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**Title:** Mini, Micro, and High-Efficiency Torches for the ICP - Toys or Tools?

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**Abstract:**

Because the inductively-coupled plasma (ICP) is expensive both to purchase and to continue in operation, many workers have sought to reduce both the radiofrequency power and coolant argon ordinarily required to sustain the discharge. In one approach, the ICP has been reduced in size, in the hope that its analytical strengths could be retained but the power and argon required for it reduced. In the second approach, the torch used to support the discharge has been modified extensively. The final and most recent approach... (Cont.)
utilizes alternative torch cooling schemes using, for example, water or high air flows as a coolant. In this paper, these alternative approaches will be reviewed and assessed in terms of their practicability and analytical capability. Prospects for future torch modification and low-flow, low-power ICP instrumentation will be considered and discussed.
MINI, MICRO, AND HIGH-EFFICIENCY TORCHES
FOR THE ICP - TOYS OR TOOLS?

by

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INTRODUCTION

Despite its obvious appeal and widespread application, the inductively coupled plasma (ICP) ordinarily requires for successful operation unfortunately high radiofrequency power input and coolant argon flows. Such high-power (>1.5kW) plasmas require bulky, expensive instrumentation, can generate substantial radiofrequency interference and, if operated incorrectly, can be hazardous. Similarly, elevated argon consumption rates (>15 L/min) are not only costly, but necessitate either frequent changes of gas cylinders or the availability of a liquid-argon dewar.

The high cost of argon is particularly troublesome and has urged many investigators to consider the use of alternative gases to support the ICP. In North America, where argon is relatively inexpensive, it can be calculated that the annual cost of each L/min increment in argon flow is approximately $1000. That is, a conventional plasma which requires for its operation 18L/min will cost approximately $18000 per year for operation. By contrast, a low-flow plasma that consumes only 5L/min will require only $5000. Clearly, strong economic urgency drives the development of high-efficiency ICP systems.

Over the past several years, a number of investigators have sought to reduce the gas flow and power requirements of the ICP through modification of the torch required to sustain the discharge. These modifications include shrinking the torch's size, optimising torch geometries and operating conditions, and employing alternative cooling using, for example, water or high-velocity jets of air. In this paper, these alternative approaches to the development of a high-efficiency ICP will be reviewed and assessed and a view toward the future offered. The review will not attempt to be comprehensive, but will include a sampling of the alternative
approaches and a discussion of the studies which the author feels are particularly significant. The discussion will not proceed chronologically, but will instead examine the above-mentioned alternative approaches individually.

MINIATURISED ICP SYSTEMS

Perhaps the most straightforward approach to reducing gas flow and power in an ICP is simply to reduce the plasma's dimensions. If it can be assumed that ICP performance is dependent on power density in the discharge, a satisfactory unit could be designed for low-power operation just by configuring a proportionally smaller torch. Presumably, necessary gas flow would also be reduced. Such an approach would yield not only a more efficient ICP in terms of required gas flows and radiofrequency powers, but might also result in less atomic dilution, a factor which could enhance sensitivity and simplify the interfacing of the plasma to ion-detection systems.

The first description of an analytically effective miniaturised torch (1) involved a rather modest reduction in the torch's dimensions; its size and operating requirements are listed in Table 1 along with those of other systems to be discussed in this narrative. The miniaturised torch had a diameter approximately 2/3rds that of the conventional (18mm i.d.) torch and, interestingly, required approximately 2/3rd the radiofrequency power to provide similar analytical performance. From the original study (1) and later reports (2), the "mini-ICP" exhibited the same detection limits and working-curve linearity expected from a conventional-sized ICP. In later studies on the same system, it was shown that vaporization and ionization interferences (3) were also minimal and that the background emission spectrum from the mini-ICP (4) was just as structured and troublesome as that from the conventional source. In short, the mini-ICP can be viewed and utilised exactly as would the conventional source, but can be operated at 2/3rds of the
radiofrequency power and at a coolant flow of less than 81./min (2). Detection limits, interferences, and other figures-of-merit of the mini-ICP are collected in Tables 2-3, where they are compared with those obtained from other high-efficiency ICP systems.

In the course of the development of reduced-size torches, an interesting and useful aid to torch development was described by Sexton, et al. (5). In the test described, flowing water was directed into each of the gas inlet ports of the constructed ICP torch; from the pattern of the exiting water flow, the uniformity and concentricity of the quartz tubes in the torch could be evaluated. For example, water directed into the "coolant" (outer) argon inlet produced in a well-constructed torch a flat "fan" of water issuing from the top of the torch. The flatness of the "fan" indicated the swirl velocity in the torch, whereas the symmetry of the "fan" revealed tube concentricity and uniformity.

A further step in reducing ICP size was described by Allemand et al. (6), who tested not only a 13-mm torch like the "mini-ICP", but also a 9-mm device. Both torches utilized a smooth contour of the flared intermediate tube and sharp torch edges for uninterrupted gas flow. The entire torch was constructed of boron nitride, enabling it to be precisely machined rather than glass-blow. Reported detection limits for the 13-mm torch were, on the average, even better than those reported in the "mini-ICP" study (1). However, the interference from easily ionized elements (EIE) was slightly worse than exhibited by a conventional-sized unit. As shown in Table 1, the system was operated on slightly higher argon flows than was the "mini-ICP".

Allemand, et al. (6) indicated stability problems with a 9-mm (i.d.) torch and found that it required at least 700W for operation. In contrast, the study by Weiss, et al. (7) used the water-flow
testing approach (5) to develop an analytically useful "micro-ICP" of 9mm in inner diameter which could operate on less than 500W of RF power and 7L/min of total argon flow. Like the conventional and "mini" ICP, the "micro" torch yielded detection limits, working curves, and most other analytical characteristics expected of the ICP. Although the temperature of the micro-plasma was somewhat lower (4000K) than reported for other ICP discharges, the unit was shown useful for the analysis of real samples; refer to Tables 2-3 for a comparison of analytical characteristics of the various miniaturised plasmas.

Unfortunately, both vaporization interferences and those caused by an EIE are somewhat greater in the 9-mm plasma than in either the "mini-ICP" or in a conventional unit. The reason for this somewhat reduced performance lies presumably in the necessary interaction which occurs between sample aerosol and radiofrequency energy coupling into such a small plasma. In all radiofrequency discharges, power is coupled into the "skin" of the discharge, with coupling decreasing exponentially with distance from the discharge boundary. This feature is ordinarily characterised by the "skin depth", which is the distance from the plasma boundary where energy coupling has fallen to 0.37 of its maximum value. For plasmas like the ICP, the skin depth lies reportedly between 2mm (7) and 3mm (8).

Because energy coupling is minimal in the centre of a large ICP, aerosol can be directed into it with minimal effect on the energy-coupling process. Consequently, changes in aerosol flow or in sample composition should produce few matrix interferences. In contrast, extremely small discharges like the "micro-ICP" could be greatly upset by aerosol introduction. Even if the skin depth were 2mm and aerosol were restricted to a 1-mm channel in the discharge centre, some 13% of the plasma's energy coupling would
<table>
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<tbody>
<tr>
<td>Coolant tube i.d. (mm)</td>
<td>13</td>
<td>13</td>
<td>9</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>17</td>
<td>13.5</td>
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<td>13.5</td>
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<td>12</td>
<td>6.4</td>
<td>12</td>
<td>5</td>
<td>16</td>
<td>9</td>
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<td>30ᵇ</td>
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<td>0.8</td>
<td>4</td>
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<td>0.76</td>
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<td>0.3</td>
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<td>0.8</td>
<td>0.15</td>
<td>0.12</td>
<td>0.15</td>
<td>0.17</td>
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<td>0.36</td>
<td>1</td>
<td>1.2</td>
<td>1.35</td>
<td>1.0</td>
<td>1.5</td>
<td>1.5</td>
<td>2</td>
<td>2</td>
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<tr>
<td>Observation height (mm above coil)</td>
<td>15</td>
<td>13</td>
<td>15</td>
<td>13</td>
<td>10(18)</td>
<td>4</td>
<td>12</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td>10</td>
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<tr>
<td>Applied rf power (W)</td>
<td>1000</td>
<td>850</td>
<td>500</td>
<td>1200</td>
<td>350(16)</td>
<td>700</td>
<td>1100</td>
<td>500ᵇ</td>
<td>450ᵇ</td>
<td>1100</td>
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<tr>
<td>Excitation temperature (K)</td>
<td>4300</td>
<td>4000</td>
<td>4000(16)</td>
<td>4500</td>
<td>7000(24)</td>
<td>5500</td>
<td></td>
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</table>

a. Flow rate of cooling water; argon flow listed as "plasma gas".
b. Flow rate of cooling air; argon flow listed as "plasma gas".
c. Adjusted from author's values cited for power dissipated in plasma.
still be affected.

Clearly, unless the skin depth of the ICP can be altered, there is little prospect of successfully reducing further the plasma dimensions. In turn, skin depth can be reduced only by altering the plasma's impedance, an unlikely event, or by raising the operating frequency of the ICP. Importantly, it has recently been shown that a 9mm ICP can be operated at 100MHz successfully and with minimal matrix interference(9). Clearly, this study heralds one of the important new directions which high-efficiency ICP systems might take.

HIGH-EFFICIENCY ICP TORCHES

Historically, some of the most dramatic reductions in RF power and argon flow required to sustain the ICP were made by modifying the torch used to support the plasma. In fact, the work by Allemand and Barnes (10) established the basis for even some of the most recent improvements in low-flow torch design. In that study, a parameter termed the "configuration ratio" was defined as an indicator of torch performance. The configuration ratio is simply the ratio of the diameters of the intermediate and outer tubes in the plasma torch. It was shown then and in later studies (6,11) that a large configuration ratio enabled a plasma to be supported on unusually low gas flows. Later, the same research group (12) demonstrated the importance of a constricted port in the coolant-gas inlet tube of an ICP torch. Such a constriction increases the swirl velocity of coolant argon, stabilizes the plasma, and promotes easier ignition. These design features were, not surprisingly, incorporated into a number of the miniaturized ICP systems described in the previous section and also in the design of high-efficiency torches for use with molecular gases (13).
Other investigators who have recently described modified torches for low-power or low-flow operation include Lowe (14) and Demers and Allemand (15). Lowe (14) employed a thick outer tube at a rather large distance from the intermediate tube in an ICP that required only 5L/min for operation. The system by Demers and Allemand (15) can operate at unusually low argon flows and applied RF powers because it was designed for use in an atomic fluorescence instrument. Consequently, the plasma is not required to ionise or excite sample atoms.

Perhaps the most dramatic improvement in operating conditions through torch design was reported by Rezaaiyan et al. (11). Using as a guide "plasma stability" curves, a number of physical dimensions of an 18-mm ICP were optimized to enable operation at unusually low power and gas flow. Such plasma stability curves are generated by reducing slowly either the applied RF power or coolant gas flow in an ignited, stable ICP. The flow or power where the plasma extinguishes is then noted and the group of minimal flow/power points so obtained is plotted on a power/flow axis system. The resulting "plasma stability" curve, which in an optimized plasma follows both axes remarkably closely, delineates boundaries of stable plasma operation. The final optimized torch (11) could sustain a stable plasma alternatively at a coolant flow of 5L/min and an RF power of 125W or a coolant flow of 3.5L/min and an RF power of 500W. Features of the torch are outlined in Table 1 and its analytical characteristics summarised in Tables 2-3. Importantly, the optimized torch exhibited the same stability when a 1% NaCl solution was introduced into it and could also be employed for the analysis of real samples. Recent results from the same laboratory (16) reveal that optimal operation occurs at an applied RF power of 350W and a coolant flow of 5L/min.
limits are comparable to those reported in other ICP investigations.

The "optimized" torch has since been used by a number of outside investigators (17-19) who report that it can indeed be used for real samples and, even more importantly, is extremely convenient when organic solvents must be employed (18,19). From these reports, the use of organic samples requires the plasma supported by the optimized torch to be operated at somewhat higher RF power levels - approximately 700 to 1000W. Under these conditions, carbon deposition is reportedly minimal and plasma stability is excellent.

It is appropriate to question whether torch miniaturisation and optimization might not profitably go hand in hand. From recent studies (16), optimized torches of reduced size perform no better than their larger counterparts, at least when sustained at radio-frequencies in the 27-40MHz range. Perhaps operation at higher frequencies (9) will alter this situation.

EXTERNALLY COOLED TORCHES

A clear alternative to the foregoing approaches is the use of externally cooled ICP torches. Presumably, if the torch could be cooled internally or externally by a relatively inexpensive gas (e.g. air) or by a more effective cooling medium (e.g. water) the total argon flow to the plasma could be vastly reduced. This approach has been explored by a number of researchers and points the way toward some of the most promising developments in high-efficiency ICP torch design.

Water-Cooled Torches

The first example of a water-cooled torch was reported by Britske et al. (20) who supported a 40 MHz, 4kW plasma on as little as 4L/min of argon. The torch was unusually large (40mm i.d.) and was
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<td>Al(III)</td>
<td>3</td>
<td>2</td>
<td>4</td>
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<td>25(17)</td>
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<td>B(III)</td>
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<td>16</td>
<td>90</td>
<td>10</td>
<td>35</td>
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<td>Cu(II)</td>
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<td>0.44</td>
<td>30</td>
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<td>Fe(II)</td>
<td>0.07</td>
<td>4</td>
<td>0.08</td>
<td>3.1</td>
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<td>9</td>
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<td>Fe(III)</td>
<td>42(1)</td>
<td>9</td>
<td>10(1)</td>
<td>7.4</td>
<td>3(17)</td>
<td>16</td>
<td>16</td>
<td>45</td>
<td>1.5</td>
<td></td>
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<td>9</td>
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<td>Co(II)</td>
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<td></td>
<td>9(17)</td>
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<td></td>
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<td>Cr(III)</td>
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<td>10(17)</td>
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<tr>
<td>Cu(I)</td>
<td>8</td>
<td>1.2</td>
<td>1</td>
<td>4.0</td>
<td>3(17)</td>
<td>250</td>
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<td>2</td>
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<td>4.7</td>
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<td>Mg(II)</td>
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<td>2(1)</td>
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<td>0.13</td>
<td>0.6</td>
<td>0.3</td>
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<td>13</td>
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<td>80</td>
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<td>0.5</td>
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<td>7</td>
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<td>Ni(II)</td>
<td>4(1)</td>
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<td>0.8</td>
<td></td>
<td></td>
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<td>26</td>
<td>7</td>
<td></td>
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<tr>
<td>Pb(II)</td>
<td>33(1)</td>
<td>20</td>
<td>25(1)</td>
<td>14</td>
<td></td>
<td>230</td>
<td>260</td>
<td>42</td>
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<td>Ti(IV)</td>
<td>2</td>
<td></td>
<td>1</td>
<td>3</td>
<td>140(1)</td>
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<td>Zn(II)</td>
<td>71</td>
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<td>12</td>
<td>8</td>
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a. Next but not all detection limits as the 3σ value.
b. Numbers in parentheses are literature references; Roman numerals in parentheses refer to atom (I) or ion (II) line.
found to be effective for rare-earth determination. However, end-on viewing was required.

The water-cooled torch of Kornblum, et al. (21) dramatically required a total argon flow of approximately 1L/min and an RF generator power of only 700W (cf. Table 1). However, interferences from Al, Na and phosphate were noted and detection limits were disappointing (cf. Table 2). The authors attributed the poor detection limits to the inability of the low-power plasma to accommodate more than 0.1L/min of aerosol gas flow. However, a later study (22) employed the same plasma with an efficient Babington-style nebuliser and yielded little improvement in sensitivity.

In contrast, the water-cooled torch of Kawaguchi et al. (23) was operated at relatively high radiofrequency power (1000-1800W) and with a somewhat modified design. Under these conditions, matrix interferences were reduced (cf. Table 3) and detection limits dramatically improved (cf. Table 2). Later work by the same authors (24) employed the same kind of top-inlet water-cooling system but substituted for the original three-tube torch a 2-tube design which was surrounded by a silica cooling jacket. The resulting plasma was found to be stable at 4L/min of coolant gas but required an RF power of more than 1100W. The excitation temperature is unusually high (7000K) and matrix interferences are reportedly low. The design has a distinct advantage over alternative water-cooled systems in that emission can be viewed in a side-on fashion without requiring light to pass through the torch itself.

Air-Cooled Torches

One of the major difficulties with the design and use of a water-cooled torch is the incidence of gas bubbles forming in the cooling water (22). When such bubbles form, water flow can be interrupted, resulting in torch devitrification or melting. Obviously, no such problem arises when the torch is air-cooled. To
<table>
<thead>
<tr>
<th>Interferent</th>
<th>Savage (1,2)</th>
<th>Allemand (6)</th>
<th>Weiss (7)</th>
<th>Massisian (11)</th>
<th>Kerblum (21)</th>
<th>Kawaguchi (23)</th>
<th>Ripsom (15)</th>
<th>Ripsom 16-mm air-cooled (28)</th>
<th>Ripsom 13.2-mm air-cooled (28)</th>
<th>Ripsom a R,0-cooled (28)</th>
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<td>Phosphate</td>
<td>-SE</td>
<td>-SE</td>
<td>≤5%</td>
<td>≤21%</td>
<td>≤5%</td>
<td>≤12%</td>
<td>none</td>
<td>none</td>
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<tr>
<td>Al</td>
<td>-42X(CaI)</td>
<td>-14X(CaI)</td>
<td>≤5%</td>
<td>-8%</td>
<td>+12%</td>
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<tr>
<td>Na</td>
<td>+9X</td>
<td>-19%</td>
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<td>≤11%</td>
<td>-20%</td>
<td>+5%</td>
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<td>+5%</td>
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a. Unless otherwise indicated, interference is on CaII emission and is calculated as the percentage increase (+) or decrease (-) in emission signal caused by 1 g/L of the interferent.
b. Interference measured on the Mn 403.3 nm line, calculated as above.
c. Not easily used with organic solvents under listed operating conditions.
promote effective air cooling. Ripson et al. (23) designed an unusual load coil constructed of two plates of water-cooled copper. Five spaced inlet ports in this modified coil then directed a high-velocity stream of air (50L/min) at the outside of an 18-mm torch. Unfortunately, at the relatively low argon flows required (1L/min), the plasma tail flame was unstable unless an extended outer tube was employed. As a result, emission had to be viewed through the quartz tube, an obvious disadvantage. Nonetheless, detection limits (cf. Table 2) were respectable and interferences (cf. Table 3) were minor. In later studies (26–28) the same authors compared their air-cooled plasma to a water-cooled unit similar to that of Kawaguchi, et al. (24). Using a combined empirical/theoretical approach, they derived power balances for both conventional and externally cooled ICP torches. From these calculations, most of the energy in a conventional plasma goes into heating the argon, except for the small amount in a conventional torch which lies against the quartz tube and outside the plasma boundary. In contrast, air-cooled and water-cooled plasmas lose most of their heat by conduction through the torch walls; heat which is subsequently carried away by the cooling medium. Of these two, the water-cooled device loses more power through the wall and is therefore less power-efficient.

These power balance calculations bear strongly on studies mentioned earlier in this review. For example, the calculations predict that an "optimized" plasma operating at 5L/min of argon should require 250W just to heat the gas to the plasma temperature (3500K). In contrast, it was shown in the earlier study (11) that 125W was sufficient to sustain the discharge. Presumably, a large fraction of the argon in the "optimized" torch passes outside the plasma boundary, is not heated greatly, and serves merely to efficiently cool the torch walls.
The authors also suggest that additional power in an ICP beyond that required to heat the argon serves in large measure to increase the degree of ionization in the plasma. This hypothesis might explain the relatively low excitation temperature reported by Weiss (7) and the poorer detection limits of Kornblum (21) than those of Kawaguchi (23) who operated his water-cooled torch at higher power levels.

Using these findings in a more directly analytical study (28), the same authors compared directly the air-cooled and water-cooled torches. Optimizing torch dimensions in a univariate manner, and using signal-to-background ratio as the optimization criterion, each torch was modified (cf. Table 1); in a number of subsequent analytical studies, the air-cooled torch was found generally to be superior. Although the water-cooled device is more immune to changes in input radiofrequency power and although the air-cooled torch is somewhat more temperamental, requiring solvent to be aspirated continuously, the air-cooled torch did not suffer from salt build-up and yielded better detection limits and lower matrix interferences. Unfortunately, detection limits were still inferior to those of a conventional plasma and neither torch functioned particularly well when fed an organic-containing aerosol. Moreover, both torches required viewing through the tube wall, a factor which could lead to long-term drift and instability in working curves.

**CONCLUSIONS**

Tables 1-3 document and compare different torch types which have been reported for high-efficiency ICP use and the analytical characteristics that they yield. From these data, several conclusions arise. First, for the near term, the "optimized" or miniaturized torches offer the best solution for ICP operation at reduced RF power and coolant-gas flow. Of these two alternatives, the 13-mm reduced-size torch is the more proven and can therefore be used with greatest
confidence. However, such a torch requires a modification in the load coil supplied with most ICP power generators; although this change is simple, it might not be undertaken by many users. In contrast, the "optimized" torches have not been used as widely, but can be directly installed in a commercial unit. An optimized torch similar to that reported in the literature (11) is now commercially available (29) and documentation on its use should be forthcoming. Future developments in torch design will no doubt see higher frequencies being employed with miniaturised torches (9). Such systems would be especially useful in detection systems for liquid chromatography, where low-flow and minimal atomic dilution are required. Obviously, interfacing with a mass spectrometer has similar requirements.

For dramatic reductions in applied radiofrequency power or argon flow, external cooling seems a necessity. Of the two alternatives already described in the literature, water-cooling seems inferior to air-cooling (28). To render air-cooling more efficient, one might expect to see in the future outer torch tubes of higher thermal conductivity. For example, BeO is a material long used in ion laser tubes because of its high thermal conductivity and low electrical conductivity. Such a material would seem to be ideal for the construction of externally cooled ICP torches. Alternatively, radiative cooling itself might be employed in the future for an ultra-low flow ICP. In the work of Kawaguchi, et al. (23), it is stated that a coolant water flow of 2.5L/min is necessary to stably cool a quartz ICP torch; as a result, the water is increased in temperature 2-5°C. From these data, it can be calculated that the water must carry away between 350 and 850W. These values are confirmed by the findings of Ripson and de Galan (26).
To effectively dissipate this 350-800W radiatively, a plasma torch would obviously have to reach a higher temperature than that expected of a conventional unit. Equation 1 can be used to calculate this necessary temperature.

\[ P = S \varepsilon \sigma T^4 \]  

(1)

In equation 1, \( P \) is the amount of power to be dissipated radiatively, \( S \) is the surface area of the radiator, \( \varepsilon \) is the emissivity of the radiating substance, \( \sigma \) is the Stefan-Boltzmann constant, and \( T \) is the radiator temperature. For a plasma torch of 18mm diameter and a radiating length of 5cm, equation 1 shows that a temperature of 1400K would have to be reached to dissipate 625W, a number expected to be reasonable for such a system. Clearly, such a temperature can be readily reached by a number of ceramics conveniently available. Such a radiatively cooled torch is now under development in our laboratory.

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