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A MODIFIED MICROWAVE-INDUCED PLASMA (MIP) DISCHARGE CHAMBER EXH--ETC(U)
JUN 77 A T ZANDER, R K WILLIAMS, G M HIEFTJE N00014-76-C-0838

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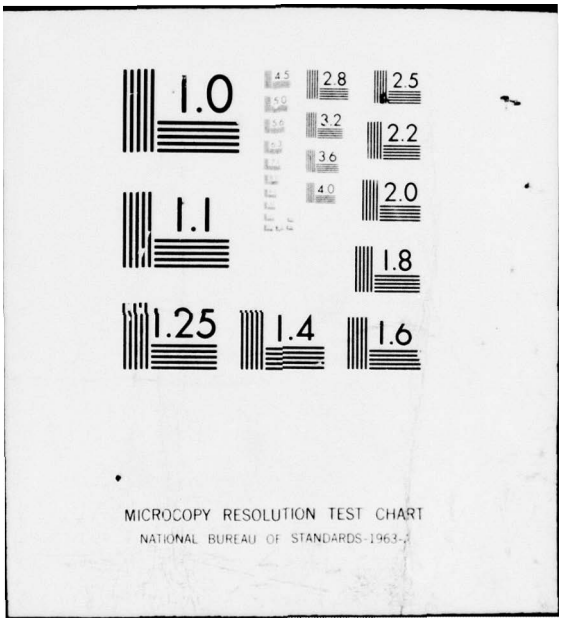
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A simple modification has been made to the discharge chamber of a microwave-induced plasma (MIP) at atmospheric pressure. The positioning of two carbon washers in approximately one-third of the region within which the MIP exists allows the formation of an auxiliary plasma which is unaffected by material entering the MIP. The auxiliary plasma provides thermal stabilization of the cavity when the primary MIP is adversely affected while solvent vapors pass through the chamber, reignites the MIP automatically, and increases MIP stability by keeping it centered in the chamber. The carbon washers do not significantly alter the spectral character of the MIP.

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TECHNICAL REPORT NO. 5

# A Modified Microwave-Induced Plasma (MIP) Discharge Chamber Exhibiting High Stability and Immunity from Sample Solvent Extinguishment

by

Andrew T. Zander, Rod K. Williams and Gary M. Hieftje

Prepared for publication in

ANALYTICAL CHEMISTRY

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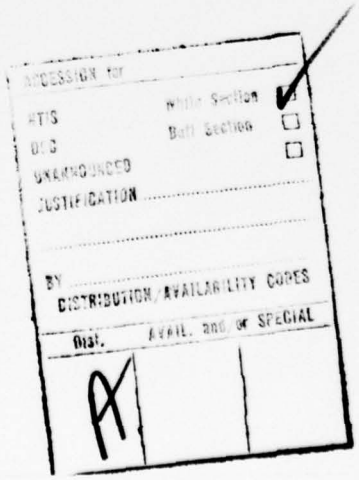

Microwave-induced plasmas (MIP's) in argon or helium possess a number of advantages for use as excitation sources in atomic emission spectrometry (1,2). These plasmas have high excitation temperatures so that a great number of elements, including the halogens and many nonmetals, can be determined at high sensitivity in the UV and visible regions. The power required for stable operation of an MIP is relatively low, generally below 200 W. Also, atmospheric-pressure argon or helium plasmas consume much less support gas than other types of plasmas, and have minimal requirements for cooling. Because of their low operating power, these plasmas often produce unusually low background molecular spectra, further enhancing their utility.

An MIP is formed in a discharge tube placed in a cavity to which microwave power is transmitted via a coaxial cable or waveguide. The most frequently used resonant cavities for operation at 2450 MHz are the 1/4-wave Evenson cavity and the 3/4-wave Broida cavity (3). The plasma can be viewed either radially or axially.

By far, the most extensive use of MIP's as emission sources has been as detectors for gas chromatographic systems (4-11). The GC carrier gas can be argon or helium and the generally used flow rates are compatible with stable MIP operation. In such an application, the MIP has been employed to excite elements such as C, H, N, P, B, O, and the halogens, providing highly selective and sensitive detection and determination.

The major limitation to using the MIP as an emission source in present configurations revolves around injection of aerosol samples into the plasma. The low power ordinarily utilized does not afford a high enough plasma energy density to evaporate and atomize aqueous droplets. Also, the stability of the plasma is degraded when even a relatively small amount of sample material is injected. These problems have not proven to be insurmountable,

but they have hindered extensive use of MIP's in optical emission analysis.

The problems associated with aerosol sample injection into MIP's have been alleviated in two ways. In the first approach, an aerosol desolvation system (12) is placed between the nebulizer and the plasma to evaporate and remove the solvent from the gas stream before the sample reaches the plasma (13,14). Although this method offers high nebulization efficiency, the MIP is still required to atomize the analyte from the resulting dry aerosol particles.

Alternatively, the liquid sample can be both desolvated and atomized prior to its introduction into the MIP (15-18). The low current, low power microarc atomizer described by Layman and Hiefjte (15) serves this purpose; analyte atoms are generated efficiently by cathodic sputtering of the sample applied to a tungsten filament external to the MIP. However, in the original configuration (15), the microarc was interfaced to the plasma chamber in such a way that the MIP extinguished when solvent was evaporated into it. To overcome this limitation, provision for automatic reignition of the plasma with a high voltage spark was made. Fricke, Rose, and Caruso (16,17) have taken advantage of the high atomization efficiencies of carbon cup and tantalum-ribbon electrothermal atomizers to release analyte atoms for injection into an MIP. In this application, the plasma was kept from being extinguished by careful control of solvent evaporation rate, thereby also lengthening the analysis time. Recently, Kirkbright (18) described a new commercial MIP system which utilizes a Ta-ribbon atomizer. In this system, solvent vapor is vented away from the MIP, enabling continuous operation of the plasma without increasing analysis time. However, this venting requires careful control of the gas flows to ensure stable plasma operation.

In the present study, a new method was developed for operating an MIP on a continuous basis, and in conjunction with an external desolvation and atomization system. With this method, the MIP is not extinguished during solvent evaporation, drying time of the applied sample is not extended, and extra venting of the evaporate is not necessary. In the new approach, a portion of the MIP is kept operating by partially isolating it from the rest of the plasma within the plasma chamber. This auxiliary or "pilot" plasma is bypassed during sample or solvent injection and is therefore not affected by such events. Of course, during solvent evaporation, the primary excitation plasma is extinguished; however, the microwave cavity is thermally stabilized during this period by the existence of the auxiliary plasma. Following desolvation, the "pilot" plasma automatically reignites the primary discharge. In addition to the convenience it provides, the auxiliary plasma eliminates the necessity of retuning the cavity.

## EXPERIMENTAL

The atmospheric pressure argon MIP was powered by a 100 W microwave generator (Model HV-15A, Scintillonics, Inc., Fort Collins, Colo.) which was stabilized by a 500 W Sola constant voltage power transformer. The 2450 MHz output is conducted via a 3/8" coaxial cable (Type RG-9, Belden Corp., Richmond, Inc.) to a 3/4-wave Broida cavity, fitted with a double-stub tuner (Model 306A, PRD Electronics, Westbury, L.I., N.Y.) for impedance matching.

The plasma exists near the tuning-stub end of the cavity inside a 6 mm i.d. quartz chamber. As shown in Figure 1, sample vapor is introduced into the plasma at a point approximately halfway between the plasma ends.

During emission measurements, the plasma is viewed axially. Into one end of the plasma chamber, a smaller quartz tube (4 mm i.d.) was inserted. Within this inner sleeve were positioned two tightly fitting carbon washers (4 mm o.d., 2 mm i.d., 2 mm long) made from spectrographic-grade graphite rod (National Carbon Co., Union Carbide Corp.); the carbon washers are spaced approximately 1 cm apart and enclose approximately 1/3 of the MIP region.

Primary argon flow to the MIP at approximately 375 mL/min is from the external sample atomization apparatus located in a direction perpendicular to the plasma chamber. An auxiliary argon flow, of about 75 mL/min, enters the chamber axially from the direction of the pilot plasma and enables a stable plasma to exist between the carbon washers. The primary MIP passes through the carbon washer at its one end; this results in stable positioning of the plasma in the center of the chamber.

The sample introduction system was based on a microarc atomizer (15); however, the microarc housing and electrode configuration were modified somewhat for improved operational and mechanical stability. This modified configuration will be described in a later communication; of course, any sample introduction system can be used which desolvates and atomizes the sample external to the MIP.

In operation, the MIP is ignited within the cavity by means of a Tesla coil. The presence of the carbon washers does not adversely affect the ignition or the tunability of the cavity, and aids in reducing plasma wander. Aqueous samples are applied with a syringe in microliter amounts to the microarc filament. The sample is then dried by heating the filament with a constant current. During drying, the evaporated solvent is carried through the plasma chamber by the primary argon flow; depending upon the

amount of solvent vapor present, the primary MIP will either be weakened or extinguished. However, the auxiliary plasma is unaffected by the passage of solvent vapor and continues to operate, keeping the chamber thermally stabilized. After removal of all solvent vapor from the cell, the primary MIP is reignited by the pilot plasma and rapidly stabilizes. The microarc is then struck to atomize the sample and send it into the discharge.

The flow rates for the primary and auxiliary inlets werechosen in this investigation to optimize sample transport to the MIP and reduce the effects of the presence of the carbon washers within the plasma chamber, while minimizing auxiliary plasma instability. Excessively high primary flow rates were found to produce a primary plasma which bent around the sample inlet port; too low a flow rate leads to an easily extinguished MIP.

The auxiliary flow rate is also critical. Below approximately 50 mL/min, the auxiliary flow produces a plasma which rotates at high speed around the edges of the carbon washer placed at the argon inlet end of the plasma. This rotation adds a high frequency fluctuation to the background signal level. Coincident with rotation, the auxiliary plasma appears bluish-green in color, indicative of emission from carbon ($C_2$) in the plasma. Above 50 mL/min the auxiliary plasma remains centered and stationary and appears identical in color and configuration to the primary MIP.

## RESULTS AND DISCUSSION

Portions of the argon MIP spectrum were scanned to determine the effect of the graphite washers on the spectral character of the plasma. The C I line at 2478.6 Å was easily observable as were most other lines, at very low intensity, of the Swan system ($A^3\pi_g - x^3\pi_u$) of the emission spectrum

of the emission spectrum of $C_2$. There was no evidence of the weaker $C_2$ systems, or any of the $C_3$ spectrum. These spectral features could all be decreased to negligible levels, except for the C I 2478.6 Å line, by appropriate adjustment of the auxiliary argon flow. The carbon pieces never become hot enough to glow and no evidence of increased continuum background emission was noted.

The excitation temperature of the MIP with and without the carbon washers in place was determined by measuring the relative radiances of argon lines having known wavelengths, energies, and transition probabilities (19). In this way, the temperature of the MIP with the graphite-contained auxiliary plasma was determined to be approximately 4300°K while the temperature of the unmodified MIP in the same cavity was 5100°K. Although the difference in excitation temperature is significant, the lower temperature of the auxiliary-plasma-aided MIP is still within the range of excitation temperatures routinely encountered with MIP's (2), and is not expected to adversely affect the capability of the MIP for excitation.

The signal levels obtained with the auxiliary-plasma-aided MIP were equivalent to those produced by the unmodified MIP. However, reproducibility of the signals was substantially improved, 3% RSD compared to 15-25% (15), probably because the unmodified MIP requires reignition after solvent evaporation by a spark. Because reignition employs as one electrode the grounded microarc sample filament, the analyte which was earlier dried on the filament might be lost or disrupted somewhat during reignition.

Table I lists representative detection limits obtained with the unmodified and modified MIP; as expected, no appreciable difference exists between the different sets.

## CONCLUSIONS

Modification of the plasma chamber for an MIP by causing an auxiliary plasma to exist between two carbon washers within the plasma chamber affords a simple and efficient means of interfacing MIP's and external sample atomization systems. The auxiliary plasma which is formed prevents the MIP from extinguishing when the vapors produced during sample drying flow into the plasma tube. Retuning the cavity for reignition of the MIP also becomes unnecessary because the auxiliary plasma automatically reignites the primary plasma after the solvent vapor has been passed. In this manner the cavity remains thermally stabilized, a situation which leads to more stable MIP operation. The carbon washers in the plasma do not significantly affect the spectral character of the MIP, act to decrease plasma wander, and keep the plasma centered in the chamber.

The auxiliary plasma does not eliminate drift of the MIP spectral background when sample vapor is carried into the chamber; even the smallest amount of solvent vapor causes such changes. However, drift severity is reduced in that the MIP is never totally extinguished.

## CREDIT

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TABLE I

Detection Limit[a] Comparison Between Unmodified and Modified MIP's

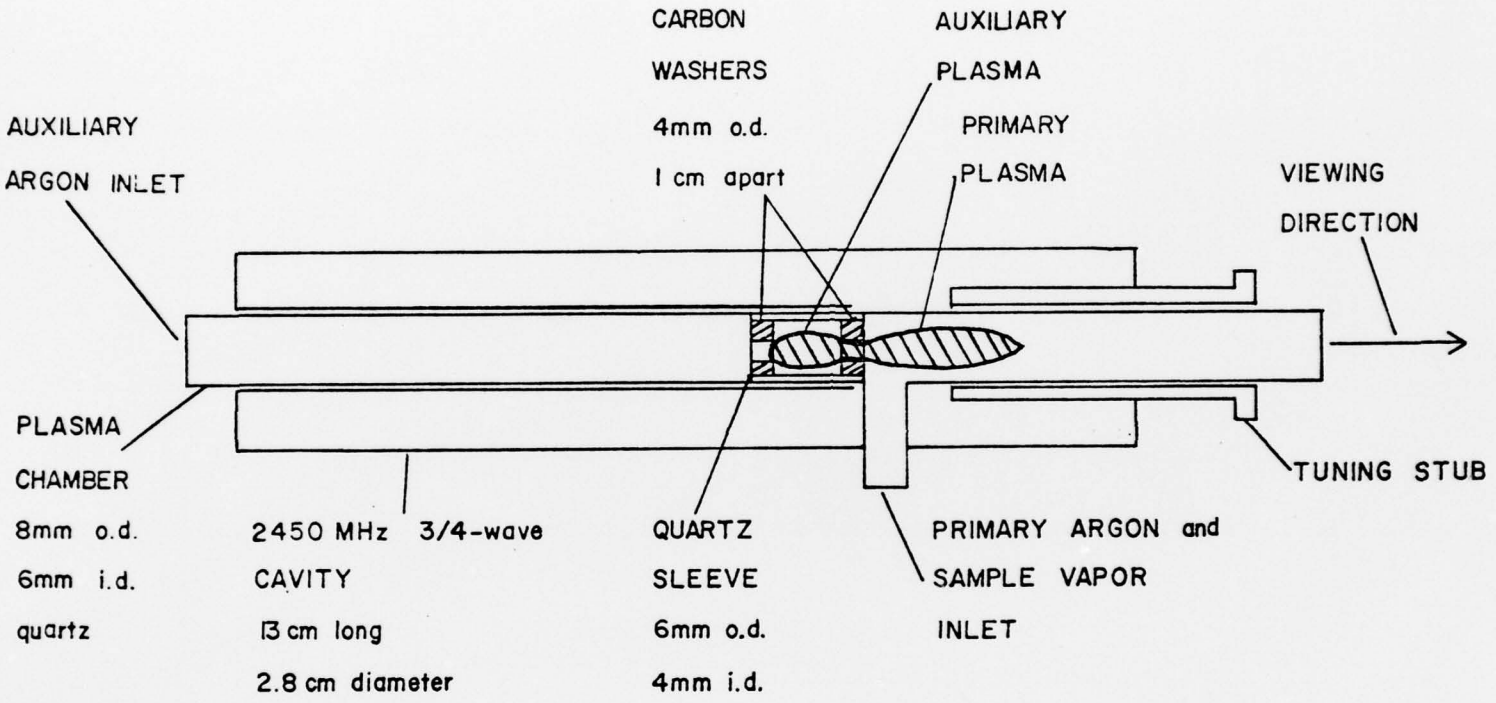
| Element | Wavelength (nm) | Unmodified MIP[b] Detection Limit (pg) | Modified MIP Detection Limit (pg) |
|---|---|---|---|
| Ca | 422.7 | 10.0 | 3.2 |
| Cu | 324.7 | 1.6 | 7.4 |
| Pb | 283.3 | 3.8 | 3.8 |

a. Detection limit taken at S/N = 2.

b. Taken from reference 15.

## FIGURE CAPTIONS

1) 3/4-wave Resonant Cavity with Modified Plasma Chamber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WASHERS
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1 cm apart
AUXILIARY
PLASMA
PRIMARY
PLASMA
AUXILIARY
ARGON INLET
VIEWING
DIRECTION
PLASMA
CHAMBER
8mm o.d.
6mm i.d.
quartz
2450 MHz 3/4-wave
CAVITY
13 cm long
2.8 cm diameter
QUARTZ
SLEEVE
6mm o.d.
4mm i.d.
PRIMARY ARGON and
SAMPLE VAPOR
INLET
TUNING STUB

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