especially when O_2 completely replaces Ar. For example, at 2.5, 4.2, and 6.5 mm above the intermediate tube, temperatures of 350, 1129, and 5931 K, respectively, are predicted for 100% O_2 in the outer gas (Fig. 2B). For 5% O_2 in the outer gas, the estimated temperatures are 350, 438, and 2060 K (Fig. 2B) at 2.5, 4.2, and 6.5 mm

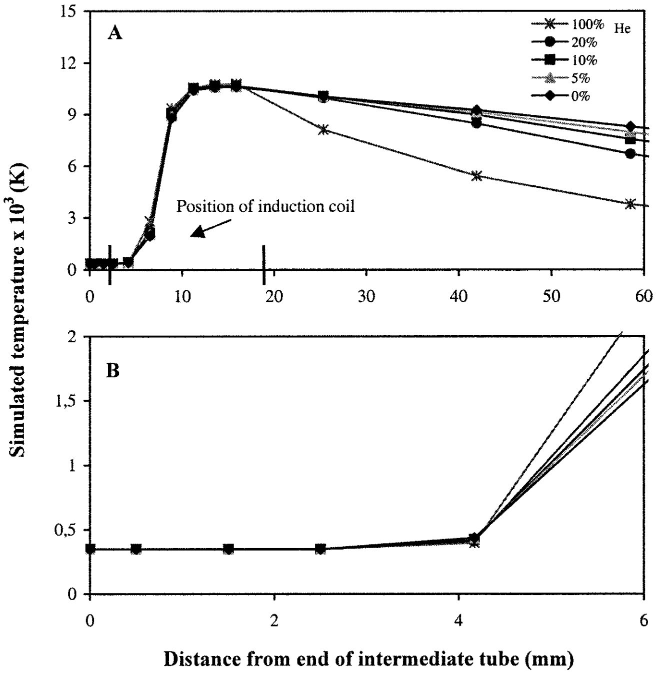

Fig. 3 Simulated plasma temperature (K) as a function of the distance from the end of the torch intermediate tube for Ar-He ICPs. RF power, nebulizer gas flow and intermediate gas flows are 1500 W, 0.15 L min^{-1} and 1.2 L min^{-1}, respectively

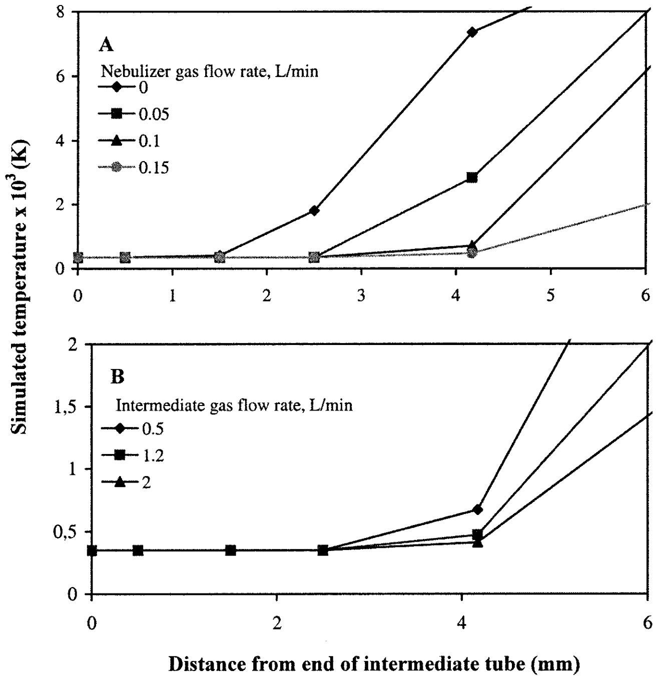

Fig. 4 Simulated plasma temperature (K) as a function of the distance from the end of the torch intermediate tube for Ar-O_2 ICP with 10% O_2 in the outer gas flow: (**A**) intermediate gas flow= 1.2 L min^{-1} at different nebulizer gas flows and, (**B**) nebulizer gas flow=0.15 L min^{-1} at different intermediate gas flows

above the intermediate tube, respectively. The wide temperature variations at the base of the plasma collectively suggested that the DIHEN nozzle should be positioned at larger distances below the intermediate tube when the percentage of O_2 in the outer gas is extensively altered; otherwise, the DIHEN nozzle would melt. Accordingly, the DIHEN nozzle was placed 3 mm below the intermediate tube for Ar-O_2 ICP as compared to 2 mm for Ar ICP. One must note, however, that the temperature rise predicted at the base of the mixed-gas plasma is useful analytically because it enhances droplet desolvation and diminishes solvent effects. Indeed, the cited issues are difficult to attack when the sample aerosol is directly injected into the plasma, especially for the large droplets.

Axial temperature profiles are shown in Fig. 3 for Ar and Ar-He plasmas. At large distances from the nebulizer (40–60 mm), the plasma temperature is reduced with the introduction of He. In contrast to the results obtained with Ar-O_2 plasmas, the predicted axial channel temperature close to the intermediate tube (Fig. 3B) does not significantly increase as more He replaces Ar in the outer gas, suggesting that the DIHEN nozzle could be safely positioned 2 mm below the intermediate tube. Based on the predicted temperatures, the spatial structures of the Ar-He ICPs and the Ar ICP are nearly identical, hence the MgII/MgI values of Ar-He ICPs should be less (see below) than those measured in Ar-O_2 plasmas.

Simulation of the axial temperature profiles at different nebulizer and intermediate gas flow rates

The predicted axial temperature profiles of the plasma at different nebulizer gas flow rates are shown in Fig. 4A for 10% O_2 in the outer tube. The plasma temperature increases significantly close to the intermediate tube when the nebulizer gas flow is reduced or stopped. These results are significant for DIHEN operation, considering that the DIHEN is typically operated at comparatively low nebulizer gas flows (0.1–0.2 L min^{-1}). A nebulizer gas flow rate of 0.15 L min^{-1} was chosen for experimental work. At lower nebulizer gas flows, either the DIHEN nozzle would gradually clog due to excessive heating or the aerosol would not penetrate the axial channel, resulting in plasma instabilities.

The effect of the intermediate gas flow rate on axial temperature distributions of the plasma is shown in Fig. 4B for 10% O_2 in the outer tube. The simulated profiles are obtained at intermediate gas flow rates of 0.5, 1.2, and 2.0 L min^{-1}. The plasma temperature increases significantly close to the intermediate tube when the intermediate gas is reduced from 2 to 0.5 L min^{-1}. For example, at an intermediate gas flow of 2.0 L min^{-1}, the predicted temperatures are 350, 414, and 1695 K at 2.5, 4.2, and 6.5 mm above the intermediate tube, respectively. At 0.5 L min^{-1}, the estimated temperatures are 350, 672, and 3875 K at 2.5, 4.2, and 6.5 mm above the intermediate tube, respectively. These results collectively illustrate that the intermediate gas flow plays, compared to conventional nebulization, a more critical role in operating a stable mixed-gas plasma with the DIHEN because the nebulizer nozzle may easily clog from excessive heating. Similar results are obtained with 10% He in the outer tube (not presented here). Based on these results, an intermediate gas flow of 1.2 L min^{-1} was used for subsequent experiments.

The above simulated data were used to establish initial operating conditions for DIHEN-ICPAES measurements using mixed-gas plasmas. The predicted results were then confirmed experimentally by using a "dummy nozzle" before installing the DIHEN. The dummy nozzle resembles the DIHEN shell, except that it does not include a solution capillary. In general, the dummy nozzle is a useful tool for establishing safe operating conditions for the DIHEN when the plasma is operated under conditions different from those commonly used for the Ar ICP. One must note that the plasma operated with a dummy nozzle has different characteristics compared to the DIHEN because effects of aerosol and nebulizer gas flow are not considered. However, the combined effort involving computer simulation and the application of the dummy nozzle is most effective in establishing initial operating conditions.

Based on the studies described above, the DIHEN was positioned 3 mm below the torch intermediate tube and was operated at the nebulizer and intermediate gas flow of 0.15 L min^{-1} or greater and 1.2 L min^{-1}, respectively, when mixed-gas plasmas were used. Under such conditions, no erosion in the DIHEN tip was noted. A recent report refers to the deterioration of the DIHEN by the plasma at very low nebulizer gas flow rates (<0.3 L min^{-1}) and 1300 W [26, 27] however, in our view, this observation is attributed to the use of a low intermediate gas flow rate (0.5 L min^{-1}).

Robustness of the plasma generated in Ar-O_2 and Ar-He mixture using DIHEN

Plots of MgII/MgI[I] ratios for Ar, Ar–O_2, and Ar-He ICPs are shown in Fig. 5 as a function of nebulizer gas flow rate for the DIHEN. The ratios are the mean of three measurements on different days and the precision is within 5%. The Ar-O_2 ICPs exhibit higher ratios compared to Ar ICP (Fig. 5A). For example, the MgII/MgI ratio is approximately 8.5 and 6 for Ar-O_2 ICP and Ar ICP, respectively, at a nebulizer gas flow of 0.15 L min^{-1}. No significant difference was observed for mixed-gas plasmas having 2.5, 5, and 10% v/v of O_2 in the outer gas flow. Fig. 5B shows similar results for Ar-He plasmas, that is, Ar-He plasmas exhibit higher MgII/MgI ratios compared to the Ar-ICP, but the ratios are slightly lower than those obtained with Ar-O_2 ICP.

The above results jointly suggest that mixed-gas plasmas improve the robustness of the ICP when a relatively small amount of the foreign gas is introduced (ca 2.5%). For higher percentages of foreign gas, no significant improvement in the MgII/MgI ratios is realized, but the hot zone of the plasma approaches the tip of the DIHEN nozzle, increasing the risk of damage to the nebulizer. A mixed-gas ICP is a viable alternative to improve the excitation conditions of the plasma in the presence of the DIHEN, especially in this study, when the instrument is operated at maximum possible RF power and minimum possible nebulizer gas flow rate.

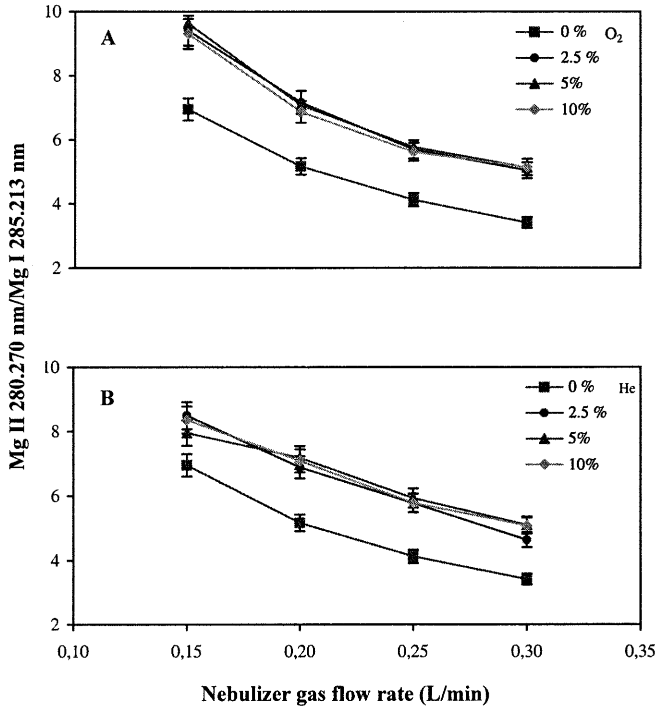

Fig. 5 Experimental ratio of MgII/MgI as a function of nebulizer gas flow rate; (**A**) Ar-O_2 ICPs and (**B**) Ar–He ICPs. RF power, nebulizer gas flow, and intermediate gas flows were 1500 W, 0.15 L min^{-1} and 1.2 L min^{-1}, respectively

Matrix effects in DIHEN-ICPAES

Introduction of an inorganic acid, such as HNO_3, or NaCl is known to suppress or enhance analytical signal in ICPAES, but the effects can be minimized for conventional nebulization by using robust plasma conditions, that is, reduced nebulizer gas flow and high RF power [35, 37, 38, 39, 47]. Table 3 includes MgII/MgI ratios for the introduction of HNO_3 solutions by the DIHEN and nebulizer-spray chamber arrangement operating under optimal operating conditions. Again, the ratios are the mean of five measurements on different days and the precision is within 5%. For the Ar ICP, the MgII/MgI ratios (Table 3) measured with the DIHEN decrease only slightly (6.6–6.2 or 6%) as the HNO_3 concentration is increased from 0 to 2 M. These data suggest that DIHEN-ICPAES is relatively robust when Ar ICP is used at 1500 W. Todolí and Mermet also reported no matrix effect by nitric acid for a 1300 W Ar ICP, but a lower solution uptake rate (30–40 µL min^{-1}) had to be used [26, 27]. Improved MgII/MgI ratios are also noted for Ar-O_2 ICP (Table 3), however the level of suppression (6%) remained unchanged when the

Table 3 Ratio of MgII 280.270 nm/MgI 285.213 nm for aqueous nitric acid and sodium chloride solutions using DIHEN and conventional nebulization

Nebulization system	DIHEN		Crossflow nebulizer-Scott type spray chamber	
Plasma	Ar	Ar-O_2	Ar	Ar-O_2
Solution				
Aqueous	6.6	8.9	8.2	7.0
Nitric acid (2 M)	6.2	8.4	7.7	6.0
NaCl (0.1%)	6.0	6.2	7.0	6.2
NaCl (1%)	Nebulizer clogs	Nebulizer clogs	5.9	5.7
Nebulizer gas flow (L min^{-1})	0.15	0.15	0.60	0.60
Solution uptake (µL min^{-1})	85	85	600	600
RF power (W)	1500	1500	1500	1500

DIHEN was used. In contrast, with conventional nebulization, acid effects are more pronounced with Ar-O_2 ICP compared to the Ar ICP, i.e., the mixed-gas plasma is less robust than the Ar ICP. The main reason for this change in plasma robustness is unclear to us. Obviously, the presence of the spray chamber makes interpretation of the result more difficult.

Table 3 also includes MgII/MgI ratios in the presence of 0.1% NaCl introduced by the DIHEN and the conventional nebulizer-spray chamber for Ar ICP and Ar-O_2 ICP. Solutions containing 1% Na were not used with the DIHEN because the nebulizer is prone to clogging. The data in Table 3 suggest that Na suppresses MgII/MgI more severely than HNO_3, both for the conventional nebulization system and the DIHEN. Importantly, the use of the Ar-O_2 ICP was not very effective in reducing Na matrix effects at 1500 W. In contrast, the Na matrix effect was negligible at 1300 W and at a solution flow rate of nearly 80 µL min^{-1} in Ar ICPAES for micronebulization with a high efficiency nebulizer-cyclonic spray chamber [26, 27]. Accordingly, to eliminate the Na matrix effect in ICPAES, the DIHEN must present a smaller amount of sample to the plasma at RF power level greater than 1500 W. This conclusion is in line with the work of Todolí and Mermet [26, 27].

The above data on MgII/MgI ratios also brings some uncertainty to the application of this ratio as an indicator of plasma robustness [31]. At least for direct injection, it is prudent to conduct further experiments to validate the usage of MgII/MgI as an indicator of plasma robustness.

Conclusions

This paper describes ways to overcome the limitations of the DIHEN. Computer simulation was applied to predict the operating conditions of mixed-gas ICPs using the DIHEN. The simulated temperature profiles show that Ar-O_2 and Ar-He plasmas provide better excitation conditions than the Ar ICP but may create a hot zone close to the DIHEN nozzle. For mixed-gas plasmas, the DIHEN should be positioned farther below the torch intermediate tube compared to its typical location in Ar ICPs. In general, the DIHEN provides robust conditions (values of MgII/MgI greater than 6) for some Ar ICPAES measurements at high RF power (ca 1500 W) and low nebulizer gas flow (ca 0.15 L min^{-1}), however, the ratios were less than those noted for a conventional nebulizer-spray chamber arrangement. Slightly larger MgII/MgI ratios could be obtained using Ar-O_2 and Ar-He mixed-gas plasmas with the DIHEN for the addition of the foreign gas to the outer gas flow; nevertheless, the level of suppression (6%) for the introduction of a solution of 2 M HNO_3 remained unchanged. With conventional nebulization, acid effects were more pronounced with Ar-O_2 ICP compared to the Ar ICP.

In general, results of these studies at 1500 W on mixed-gas ICPAES with the DIHEN agree with the work of Todolí and Mermet who operated a 1300 W Ar ICP [26, 27]. Clearly, better MgII/MgI ratios were obtained because the ICP was operated at 1500 W. It was also demonstrated that the plasma required RF power above 1500 W in the presence of the DIHEN to run under robust conditions, but only 1300 W was necessary for a pneumatic nebulizer-spray chamber arrangement. Todolí and Mermet also concluded that the acid effects are eliminated for the DIHEN, but only at a solution uptake rate of 30–40 µL min^{-1} [27]. Operation at 1500 W, as demonstrated in this work, allows introduction of 80 µL min^{-1} with the DIHEN with nearly no HNO_3 effect. At 1300 W, Todolí and Mermet reported minimal Na matrix effect with the DIHEN, but only for spectral lines possessing low E_{sum} [27]. For lines having high E_{sum} values, as shown in this work, the Na matrix effect could not be remedied at 1500 W or through the use of mixed-gas plasma. To create a robust plasma condition for direct injection, one must reduce the amount of aerosol and decrease the droplet size introduced into the ICP to the level prevalent in conventional pneumatic nebulization (20–40 mg min^{-1}), increase the RF power beyond the level required for conventional nebulization, and enhance plasma–sample interaction by operating a mixed-gas plasma.

It would be interesting to introduce a foreign gas to the nebulizer gas flow as no report is currently available on the efficiency of the DIHEN with a large proportion of such a gas. In this case, the axial channel would be wider [3], but an increase in thermal conductivity may result in the central channel. Work in this area is in progress in our laboratory.

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