DEVELOPMENT AND CHARACTERIZATION OF A 9-mm INDUCTIVELY-COUPLED ARGON PLASMA SOURCE FOR ATOMIC EMISSION SPECTROMETRY

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SUMMARY

A new 9-mm (i.d.) inductively-coupled plasma (ICP) torch is described which supports a stable, analytically useful plasma at less than 500 W of r.f. power and 7 l min^{-1} total argon gas flow. Detection limits, working curves and other analytical characteristics of the new device are compared with those of both a miniature (13-mm i.d.) and conventional (19-mm i.d.) ICP. Although temperatures of the new plasma are somewhat lower than those in the larger plasmas, the new system offers promise for future, miniaturized ICP instruments.

The current acceptance of the inductively-coupled plasma (ICP) has been stimulated by a number of favorable performance characteristics [1–6]. However, the high initial and operating costs and large physical dimensions of such devices have limited their use mostly to larger laboratory facilities with high sample throughput. In order to expand the use of ICP systems, numerous workers have focussed upon improving the plasma efficiency by reducing both its power and gas-flow requirements.

Several new torch designs have been introduced which operate on lower power and argon gas consumption without sacrificing the analytical capabilities of the ICP. A substantial reduction in argon consumption has been realized by employing water rather than gas for cooling the outer tube of the torch [7]. The water-cooled plasma could be sustained on as little as 2 l min^{-1} argon, but yielded low sensitivity. Allemand and Barnes [8] used computer modelling to design torches which not only consumed less gas, but also ignited more easily. Genna et al. [9], by modifying the tangential coolant tube inlet of a torch, were able to produce higher swirl velocities and thereby allow the plasma to be sustained at a 30–40% lower argon flow rate. This latter modification also improved the discharge performance of the plasma.

An alternative approach toward reducing the argon consumption and power requirement of an ICP has been to decrease the size of the torch. Savage and Hieftje [1] have described a reduced-size ICP which operates at less than 1 kW of r.f. power and an argon flow of 8 l min^{-1} . Significantly,

these economies have been realized without degrading analytical performance. There appears to be no fundamental reason why a further reduction in the size of the ICP could not be achieved. Allemand et al. [10] have reported the development and characterization of both 13-mm and 9-mm ICP torches. The 13-mm ICP performed similarly to conventional ICP's, but with 20% lower argon consumption and 23% less r.f. power. The 9-mm ICP yielded poorer detection limits, particularly at lower r.f. power levels (700 W). Other performance characteristics of the 9-mm ICP were not discussed in the communication.

In the present study, a new 9-mm torch is reported which supports a plasma at approximately 1/3 the r.f. power and less than half the argon flow of a conventional torch. Although the resulting plasma yields somewhat greater interelement interferences than its larger counterpart, it offers excellent sensitivity and linearity. Moreover, with its low operating requirement (500 W, 7 l Ar min⁻¹), it suggests the future development of compact, inexpensive instrumentation for ICP spectrometry.

Preliminary considerations on the selection of plasma size and operating power

It is appropriate to ask the degree to which the ICP can be reduced in size and yet remain a viable analytical tool. Although several considerations necessary to answer this question have been offered before [8, 9], a fundamental limit is posed by the "skin-effect" exhibited by all high-frequency discharges. According to the skin-effect model, most of the energy in such discharges is introduced near the outer boundary (or skin) of the plasma; the energy introduction decreases in an approximately exponential fashion toward the plasma center. As a result, the conditions (temperature, conductivity, etc.) in the plasma center do not markedly influence the coupling of r.f. energy into the discharge; this feature is responsible in part for the relative immunity of the ICP to changes in sample aerosol composition.

The distance into the plasma penetrated by the energy-coupling field is characterized by the "skin depth" which, by definition, is the depth where the r.f. energy has been reduced to 36.8% (1/e) of its surface (skin) value. For a plasma operating at 27.12 MHz, the skin depth is approximately 2 mm. Therefore, at a distance of 4 mm from the discharge surface, the r.f. energy addition should be only $(0.37)^2 = 0.13$ of its surface value. Stated differently, sample sent into the plasma a distance of 4 mm from its surface should have less than a 13% effect on energy coupling. Taking this degree of perturbation to be the maximum permissible, the plasma must have a diameter at least 8 mm greater than that of the aerosol stream sent into it. Assuming nearly laminar aerosol flow, and given the 0.75–1.0 mm sample tube found in most torches, one then calculates a minimum plasma diameter of 9 mm, the size of torch chosen for the present work.

Because it is desirable that the 9-mm plasma operates as well as a conventional one, the smaller torch was sustained at comparable power density.

Using the toroidal model for plasma volume described earlier [1] and inner and outer toroid radii of 1.5 and 3.5 mm, respectively, a plasma volume of 49 mm^3 was calculated. To produce in this discharge the same power density of 11.7 W mm^{-3} computed for larger (miniature and conventional) plasmas, an r.f. input of approximately 570 W is needed.

An empirical means of establishing the optimal ICP input power was offered by Greenfield and Burns [11] who suggested that sources be compared on the basis of the signal-to-background (S/B) ratios that they provided. Figure 1 shows the relationship between S/B and r.f. power input for the torch used in the present study. From a third-order spline fit to these data, an applied r.f. power of 570 W seems optimal.

The foregoing considerations argue that a 9-mm torch operated at an applied r.f. power near 570 W should provide the most efficient ICP design. However, practical considerations urge that even lower powers be utilized, if they are viable. In particular, extremely inexpensive r.f. power supplies of 500 W capabilities have been developed for use in amateur radio transmissions. Moreover, at power levels of 500 W and below, compact solid-state supplies can be employed. For these reasons, the new 9-mm torch was tested at an applied power of 500 W, with the anticipation that a slight worsening in analytical characteristics might result.

EXPERIMENTAL

Instrumentation

Most of the experimental system used in this study is identical to that described previously [1]. Details concerning slight alterations are discussed below.

Load coils. In order to increase both the electric field strength and the

Fig. 1. Effect of applied r.f. power on the signal-to-background ratio of the new torch at the 422.7-nm Ca line. An aqueous solution of calcium ($10 \mu\text{g ml}^{-1}$) was aspirated into the plasma during all signal measurements; background readings were taken at the same wavelength with a blank being aspirated.

magnetic flux density needed to sustain a smaller plasma [3, 8, 12, 13], a new water-cooled load coil was constructed. The new coil consisted of four turns of 1.6-mm copper tubing, which covered a length of 1 cm in the plasma and had a diameter of 2 cm, to accommodate the smaller plasma torch. A spark from a Tesla coil served as the plasma igniter.

Plasma torch. The basic configuration of the torch used in this study, shown in Fig. 2, is the same as that in both the miniature and conventional ICP [1] except for a reduction in size. In all phases of the development and construction of this device, hydrodynamic techniques were utilized to insure proper function [14].

Several design features of the new torch are critical to its proper operation. The quartz tangential inlet tubes for both the plasma and coolant gases were constricted to 1.5 mm to increase the swirl velocity. Also, the outer diameter of the flared-out portion of the plasma tube was increased to force the coolant gas against the coolant tube and thereby shield the tube from the plasma and further increase the swirl velocity. The length (3 mm), shape, and smooth taper of the flared-out portion also proved to be critical to maintain a stable vortex.

The 0.75-mm center capillary injection tube extended from the base of the torch to the top of the plasma tube to produce a laminar jet of sample aerosol. Injection tube diameters from 0.60 to 0.75 mm were examined successfully with the larger diameter being ultimately selected. This larger diameter permits longer sample residence times in the plasma, but seems not markedly to affect r.f. energy coupling into the discharge. As mentioned earlier, the size of the sample channel is especially critical in this smaller

Fig. 2. Design features of 9-mm ICP torch. (A) Torch construction; except for capillary injector, all tubing is of 1-mm wall thickness. (B) Photograph of torch.

ICP because of the likelihood of the sample aerosol intercepting the energy-coupling "skin" region. The coolant tube extended at least 12 mm above the plasma tube to minimize optical background caused by entrained air components.

Nebulizer and spray chamber. Sample was introduced into the plasma by means of a cross-flow nebulizer (Model TN-1, Plasma-Therm Inc., Kresson, NJ). The nebulizer was mounted in a teflon cap which fits over one end of a dual-tube spray chamber similar to type 2C described by Schutyser and Janssens [15]. Sample solution was delivered at a rate of 0.85 ml min^{-1} by a peristaltic pump. No desolvation apparatus was employed.

Procedures

Detection limit calculations and analyses of SRM. The 9-mm ICP was utilized to establish detection limits of various elements and their concentrations in NBS standard reference materials (SRM). Operating parameters for these determinations are given in Table 1. For detection limit investigations, the viewing region in the plasma was optimized for each element by rotating the 150-mm (diameter) collection mirror. During the determination of eight elements in NBS standard 1571, a compromise viewing region was selected for the elements of interest. All standard solutions and blanks were appropriately matrix-matched for SRM analyses.

Nebulizer flow rate was limited in all cases to 0.86 l min^{-1} , above which the plasma had a tendency to extinguish; moreover, below 0.60 l min^{-1} the pneumatic nebulizer was found not to function efficiently. Five measurements of both the sample and blank were used to calculate the detection limit for each element according to the procedure outlined by Winefordner et al. [16].

Plasma excitation temperature measurements. Excitation temperatures in the 9-mm plasma were determined by using the slope or Atomic Boltzmann Plot method [17]. Background-corrected intensities were obtained for three

TABLE 1

General operating conditions for 9-mm ICP

	Plasma ignition	Plasma operation
R.f. power	1.0 kW	500 W
Ar flows (l min^{-1})		
coolant	9.8	6.4
plasma	0.42	—
nebulizer	—	0.75
Sample uptake rate	—	1.2 ml min^{-1}
Monochromator slits	width $50 \mu\text{m}$ ($0.2 \text{ \AA}$ spectral band width), height 5 mm	
Time constant	1 s	

iron emission lines whose wavelengths, excitation energies, statistical weights, and relative transition probabilities have been documented elsewhere [18]. The iron(III) sulfate solution employed contained $1000 \mu\text{g Fe ml}^{-1}$. Conditions used during temperature measurements are identical to those in Table 1 except for a narrowing of the monochromator slits to $40 \mu\text{m}$ for better resolution. The observation zone was centered at 15.5 mm above the load coils and encompassed a 4.1-mm vertical segment of the plasma.

Plasma spectral background scans. The optical arrangement used for spectral background scans has been described elsewhere [19]. With this design, the viewing region was a rectangle 8 mm high by $80 \mu\text{m}$ wide centered 11 mm above the load coils. Operating conditions for these scans are listed in Table 1. Spectral background scans were obtained while a solution containing $100 \mu\text{g Mn ml}^{-1}$ and $10 \mu\text{g Ca ml}^{-1}$ was being sprayed into the plasma.

Plasma interference experiments. Classical interferences were examined with the modified optical design and silicon intensifier tube (SIT) detection system described previously [20]. A minor alteration was the placement of a neutral-density filter in front of the entrance slit of the monochromator to prevent saturation of the detector.

Reagents

Stock solutions were prepared as described by Dean and Rains [21]. All salts and acids were reagent-grade and water used in dilution was distilled-deionized. Where necessary, solutions and blanks were matrix-matched by addition of the appropriate salt and acid.

RESULTS AND DISCUSSION

Plasma ignition and operating characteristics

Plasma ignition was relatively simple under the conditions listed in Table 1. The best method for ignition was to form initially a filamentary plasma [9, 12] at low r.f. power (300 W). Once the filamentary plasma had been formed, the r.f. power was increased to ca. 1 kW and the now conventional toroidal plasma stabilized. Next, the nebulizer gas flow was initiated [cf. Table 1]; occasionally (30% of the time), initiation of nebulizer gas flow would extinguish the plasma, requiring the ignition procedure to be repeated. Operating conditions were then set for the particular experiment.

During operation, the 9-mm plasma would readily accept sample solutions up to $10000 \mu\text{g ml}^{-1}$ without difficulty. However, it was found that salt build-up in the tip of the capillary tube occasionally required ultrasonic cleaning in a dilute acid bath.

Excitation temperature

An excitation temperature of 4000 K was measured in the 9-mm plasma at a height of 15.5 mm above the load coils. This temperature is considerably

less than the 5000 K assigned to the conventional (19-mm) ICP [1], but not significantly lower than the 4300 K of the miniature (13-mm) discharge [1]. Partly responsible for this lower temperature is the reduced power density (500 W rather than 570 W) at which the 9-mm plasma operates. Moreover, the uncertainty associated with this method of determining excitation temperatures ($\pm 10\%$) lessens significantly the difference between the 9-mm ICP and the larger versions.

Background spectrum

As with the miniature and conventional ICP's, the background of the 9-mm discharge (cf. Fig. 3) was found to be complex and consisted of three types of spectral features: (1) continuum, (2) line spectra, and (3) band spectra. The detailed discussion of these features as they relate to the miniature ICP [22] is also applicable to the 9-mm ICP.

Detection limits and calibration curves

Table 2 lists detection limits for a number of elements determined in the 9-mm plasma, the 13-mm ICP, a conventional (19-mm) ICP and literature values. For every element but iron, detection limits obtained with the 9-mm torch are not significantly different from those obtained with the larger plasmas. No explanation can be given for the slightly poorer performance of the smaller discharge for iron determination.

For the conventional ICP the linearity of the calibration curves is over 5–6 orders of magnitude; similar results have been obtained with the miniature ICP [1]. Calibration curves for the 9-mm ICP, shown in Fig. 4, indicate the same wide dynamic range expected from other ICP systems. The straight lines (Fig. 4) were obtained from a least-squares fit to the original data using the equation $\log I = (a \pm S_a) + (b \pm S_b) \log c$, where I is the measured intensity, C is the analyte concentration ($\mu\text{g ml}^{-1}$), a and b are the intercept and slope, respectively, of the calculated line, and S_a and S_b are the calculated standard deviations in the intercept and slope. These least-squares parameters, cited in the legend to Fig. 4, reveal the near-unity slope of the calibration curves and their small departure from linearity, even over this extended concentration range. The least squares equation is also included for copper, although no plot is drawn because of overlap with the sodium curve.

Interferences

To examine the susceptibility of the 9-mm ICP to classical solute vaporization interferences, the influence of phosphate on the spatial emission profiles of the Ca I and Ca II lines was investigated. These effects were examined at two different r.f. power levels. Figure 5 (I) illustrates the influence of phosphate on the Ca I (422.7-nm) line; curve A was obtained from a solution containing $50 \mu\text{g Ca ml}^{-1}$ while curve B is from the same solution but with phosphate added at a molar ratio of 50 to 1 ($\text{PO}_4^{3-}:\text{Ca}$).

Fig. 3. Typical background spectrum of 9-mm ICP with $100 \mu\text{g Mn ml}^{-1}$ and $10 \mu\text{g Ca ml}^{-1}$ aspirated into it.

Profile X was obtained at 500 W r.f. power and profile Y at 750 W. The addition of phosphate as a matrix interference clearly causes a shift in the Ca I emission to regions higher in the plasma. Also, at higher r.f. power the profile shifts toward lower regions of the plasma. From these profiles, it is evident that, at any applied power, phosphate has an effect on Ca I emission,

TABLE 2

Detection limits (ng ml⁻¹) in various ICP sources

Element	Spectral line (nm)	9-mm ICP	13-mm ICP [1]	Conventional (19-mm) ICP [1]	19-mm torch	Reference
Al	396.15	4	5	3	2	[2]
Ba II	455.50	0.6	— ^a	— ^a	0.1	[3]
Ca II	393.37	0.08	0.07	0.04	0.07	[3]
Cd	228.80	10	42	13	30	[2]
Cu	324.75	1	8	2	1	[3]
Fe	371.99	51	10	12	5	[2]
Mg	285.21	2	6	2	0.7	[3]
Na	588.49	0.5	0.7	0.2	0.2	[3]
Ni	352.45	8	4	15	6	[2]
Pb	405.78	25	33	40	8	[2]
Zn	213.86	10	71	23	10	[12]

^aNot determined.

Fig. 4. Calibration curves obtained with the 9-mm ICP. Least-squares equations included for clarity (see text for discussion). (○) Ba II (455.4 nm) $\log I = 3.74 \pm 0.06 + (0.96 \pm 0.03) \log C$; $S_{yx} = 0.11$; (◻) Na I (588.9 nm) $\log I = 2.82 \pm 0.08 + (0.96 \pm 0.03) \log C$; $S_{yx} = 0.14$; (Δ) Ba I (553.6 nm) $\log I = 1.96 \pm 0.03 + (1.01 \pm 0.02) \log C$; $S_{yx} = 0.06$; (◊) Fe I (371.9 nm) $\log I = 1.36 \pm 0.16 + (0.94 \pm 0.01) \log C$; $S_{yx} = 0.03$; Cu I (324.7 nm) $\log I = 2.77 \pm 0.11 + (0.92 \pm 0.05) \log C$; $S_{yx} = 0.20$.

but that a viewing region can be selected where the influence would be minimal or nonexistent.

The profiles in Fig. 5(II) indicate that phosphate causes a significant depression of the Ca II signal rather than just a spatial shift in intensity. Moreover, changes in applied r.f. power have little effect upon the degree of the depression. Because of this reduction in intensity, the interference of phosphate on Ca II emission cannot be nullified by spatial selection in the plasma, as was possible for the Ca I line. Although no mechanism can be offered here for these findings, the Ca I emission line would clearly offer the

Fig. 5. Effect of phosphate on the emission profiles of (I) the Ca I (422.7 nm) line and (II) the Ca II (393.4 nm) line, with changing r.f. power levels (Frames X, 500 W; Y, 750 W). Curves A represent analyte ($50 \mu\text{g Ca ml}^{-1}$) signal and curves B analyte plus interferent ($50:1$ molar ratio $\text{PO}_4^{3-}:\text{Ca}$). Relative scales X, 10^4 ; Y, 10^5 .

better conditions for minimizing the interference of phosphate in a practical analysis.

The effects of sodium and cesium on calcium emission were also examined in the 9-mm ICP. Profiles were obtained for both the Ca I and Ca II lines at r.f. powers of 500 W and 750 W. Figure 6(I) shows the influence of cesium on Ca I emission; in the profiles, curve A represents a $5 \mu\text{g Ca ml}^{-1}$ solution and curve B the same solution but with cesium added at a molar ratio of 140:1 (Cs:Ca). At both 500 W and 750 W, there is a significant enhancement of the Ca I emission when cesium is present although the enhancement at 750 W is somewhat lower. The influence of cesium on Ca II emission is shown in Fig. 6(II). At 500 W there is a significant depression of the Ca II emission while at 750 W there is relatively little effect (a downward shift of emission occurs as power is increased). The influence of sodium on calcium emission follows the same pattern as that discussed for cesium.

Based on these results, viewing regions can be selected to minimize the effect of an easily ionized species upon calcium. The influence on the Ca II emission is considerably less than on Ca I, particularly at higher r.f. power levels and would provide the best analytical conditions. The pattern displayed by these profiles strongly suggests that the smaller ICP suffers a greater degree of "ionization" interference than a larger ICP.

It is interesting in Figs. 5 and 6 that Ca II profiles peak higher in the plasma than Ca I profiles under any given set of operating conditions. Also, although the profiles of both lines are shifted downward by increases in r.f. power, the shift for the ion line is greater. These trends are the same as those expected from experience in an analytical flame, where ionization often lags behind atom formation and is strongly influenced by source temperature. In the ICP, however, it is doubtful that these straightforward mechanisms prevail, and further evidence will be needed to completely explain the observed behavior.

Determination of various elements in NBS SRM 1571 Orchard Leaves

To assess the performance of the 9-mm ICP system, the determination of several elements in a "real" sample was undertaken. Table 3 lists the determined values for eight elements along with the corresponding certified values for NBS SRM 1571. For all elements but manganese the values obtained were within the uncertainty range of the certified values. The manganese determination was only slightly higher than the acceptable certified value. The results indicate that the 9-mm ICP performs with good sensitivity and accuracy in the routine analysis of biological material.

Conclusions

Further reductions in the consumption of argon gas and r.f. power have been achieved through scaling down the ICP torch with little loss of analytical performance. The 9-mm torch can support a stable plasma under more economical operating conditions while accepting sample solution

Fig. 6. Effect of cesium on the emission profiles of (I) the Ca I (422.7 nm) line and (II) the Ca II (393.4 nm) line, with changing r.f. power levels (Frames X, 500 W; Y, 750 W). Curves A represent analyte ($5 \mu\text{g Ca ml}^{-1}$) signal and curves B analyte plus interferent (140:1 molar ratio Cs:Ca). Relative scales (I) X, 10^3 ; (I) Y, 10^4 ; (II) X, 10^4 ; (II) Y, 10^5 .

TABLE 3

Results for NBS SRM 1571 Orchard Leaves with 9-mm ICP torch^a

Element	Present study ($\mu\text{g g}^{-1}$)	Certified value ($\mu\text{g g}^{-1}$)	Element	Present study ($\mu\text{g g}^{-1}$)	Certified value ($\mu\text{g g}^{-1}$)
Ca	2.11 ^b	2.09 $\pm$ 0.03 ^b	Mn	96	91 $\pm$ 4
K	1.48 ^b	1.47 $\pm$ 0.03 ^b	Pb	47	45 $\pm$ 3
Mg	0.64 ^b	0.64 $\pm$ 0.02 ^b	Zn	25	25 $\pm$ 3
Fe	313	300 $\pm$ 20	Cu	11	12 $\pm$ 1

^aDigestion by standard methods [23]. ^b% (w/w).

readily. The ability to operate the smaller ICP stably at 500 W offers the prospect of solid-state ICP r.f. generators, which would reduce both cost and physical size of ICP-AES systems.

However, interferences in the current system are somewhat worse than in conventional plasmas. Because interferences from such disparate concomitants as Al, Cs, Na and phosphate were found to persist in the mini-ICP even at elevated r.f. power levels (750 W), they are believed to arise in part from the effect of sample components on the efficiency of energy coupling into the discharge. If this assumption is correct, operating the 9-mm ICP at higher frequencies (e.g. 40.68 MHz) should improve performance; at this higher frequency, the skin depth would be reduced and intrusion of sample material into the energy-coupling region would be lessened.

This paper is taken in part from the M.S. thesis of A. D. Weiss and from the Ph.D. thesis of R. N. Savage. The work was supported in part by the National Science Foundation through grants CHE 79-18073 and CHE 77-22152 and by the Office of Naval Research.

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