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Investigation of the direct injection high efficiency nebulizer for axially and radially viewed inductively coupled plasma atomic emission spectrometry

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A direct injection high efficiency nebulizer (DIHEN) is explored for introduction of the sample aerosol into the central channel of the axially and radially viewed inductively coupled plasma (ICP) of a commercial ICP atomic emission spectrometer (ICPAES). The DIHEN is a micro-nebulizer that requires very low solution uptake rates (1–100 μL min^{-1}) and nebulizer gas flow rates ($<$0.2 L min^{-1}) compared to conventional nebulizer-spray chamber arrangements ($\sim$1.0 mL min^{-1} and $\sim$1.0 L min^{-1}, respectively). Signal-to-background ratios (SBRs), detection limits, and precision of the DIHEN are comparable or superior to those of the conventional sample introduction system, but the Mg II 280.270/Mg I 285.213 nm ratios are lower with the DIHEN, indicating that the DIHEN is more susceptible to matrix effects than the conventional nebulization system, for both the axial and radial ICPAES systems. Matrix effects are further investigated by comparing intensity ratios with and without 0.1% and 0.5% Na for several spectral lines having energy sum ranging from 7.93 to 14.79 eV. Replacement of Ar with Ar–O_2 and Ar–N_2 mixtures in the outer gas flow of the plasma improves SBRs and Mg II 280.270/Mg I 285.213 nm ratios of the DIHEN, and reduces matrix effects. By reducing solution uptake rate from 60 to 30 μL min^{-1}, matrix effect is also reduced. Operation of the radial instrument at 1700 W reduces matrix effect compared to the effect noted for the axial instrument at 1500 W. Finally, the utility of the technique in practical ICPAES studies is demonstrated using a custom made organo-metallic standard for As, Hg, and Pb in xylene.

Introduction

In a recent report,[1] we described the first investigation of mixed-gas inductively coupled plasmas for direct nebulization of sample aerosol in atomic emission spectrometry (AES).[2] Direct nebulization of the aerosol into the plasma by devices such as the direct injection high efficiency nebulizer (DIHEN)[3,4] and the large bore DIHEN (LB-DIHEN)[5] exhibits potential benefits compared to traditional nebulizer-spray chamber arrangements: (i) 100% analyte transport efficiency into the plasma; (ii) elimination of spray chamber related interferences and noise; (iii) no solution waste production; (iv) low dead volume ($<$10 μL), hence reduced memory effects and rapid response times; and (v) low nebulizer gas flow rates ($<$0.2 L min^{-1}) and solution uptake rates (1–100 μL min^{-1}) compared to conventional nebulizer-spray chamber arrangements ($\sim$1.0 L min^{-1} and $\sim$1.0 mL min^{-1}, respectively). These attributes are essential in the analysis of limited volume, expensive, and hazardous samples, or in coupling with separation techniques such as high performance liquid chromatography[6] and capillary electrophoresis.[7] Several reports have been published investigating the utility of the DIHEN in ICP mass spectrometry,[5–14] however such studies with ICPAES are scarce.[1,15] In this connection, one aim of this work is to investigate the performance of the DIHEN in axially and radially viewed ICPAES, and to examine whether or not the characteristics noted in ICPMS in terms of operating conditions, ease of use, and analytical performance are common or extendable to ICPAES. The study is important because introduction of sample solutions into plasma spectrometers has implications for instrument performance in terms of detecting power, accuracy and precision. The performance of sample introduction devices also depends on the sample matrix. Clearly, not all devices have the same performance characteristics, and it is probably true that no one nebulizer is the best choice for all sample materials. Thus, it is useful for the community of users of ICP instrumentation to have access to the results of the evaluation of the performance of relatively new nebulization systems such as the DIHEN so that sensible decisions about the choice of nebulizer, ICP instrument, and operating conditions can be made.

Argon supported mixed-gas plasmas are formed when gases such as O_2, N_2, He, or H_2 are mixed with the argon in the nebulizer, intermediate, or outer gas flows of the ICP torch.[16–18] The introduction of such gases improves energy transfer from the plasma to the sample, and reduces matrix effects and spectral interferences,[18–20] characteristics important in direct solution nebulization. In this report, we investigate the analytical potentials of axially viewed Ar–O_2 and Ar–N_2 plasmas compared to the Ar ICP, for direct nebulization with a DIHEN. The report includes studies of matrix effects produced by sodium and mineral acids and measurement of Mg II 280.270/Mg I 285.213 nm data to gauge the robustness of the plasmas.[21] The potentials and the limitations of the DIHEN-ICPAES are also examined in the analysis of a custom-made organo-metallic standard.

Table 1 Operating conditions for DIHEN using axial- and radial-ICPAES instruments

ICP instrument	Vista instruments, models AX and RL (Varian, Palo Alto, CA)
Rf power/W	1000–1700[a]
Nominal frequency/MHz	40 $\pm$ 0.2
Rf generator type	Free-running using a direct serial coupling system
Dispersive system	Based on the use of Echelle grating (94 lines mm^{-1}) with a CaF_2 prism-based cross dispersion. A 2D spectrum is obtained which displays the spectral orders 19–88
Detection system	Diagonal linear array (DLA) CCD detector. Each DLA covers one of the 70 orders in the 2D spectrum. The total number of pixels is 70,000 with a pixel width of 12.5 and 25 μm
Outer gas flow rate/L min^{-1}	15 Ar, and mixture of Ar–O_2 (5% v/v). Matheson gas proportioner (Model MFMR-0800-AA, with tubes E200/E300) was used to mix gases
Intermediate gas flow rate/L min^{-1}	2–4 (see text)
Nebulizer systems	DIHEN (Model DIHEN 170-AA, Meinhard Glass Products, Analytical Reference Materials International Corp., Golden, CO) and concentric nebulizer-cyclonic spray chamber (Glass Expansion, Hawthorn, Australia)
Nebulizer gas flow/L min^{-1}	DIHEN (0.12–0.26), concentric nebulizer (0.5–1.15)
Solution flow mode	Continuous
Solution uptake rate/μL min^{-1}	DIHEN (5–85), concentric nebulizer (900)
Observation position	The plasma was viewed in radial and axial mode. The entrance slits of the spectrometers are 25 μm wide with 50 μm height
Observation height/mm	1–19 (above the last turn of the load coil) for the radial instrument

[a]Rf power of 1700 W is only feasible with the radially viewed instrument. The maximum Rf power for the axial instrument is 1500 W.

Experimental

The axially- and radially-viewed ICPAES instruments (Varian Vista, Models AX and RL, Palo Alto, CA) were used under the operating conditions listed in Table 1. The outer tube of the torch for the axial instrument was cut by 2 cm to produce shorter, denser plasma, thus reducing electrical interaction with the optical sampling port, which was found to enhance plasma stability for operation with the DIHEN. The DIHEN (Model DIHEN-170 AA, Meinhard Glass Products, Analytical Reference Materials International Corp., Golden, CO) replaces the injector tube of the demountable ICP torch, allowing the sample to be introduced directly into the plasma.[3] The DIHEN used is one-inch shorter than the regular DIHEN[3] to facilitate installation within the torch box of the axial ICPAES instrument. For this work, the DIHEN tip is positioned 4 mm below the top of the intermediate tube to facilitate plasma ignition and also to shield it from the hot zone of the mixed-gas plasma.[1] Visual observation of the yttrium bullet was used to ensure that the aerosol was confined to the axial channel of the plasma. For operation of the DIHEN, the intermediate gas flow of the plasma was controlled externally using a gas flow meter (Model MFMR 0800-AA, Matheson Tri-Gas Inc., Montgomeryville, PA) while the nebulizer gas was supplied to the DIHEN *via* an external mass flow controller (Model 8270, Matheson Tri-Gas Inc). The sample was delivered to the nebulizer using a four-channel peristaltic pump (Model Rabbit, Rainin Instrument Co. Inc., Woburn, MA). A concentric nebulizer (Model Micromist AR30-1-FM1, Glass Expansion, Hawthorn, Australia) and spray chamber arrangement (Model Cinnabar Cyclonic, Glass Expansion) was used as the conventional sample introduction for comparison purposes.

Multi-element test solutions, prepared by diluting 1000 μg mL^{-1} stock solutions (Spex Certiprep Inc., Metuchen, NJ), were used to evaluate the performance of the plasmas. The line intensity ratio, Mg II/Mg I, was measured to gauge the robustness of the ICP. The Mg II/Mg I ratios were corrected for differences in the efficiency of the Echelle grating by dividing the ratios by a factor of 0.56.[22,23] To evaluate analytical performance, an organo-metallic standard containing 10 μg g^{-1} As, Hg, and Pb in xylene (VHG LABS, Manchester, NH) was analyzed.

Plasma ignition with the DIHEN

Table 2 presents the ignition sequence recommended by the manufacturer for the nebulizer-spray chamber arrangement and the new sequence proposed in this work for operation with the DIHEN. The default ignition process for the conventional nebulizer is changed because it involves drastic changes in the intermediate and outer gas flows, which would melt the DIHEN nozzle. For the default ignition sequence, the maximum Rf power (2000 W) is applied while the igniter spark seeds electrons through the outer gas flow for approximately 3 s. At this stage, the outer gas is reduced to 1.5 L min^{-1} while the intermediate gas (so called auxiliary boost by the manufacturer) is increased to 26 L min^{-1}. Once the plasma is ignited, the default condition changes to the run transition mode by setting the intermediate gas flow temporarily to zero (to eliminate capillary plasmas or streamers formed during ignition). This transition stage creates plasma conditions, which would damage the DIHEN nozzle due to excessive heating. The new ignition sequence used in this work eliminates this problem by fixing the intermediate gas and the outer gas at 4 L min^{-1} and 20 L min^{-1}, respectively, using external gas controllers. Once the plasma is ignited, the outer and intermediate gases are reduced to 15 and 2 L min^{-1},

Table 2 Ignition and operating conditions for the DIHEN and conventional nebulization used on the Varian Vista radial and axial ICPAES instruments

	Ignition procedure recommended by Varian for conventional nebulization		Ignition procedure used in this work for the DIHEN	
Parameters	Ignition mode	Run mode	Ignition mode	Run mode
Rf Power/W	2000	1200	2000	1500–1700[a]
Outer gas flow rate/L min^{-1}	1.5	15	20	15
Intermediate gas flow rate/L min^{-1}	~26	1.5	4	2
Nebulizer gas flow rate/L min^{-1}	0	0.90	0	0.15

[a]Radial instrument may be operated at maximum Rf power of 1700 W.

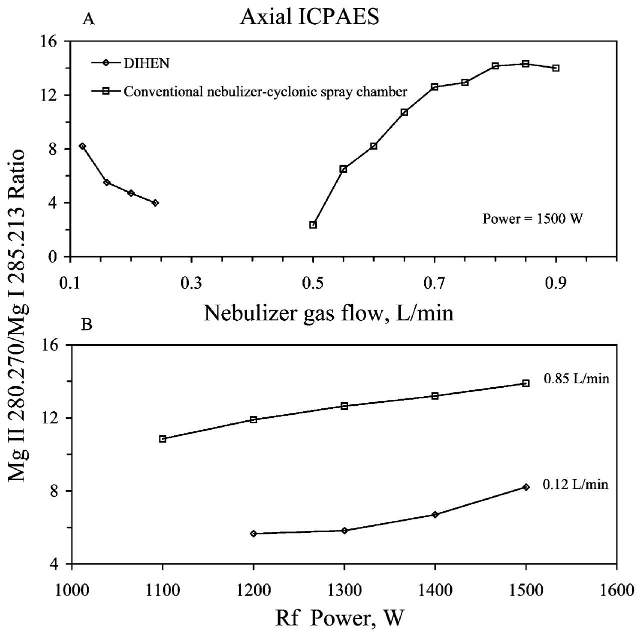

Fig. 1 Ratios of Mg II/Mg I measured with the DIHEN and the conventional nebulizer-spray chamber arrangement as a function of nebulizer gas flow rate (A) and rf power (B). The axially viewed instrument was used. Solution uptake rate for conventional nebulizer-spray chamber = 900 μL min^{-1} and for DIHEN = 60 μL min^{-1}.

respectively. No transition stage is necessary and the plasma smoothly ignites without the risk of melting the nebulizer tip.

Results and discussion

Plasma robustness

In ICPAES, the efficiency of energy transfer in the plasma is measured by plasma robustness. Under robust conditions, no significant variation in the analyte signal intensities is observed when the matrix or reagent composition changes. 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/Mg I, is commonly used to estimate plasma robustness, with higher ratios indicating more robust plasma.[22,24–33] In this connection, experiments are conducted to explore the robustness of the plasma in the axial and radial mode for direct injection of the aerosol using the DIHEN in comparison with conventional nebulization.

Fig. 1 presents a comparison of the Mg II/Mg I ratios obtained for the axially viewed plasma using the concentric nebulizer-cyclonic spray chamber arrangement and the DIHEN as a function of nebulizer gas flow rate (Fig. 1A) and Rf power (Fig. 1B). Higher Mg II/Mg I ratios are observed at higher Rf powers. The best Mg II/Mg I ratios for the DIHEN are obtained at an rf power of 1500 W and nebulizer gas flow rate of 0.12 L min^{-1}. At less than 0.12 L min^{-1}, a stable aerosol could not be produced with the DIHEN. Under optimum nebulizer gas flow rate and at 1500 W, the Mg II/Mg I ratios obtained with conventional nebulization are significantly higher than the values obtained with the DIHEN. In addition, the ratios obtained with the DIHEN exhibit a slightly greater slope as a function of the Rf power, indicating that the excitation conditions of the plasma operated with the DIHEN are more sensitive to changes in plasma properties. Note that the maximum Rf power in the axial instrument is limited to 1500 W whereas for the radial instrument, the maximum Rf power is 1700 W. The Mg II/Mg I ratio obtained for the DIHEN using the axially viewed instrument is similar to that obtained with the Elan 5000 generator in our previous

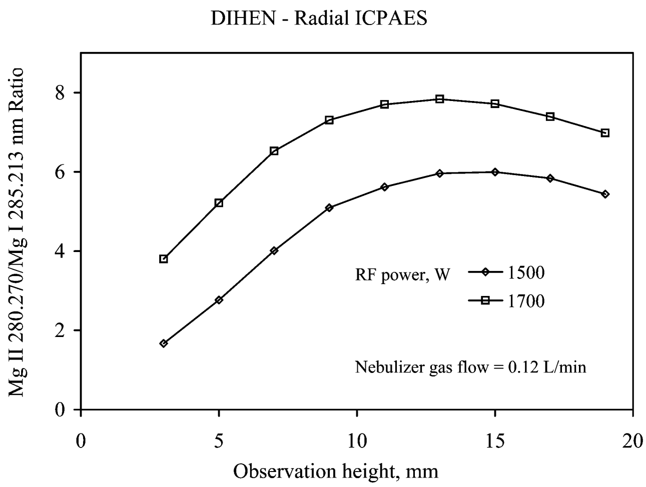

Fig. 2 Ratios of Mg II/Mg I measured with the DIHEN as a function of observation height in the radially viewed instrument. Nebulizer gas flow rate = 0.12 L min^{-1} and solution uptake rate = 60 μL min^{-1}.

ICP-AES work (8.3 *vs.* 7.1 under optimum operating conditions).[1] In both the axially and radially viewed instruments, the plasma is less robust when the aerosol is introduced directly into the plasma, compared to conventional nebulization.

Fig. 2 shows ratios of Mg II/Mg I as a function of observation height for the radially viewed Ar ICP operated with the DIHEN at two power levels. As shown earlier, high rf power and low nebulizer gas flow rate are necessary in direct nebulization of the aerosol. The Mg II/Mg I ratios obtained at higher Rf power (1700 W) are significantly improved, with the optimum observation height occurring at 13 mm.

Signal-to-background ratio, detection limit, and precision using the DIHEN and conventional nebulization system

Table 3 presents signal to background ratios (SBRs), detection limits, and precision for a number of elements measured for a concentration of 1 μg mL^{-1} in the axially viewed mode using the DIHEN and conventional nebulizer-cyclonic spray chamber arrangement. Generally, SBRs obtained with the conventional nebulizer are 2 to 4 times lower than those values obtained with the DIHEN. For both nebulization systems, SBRs obtained with the axially viewed instrument (Table 3) are nearly 10 times better than those obtained with the radially viewed instrument (not shown), which is in agreement with previous studies using conventional nebulization.[22,28,31–33] Detection limits achieved with the DIHEN are similar or superior, by up to a factor of 3, to those obtained with the conventional set-up. Precision values obtained in DIHEN-ICPAES are comparable with conventional nebulization. In general, figures of merit measured in this work for Ar ICP are similar to those previously reported for the DIHEN and conventional nebulization system.[15]

Matrix effects from sodium and nitric acid in Ar ICPAES with the DIHEN

Matrix interferences due to the presence of easily ionized elements are well documented in conventional nebulization.[28–31] The presence of easily ionized elements may result in either an enhancement or a depression of the analyte signal intensity, which can be minimized using robust plasma conditions. In this study with the DIHEN, a sodium chloride solution (0.1% and 0.5% w/w) is introduced into the axially viewed ICP. Higher sodium concentrations are not recommended for the DIHEN because of the possibility of clogging the nebulizer.[1]

Fig. 3 presents the line intensity ratios with and without the presence of 0.1% and 0.5% Na for the concentric

Table 3 Figures of merit measured for the DIHEN compared to the conventional nebulizer-cyclonic spray chamber arrangement using the axial Varian Vista ICPAES instrument

		Signal-to-background ratio		Detection limit/ng mL^{-1}		Precision (%RSD)	
Emission lines/nm	E_{sum}/eV	Conventional nebulizer-spray chamber	DIHEN	Conventional nebulizer-spray chamber	DIHEN	Conventional nebulizer-spray chamber	DIHEN
Cr I 357.860	3.46	3	12	3	1	0.5	0.5
Al I 396.152	3.90	3	4	4	2	0.3	0.4
Cd I 228.802	5.42	22	50	0.4	0.2	0.7	1
Ba II 493.408	7.72	24	105	0.3	0.1	1	0.8
U II 385.957	9.43	2	4	28	29	0.3	0.5
Mg II 280.270	12.07	207	479	0.1	0.03	0.8	1
Mn II 257.610	12.25	107	269	0.1	0.04	1	1
Tl II 190.794	12.60	5	10	5	5	0.7	0.5
Co II 238.892	13.46	18	47	0.6	0.4	0.7	0.4
Ni II 230.229	14.60	10	20	1	0.6	0.7	0.9
Pb II 220.353	14.79	10	19	2	1	0.6	0.4
Zn II 202.548	15.50	98	143	0.2	0.2	0.5	0.4
Uptake rate/μL min^{-1}		900	60				
Nebulizer gas/L min^{-1}		0.85	0.12				
Rf power/W		1500	1500				
Replicate read time/s		10	10				
Replicates		10	10				

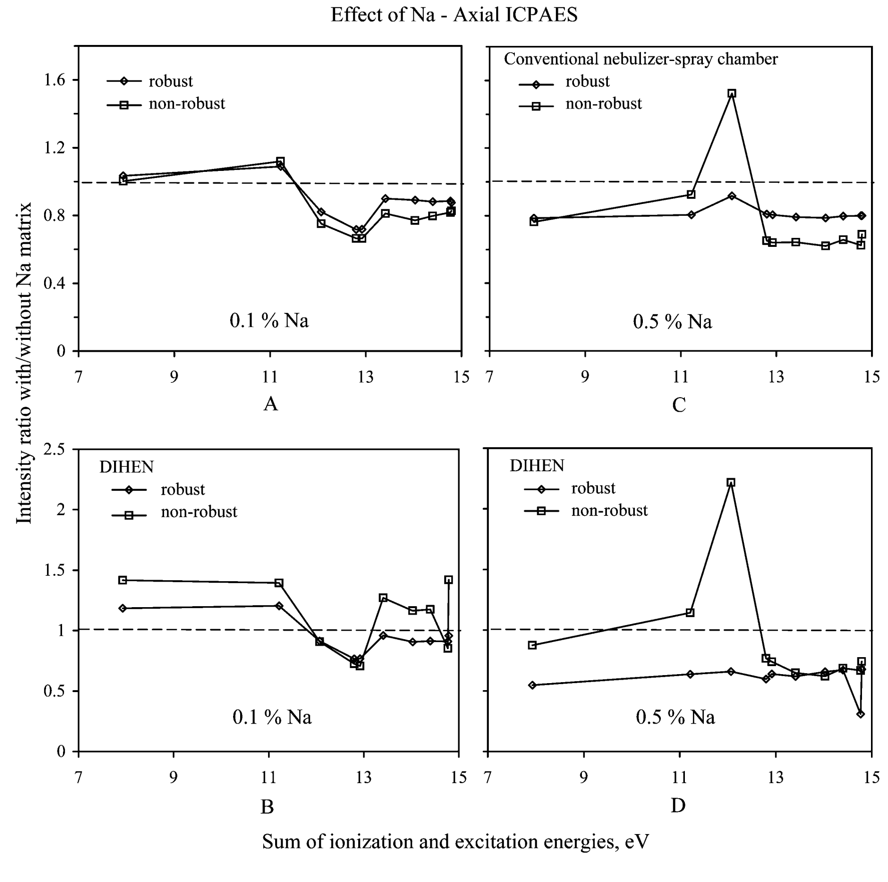

Fig. 3 Matrix effects using 0.1% Na (A and B) and 0.5% Na (C and D) with the DIHEN and the conventional nebulizer-spray chamber arrangement for the axially viewed instrument. Operating conditions for conventional nebulizer-spray chamber are: 1500 W, 0.85 L min^{-1}, and 900 μL min^{-1} (robust) and 1000 W, 1.15 L min^{-1}, and 900 μL min^{-1} (non-robust) and for DIHEN are 1500 W, 0.12 L min^{-1}, and 60 μL min^{-1} (robust) and 1000 W, 0.26 L min^{-1}, and 60 μL min^{-1} (non-robust) for Rf power, nebulizer gas flow rate, and solution uptake rate, respectively.

nebulizer-spray chamber and the DIHEN, as a function of the energy sum (*i.e.* the sum of ionization and excitation energies) of the spectral lines listed in Table 4, under robust and non-robust plasma conditions. For the conventional set-up, a robust condition is achieved by using an Rf power and nebulizer gas flow rate of 1500 W and 0.85 L min^{-1}, respectively, while non-robust condition is obtained using Rf power and nebulizer gas flow of 1000 W and 1.15 L min^{-1}, respectively. Similarly, for the DIHEN, Rf powers and nebulizer gas flows of 1500 W and 0.12 L min^{-1} (robust) and 1000 W and 0.26 L min^{-1} (non-robust) are used. The matrix effect profiles exhibit a complex behavior with energy

Table 4 Emission lines used in Figs. 3, 4, 5, and 7

Emission lines/nm	E_{sum}/eV
Ba II 455.403	7.93
Ba II 233.527	11.22
Mg II 280.270	12.07
Cr II 205.560	12.80
Cr II 267.716	12.92
Co II 238.892	13.41
Ni II 231.604	14.03
Ni II 216.555	14.40
Cd II 214.439	14.77
Pb II 220.353	14.79

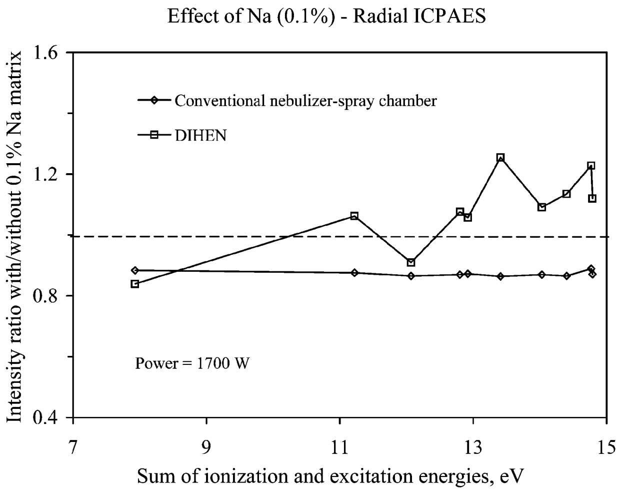

Fig. 4 Matrix effects using 0.1% Na with the DIHEN and the conventional nebulizer-spray chamber arrangement for the radially viewed instrument. Operating conditions for conventional nebulizer-spray chamber are 1700 W, 0.75 L min^{-1}, and 900 µL min^{-1} and for DIHEN are 1700 W, 0.12 L min^{-1}, and 60 µL min^{-1} for Rf power, nebulizer gas flow rate, and solution uptake rate, respectively.

sum and matrix concentration, however, in general, a non-robust condition creates a greater deviation and scatter from 1 for both the DIHEN and the conventional set-up, with greater deviation noted for the DIHEN, as a function of the energy sum. Under robust conditions, the response function is generally closer to 1, showing less matrix effect for the conventional set-up compared to the DIHEN.

The effect of 0.1% Na matrix is shown (Fig. 4) using the DIHEN and conventional nebulizer-spray chamber under robust conditions, for the radially viewed ICP. Again, a less severe matrix effect is found with the conventional nebulizer-spray chamber arrangement compared to the DIHEN. Also, with the radially viewed instrument, operating at 1700 W, less matrix effect is observed compared to the axially viewed instrument at 1500 W (Fig. 3). Fig. 5 shows the impact of the solution uptake rate on 0.5% Na matrix effect with the DIHEN under a robust plasma condition using the axial ICP-AES instrument. At 30 µL min^{-1}, signal suppression is less severe and a response function close to 1 is observed, mainly because less Na and solvent are introduced into the ICP at lower solution uptake rates.

The introduction of acidic solution to the plasma suppresses the analytical signal in ICPAES.[33,34] However, the robustness of the ICP for introduction of nitric acid solution could not be investigated because the plasma was not sustained with the DIHEN at acid concentrations greater than 2%. This instability is not observed with the conventional nebulization or with a homemade ICPAES instrument operated with the DIHEN[1] or in DIHEN ICPMS studies.[3–12] The reason for this limitation is unclear at this moment for the Varian ICPAES, but two tentative

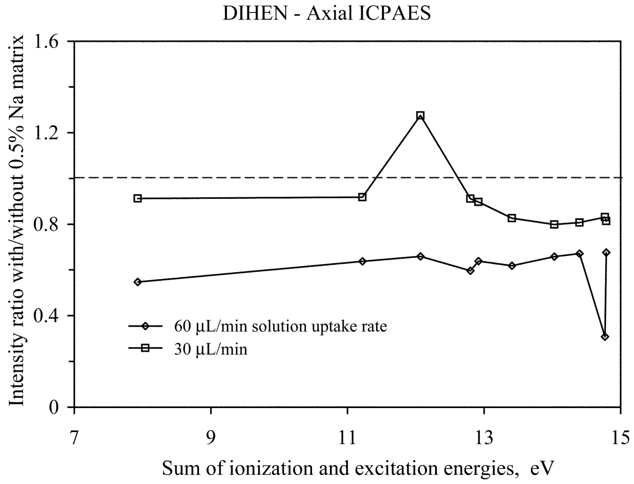

Fig. 5 Matrix effect at 30 and 60 µL min^{-1} solution uptake rate using the DIHEN-axial instrument for the introduction of 0.5% Na. The plasma was operated at Rf power = 1500 W and nebulizer gas flow = 0.12 L min^{-1}.

explanations may be considered. Perhaps, direct solution nebulization alters the frequency of the free-running generator beyond the frequency range of the current instrument. This range (40 ± 0.2 MHz) is smaller than the frequency limits of the Elan 5000 Rf generator (40 ± 1 MHz) for which the plasma tolerates even a 2 M nitric acid solution using the DIHEN.[1] Alternatively, the sudden increase in plasma electrical conductivity with the introduction of acid using the DIHEN leads to enhanced interactions between the plasma tail flames and the optical sampling port, and thus causing plasma shutdown.

Mixed-gas ICP studies and the DIHEN

In our previous report, we briefly explored the potential of mixed-gas plasmas for increasing the robustness of the ICP in direct liquid introduction with the DIHEN.[1] The current study expands beyond the earlier work by including several spectral lines having energy sum ranging from 3.14 to 15.51 eV. The improvement in SBRs for 15 spectral lines is presented in Table 5 for the introduction of 5% v/v of oxygen to the outer plasma gas flow using an axially viewed ICPAES with the DIHEN and conventional nebulizer-spray chamber arrangement. The use of oxygen improves the SBRs to some extent for

Table 5 Improvement in signal to background ratios for Ar–O_2 ICP over Ar ICP for axially viewed Varian Vista ICPAES using two nebulization systems

		SBR improvement factor	
Emission lines/nm	E_{sum}/eV	DIHEN	Nebulizer-cyclonic spray chamber
Al I 396.152	3.14	1.3	1.7
Mg I 285.123	4.35	4.0	0.7
Zn I 213.587	5.80	4.3	0.6
Se I 203.985	6.32	2.2	0.3
As I 188.980	7.87	1.5	0.6
Ba II 455.403	7.93	2.5	0.4
Ba II 233.527	11.22	0.9	0.6
Mg II 280.270	12.07	5.7	0.7
Mn II 257.610	12.25	4.6	0.7
Cr II 205.560	12.80	1.8	0.5
Co II 238.892	13.41	2.4	1.6
Ni II 216.555	14.60	2.3	0.2
Cd II 214.439	14.77	8.7	0.8
Pb II 220.353	14.79	2.9	1.2
Zn II 202.548	15.51	12.4	0.7
Uptake rate/µL min^{-1}		60	900
Nebulizer gas/L min^{-1}		0.12	0.75
Rf power/W		1500	1500

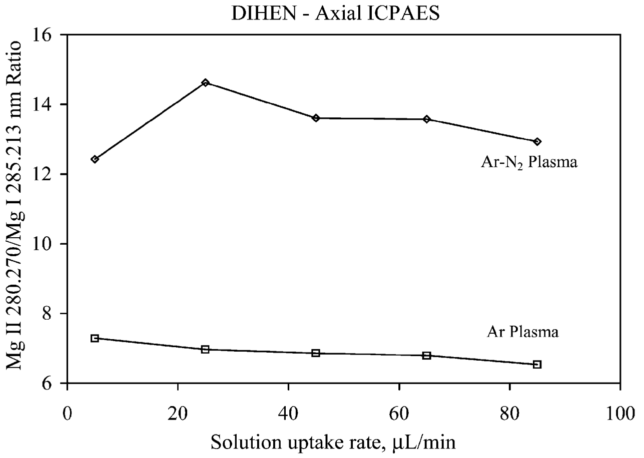

Fig. 6 Effect of solution uptake rate on ratios of Mg II/Mg I for Ar and Ar–N_2 plasma using the DIHEN-axial instrument. The plasma was operated at Rf power = 1500 W and nebulizer gas flow = 0.12 L min^{-1}.

the DIHEN, particularly for hard spectral lines such as Cd 214.439 nm and Zn 202.548 nm, but not for conventional nebulization.

Fig. 6 shows Mg II/Mg I ratios measured for Ar ICP and Ar–N_2 ICP, with 5% N_2 in the outer gas flow, as a function of solution uptake rate for the axially viewed plasma using the DIHEN. An increase in Mg II/Mg I ratio is observed for the Ar–N_2 ICP, providing ratios up to 14.6, indicating a more robust plasma. A slight decrease in Mg II/Mg I ratio is observed with increasing solution uptake rate, *i.e.* increasing solvent load to the plasma. For the Ar–N_2 ICP, the plasma is unstable at very low solution uptakes rates, causing a drop in Mg II/Mg I ratios (12.5 obtained at 5 μL min^{-1}).

Fig. 7 shows the line intensity ratio with and without Na (0.5%) as a function of the energy sum of the spectral line using the DIHEN-axially viewed instrument. Addition of oxygen or nitrogen to the outer gas flow moderates the effect of sodium when the DIHEN is utilized. A response function with less deviation from 1 is obtained for the Ar–N_2 and Ar–O_2 plasmas compared to the Ar ICP. This behavior is indicative of the greater robustness of the Ar–N_2 and Ar–O_2 plasma, where higher Mg II/Mg I ratios are observed.

Analysis of trace elements in organo-metallic standard

To examine the utility of the DIHEN-ICPAES approach, a custom made organo-metallic standard (VHG LABS) containing

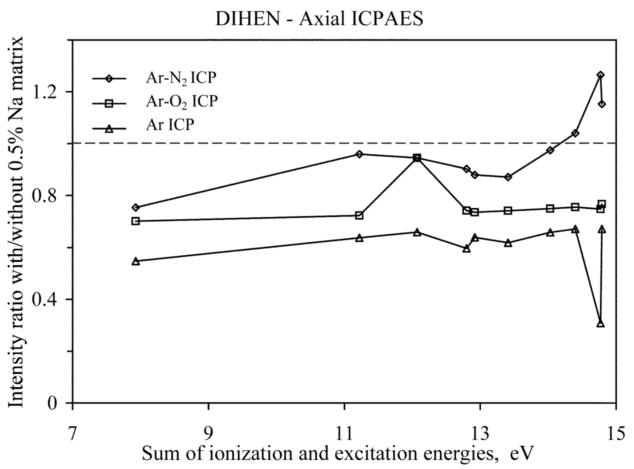

Fig. 7 Matrix effect in Ar, Ar–O_2, and Ar–N_2 plasmas using the DIHEN-axial instrument for the introduction of 0.5% Na. The plasma was operated at Rf power = 1500 W, nebulizer gas flow = 0.12 L min^{-1}, and solution uptake rate = 60 μL min^{-1}.

Table 6 Analysis of organo-metallic standard in xylene using the DIHEN-axially viewed Varian Vista ICPAES

Spectral line	Certified concentration/μg g^{-1}	Measured concentration[a]/μg g^{-1}
As 193.696	10.1 ± 0.1	11.4 ± 0.7
Hg 184.887	10.1 ± 0.1	9.1 ± 0.8
Pb 220.353	10.1 ± 0.1	11.0 ± 0.4

[a] Rf power = 1500 W, nebulizer gas flow rate = 0.12 L min^{-1}, solution uptake rate = 10 μL min^{-1}, outer gas flow rate = 15 L min^{-1} (10% oxygen), average of 5 determinations. The concentration uncertainties represent 1 σ.

10 μg g^{-1} As, Hg, and Pb in xylene was analyzed using a four-point standard addition technique. The standard was diluted to 5 μg g^{-1} for analysis. Concentrations found are illustrated in Table 6 along with the certified values for As, Hg, and Pb. In order to prevent carbon build-up on the DIHEN and to moderate the effects of the organic solution on the plasma, 10% O_2 was introduced into the outer gas flow of the plasma at a solution uptake rate of 10 μL min^{-1}. These ICPAES conditions are less restrictive than those used in DIHEN-ICPMS for similar analyses.[12] However, the data presented here are the best that can be obtained at this time with the current DIHEN-ICPAES set-up. Using a similar DIHEN, the sample has also been analyzed on an ICPMS system with much better precision[12] than the ICPAES system, perhaps due to design differences in generators and sampling interfaces.

Conclusions

The direct injection high efficiency nebulizer was coupled to radially and axially viewed ICPAES spectrometers by slight modifications to the commercial instrument. The plasma ignition process was modified significantly, simplifying operation with the DIHEN and also preventing damage to the DIHEN nozzle. The plasma required high Rf power (up to 1700 W), low nebulizer gas flow rate (0.12 L min^{-1}), and low solution uptake rate (30 μL min^{-1}) for operation of the DIHEN under robust conditions. These conditions differed markedly from those required for a conventional nebulizer-spray chamber arrangement. Signal-to-background ratios, detection limits, and precision values obtained with the DIHEN were similar or superior to those obtained with the conventional nebulizer-spray chamber arrangement. Studies of matrix effects with sodium solutions showed that the DIHEN was more susceptible to changes in matrix compared to the conventional nebulizer-spray chamber arrangement, as indicated by the difference in Mg II/Mg I ratio. The Mg II/Mg I ratios and signal to background ratios were improved in mixed-gas plasmas, resulting in reduced matrix effect, thus showing the benefits of mixed-gas ICPs for direct solution nebulization.

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