Spectroscopic Diagnostics of an Atmospheric Microwave Plasma for Monitoring Metals Pollution

P. P. Woskov, K. Hadidi, M. C. Borrás, P. Thomas, K. Green, G. J. Flores

Plasma Science and Fusion Center, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Abstract

A 1.5 kW, 2.45 GHz microwave sustained plasma in a flowing sample of stack exhaust gas has been shown in recent DOE/EPA testing to be an accurate monitor of trace hazardous metals (in the part per billion range) such as lead, chromium, and beryllium. Optical-UV spectroscopic studies are being carried out to better understand this particular atmospheric pressure plasma torch. An experimental device has been modified with extra visible access for radial and axial profile measurements. Diffraction limited fiber optic plasma views and high-resolution grating spectrometer instrumentation for molecular rotational and atomic excitation temperature (T_{rot}, T_{exc}) measurements are being used for plasma studies. Initial chord averaged measurements have been made of the $N_2^+(0,0)$ first negative system for T_{rot} and Fe I levels for T_{exc} in nitrogen and air plasmas, respectively.

I. Introduction

There is currently significant interest in the development of a real-time monitoring technology for trace metals pollution in the stack exhaust of high temperature processes such as those used for waste remediation, power production, and manufacturing. Present air pollution compliance measurements rely on the collection of stack samples followed by laboratory analysis, which can take many days to obtain results [1]. Future regulations will require continuous real-time compliance. At a minimum, a metals continuous emissions monitor (CEM) must be capable of detection of the six hazardous metals: arsenic, beryllium, cadmium, chromium, lead, and mercury with a detection limit of < 5 $\mu g/m^3$ (a few parts per billion).

The most promising approaches for achieving a practical multi-metal CEM utilize atomic emission spectroscopy of an atmospheric pressure plasma generated in, or with an extracted flowing sample of, the stack exhaust. The plasma volatizes and atomizes small particulates and molecular species entrained in the exhaust and excites the atoms to emit UV-optical radiation from which the metals are identified and quantified. A variety of plasma generation methods including laser spark, induction coupled plasma (ICP), and microwave discharge are being tested for this application [2]. Atmospheric pressure plasmas have long been used for analytic chemistry applications in the laboratory. ICP [3,4] and low power microwave discharges [5,6], usually operating with an argon or helium gas, have been well studied under ideal laboratory conditions.

Recently a high-power (>0.5 kW) microwave sustained plasma in undiluted stack off gas has been shown to be a promising approach for a multi-metal CEM [2,7]. It was shown to be a robust plasma in air and stack exhaust and highly sensitive to at least three of the hazardous metals in fast flowing gases. Future improvements in the performance of this plasma as a multi-metal CEM would benefit from an improved understanding of the plasma parameters. Measurements are needed of electron temperature, electron density, neutral gas temperature, spatial profiles of these parameters, and their relationship to trace metals atomic emission strengths. Questions of the degree of thermal equilibrium in the plasma need to be answered, as well as plasma conductivity, microwave power absorption skin depth, and the effect of gas composition and particle loading.

Spectroscopic measurements of the UV-optical plasma radiation can provide much of the information that is needed. In this report we describe the microwave plasma and spectroscopic diagnostic instrumentation being used, and some of the measurements being made of atomic excitation and molecular rotational temperatures, along with spatial profiles.

II. Microwave Plasma

The microwave plasma is sustained inside a shorted section of WR284 waveguide that is tapered down to inside dimensions of 72.1 x 34.0 mm. A cross-sectional view of the microwave plasma device is shown in Figure 1. A microwave transparent dielectric tube with approximately a 32 mm outside diameter penetrates through the wide waveguide walls one quarter wavelength back from the short. The plasma operating gases are directed through this tube and include the sample gas containing the entrained metals to be monitored and a swirl gas, which keeps the plasma off the walls and centered in the tube. The dielectric tube is usually a 25.4 mm i.d. boron nitride tube, but is replaced by a 28.5 mm i.d. fused quartz tube for some of the radial profile measurements.

One of two ASTeX microwave power generators Model S-1500 or Model AX2050 with circulator isolation and three-snub tuner are used to sustain the plasma. Plasma operation is possible with forward microwave power in the 0.3 – 2.0 kW range with 1.5 kW nominally used in recent CEM tests [7]. Backward reflected power when the plasma is on is typically less than 5% without adjustment of the snub tuner.

The viewing access for spectroscopic measurements is illustrated in Figure 1. Most trace metal measurements for the CEM application are made via the axial view through a lens that focuses the light onto a fiber optic for transmission to a spectrometer. Two lenses to directly image the plasma onto the entrance slit of a spectrometer without a fiber optic cable have also been used to improve UV transmission at wavelengths <250 nm. Radial views are accessible by a point view 10 mm downstream from the waveguide, used in earlier trace metals measurements [7], and by a 32 x 2.5 mm slit in the side wall of the waveguide for profile measurements. This slit is covered with a fine 110 wires per inch electroformed copper mesh to prevent microwave leakage.

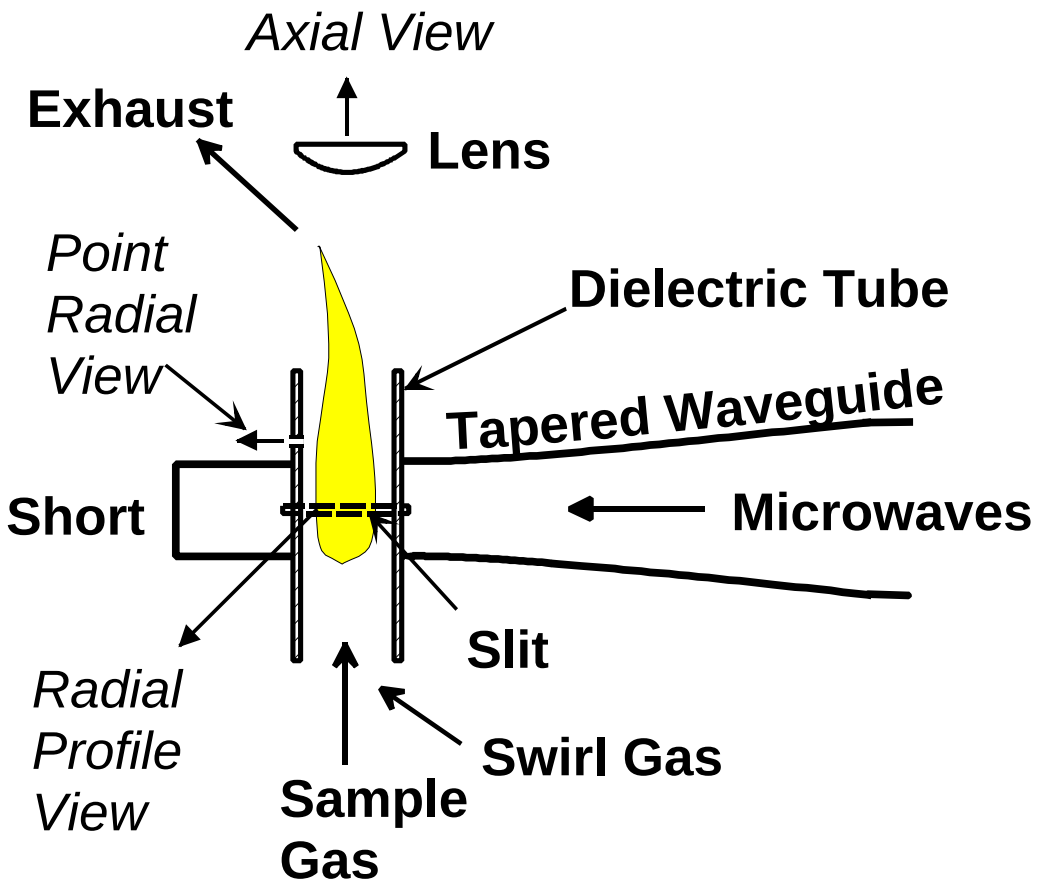

Figure 1. Cross-sectional view of the microwave plasma device.

III. Spectroscopic Instrumentation

Two grating spectrometer systems are being used for the analytical measurements of the plasma light emission. One is a commercially available ISA Jobin Yvon Spex Model THR640 and the other is a custom designed MIT multi-band system. The major parameters of these spectrometers are listed in Table 1. Each spectrometer uses one or more linear array detectors for instantaneous measurements of finite spectral bands.

Most determinations of plasma temperatures, which require relative intensity measurements of emission transitions, are done with the ISA spectrometer. This spectrometer can be easily tuned to a desired 6 – 7 nm wide band in the spectral range of 190 – 600 nm. The light is imaged onto the detectors so that the response can be assumed to be approximately flat over the instantaneous bandwidth, with only a small correction for grating efficiency. Sensitivity is very good with the intensified UV enhanced Princeton Instruments silicon detector array. This spectrometer is also useful

for studies of trace metals emission, but typically only one metal can be monitored at a time because of the limited instantaneous bandwidth.

Table 1. Spectrometers

Parameter	ISA Model TH640	MIT Multi-Band
Type	Czerny-Turner	Custom
Approx. Spectral Range	190 - 600 nm	190 – 460 nm
Bands	One, tunable	Four, fixed
Instantaneous Width/Band	~ 6.5 nm	4.5 – 9 nm
Grating	2400 grooves/mm	3600 grooves/mm
Slit	Variable	Fixed: 10, 25, 50 μm
Input Aperture	F/5.6	F/4
Output Focal Length	0.64 m	0.84 m
Dispersion	0.6 nm/mm[1]	0.3 nm/mm[1]
Detectors	Princeton Instruments IRY-512 intensified Si linear array	StellarNet 1024 and 2048 uv enhanced ccd linear arrays
Pixel width	25 μm	13 μm and 25 μm
Approx. Resolution	0.05 nm[1]	0.012 nm[1,2]

[1] at 300 nm

[2] with 10 μm slit and 13 μm pixels

The MIT multi-band spectrometer was developed to provide simultaneous multi-metal monitoring capability in one affordable spectrometer system. This spectrometer achieves both high-resolution (< 0.02 nm) and wide spectral range (190 – 460 nm) coverage with multiple non-contiguous spectral bands. It is possible to monitor metals such as As at 193 nm and Pb at 405 nm simultaneously with minimal spectral interferences. This spectrometer also has higher resolution than the ISA unit, which can be useful to some of the plasma parameter studies. Inexpensive UV-enhanced StellarNet linear ccd arrays provide good sensitivity at low cost in each of the bands.

The lay out of the MIT spectrometer is illustrated in Figure 2. Only three output bands are shown here for clarity. The actual spectrometer has been set up with up to four bands. The components are fixed to a breadboard so the operating spectral bands need to be preset prior to the start of measurements, but can be rearranged for subsequent experiments. Low-pressure metal vapor lamps are used for alignment. The input focal length is shorter than the output focal length to enable a more convenient faster optics system. Maximum spectral resolution is therefore achieved with a slit narrower than the detector pixel width due to the magnification of the slit by the optics. One of several laser-drilled slits from National Aperture, Inc. is used in the input.

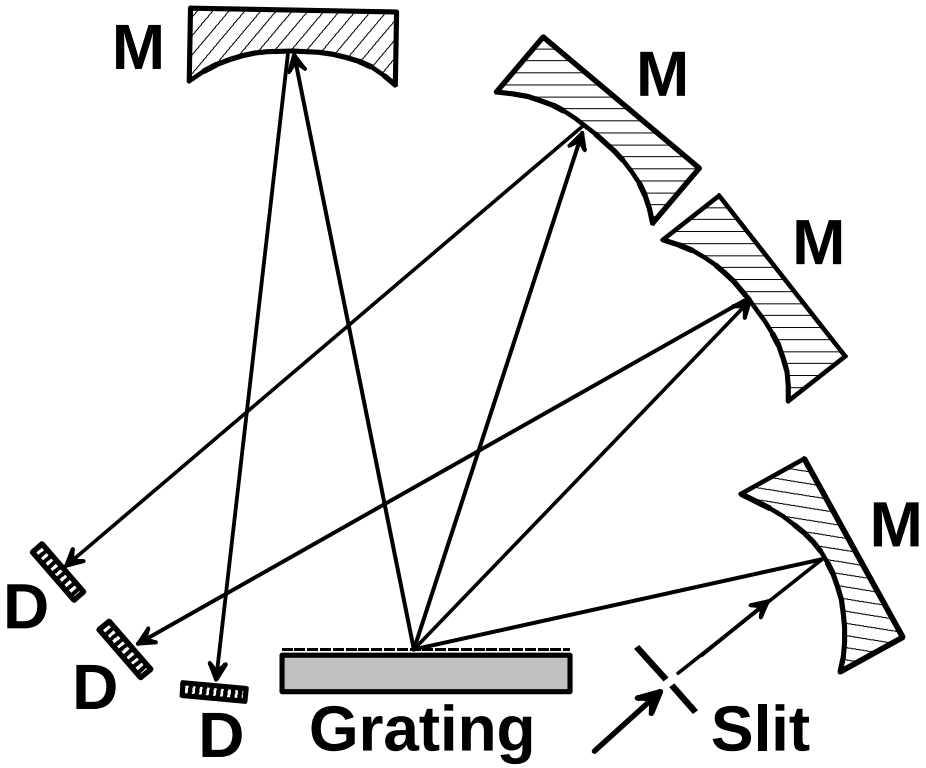

Figure 2. MIT multi-band spectrometer arrangement.

IV. Spectroscopic Measurements

The primary spectroscopic plasma measurements that have been performed so far, besides trace metals monitoring, have been the atomic excitation temperature, T_{exe}, and the molecular rotation temperature, T_{rot}. The atomic excitation temperature was obtained by introducing an iron aerosol into the sample gas stream with a pneumatic nebulizer. Iron is used because the oscillator strengths (f) and statistical weights (g) for this atom are well documented and because this particular atom has a history of use for T_{exe} measurements in many previous works [3,4,8]. A plot of $\log(Il^3/gf) \propto E_{exe}$ has a slope equal to $-0.625/T_{exe}$, where I is the observed line intensity and E_{exe} is the energy of the upper transition level in cm^{-1} units and T_{exe} is in K.

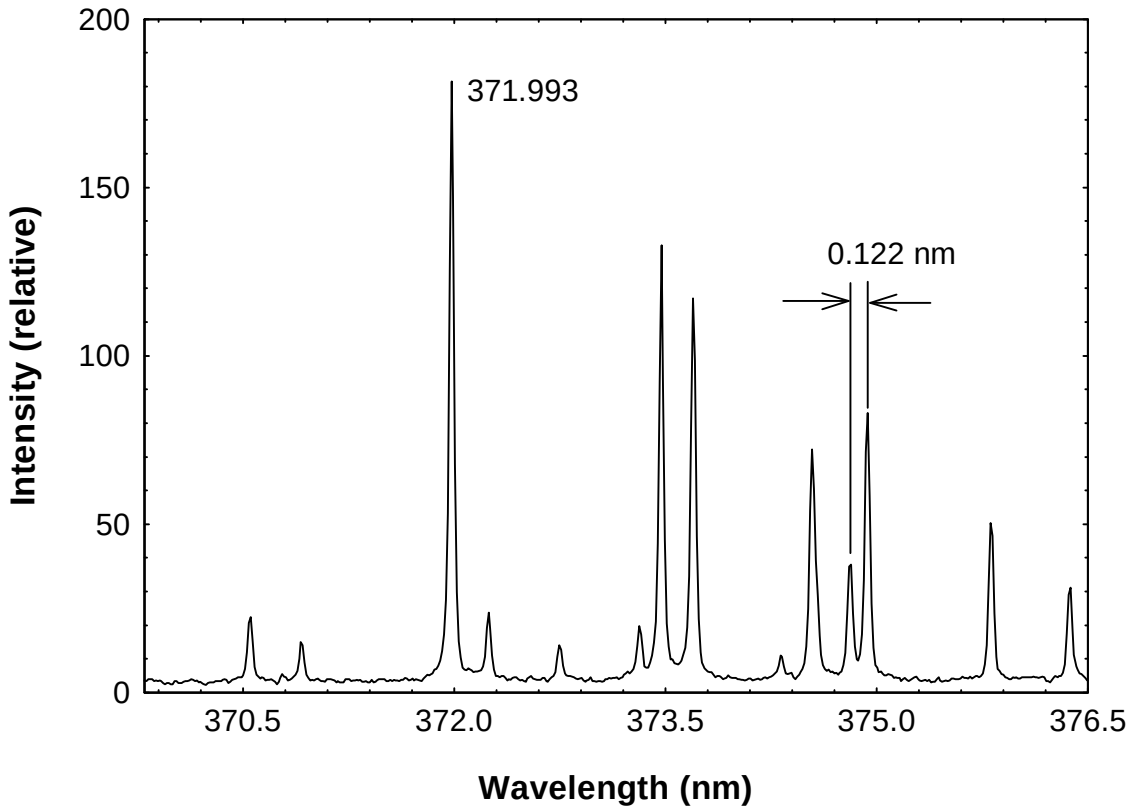

Figure 3. Iron spectrum taken with the ISA spectrometer.

An iron spectrum taken with the ISA spectrometer is shown in Figure 3. The microwave plasma forward power was 1.5 kW, reflected power less than 60 W, sample and swirl gas flows each approximately 14 l/min of nitrogen with some leakage of air. It was known that air was present in the gas matrix because these iron lines are not normally detected in pure nitrogen plasmas. The view into the plasma was along the axis and this spectrum is therefore axially integrated emission. Note the resolution of the spectrometer is less than 0.1 nm as expected. The excitation temperature obtained for this spectrum and other similar data in air plasmas corresponds to approximately 6000 ± 500 K.

The molecular rotational temperature was obtained by observations of the first negative system of the N_2^+ molecule [9]. This is a very prominent spectrum in pure nitrogen plasmas, but is quickly quenched with the introduction of other gases such as air or oxygen. Figure 4 shows a small region of the 0-0 band emission spectrum taken with one of the fixed bands of the MIT spectrometer. The plasma conditions and view are similar to those for the iron spectrum in Figure 3 except there is no air leak in this case. A helium emission line at 388.865 nm from a calibration lamp is superimposed onto the spectrum. Note that the experimental resolution appears to be about 0.02 nm.

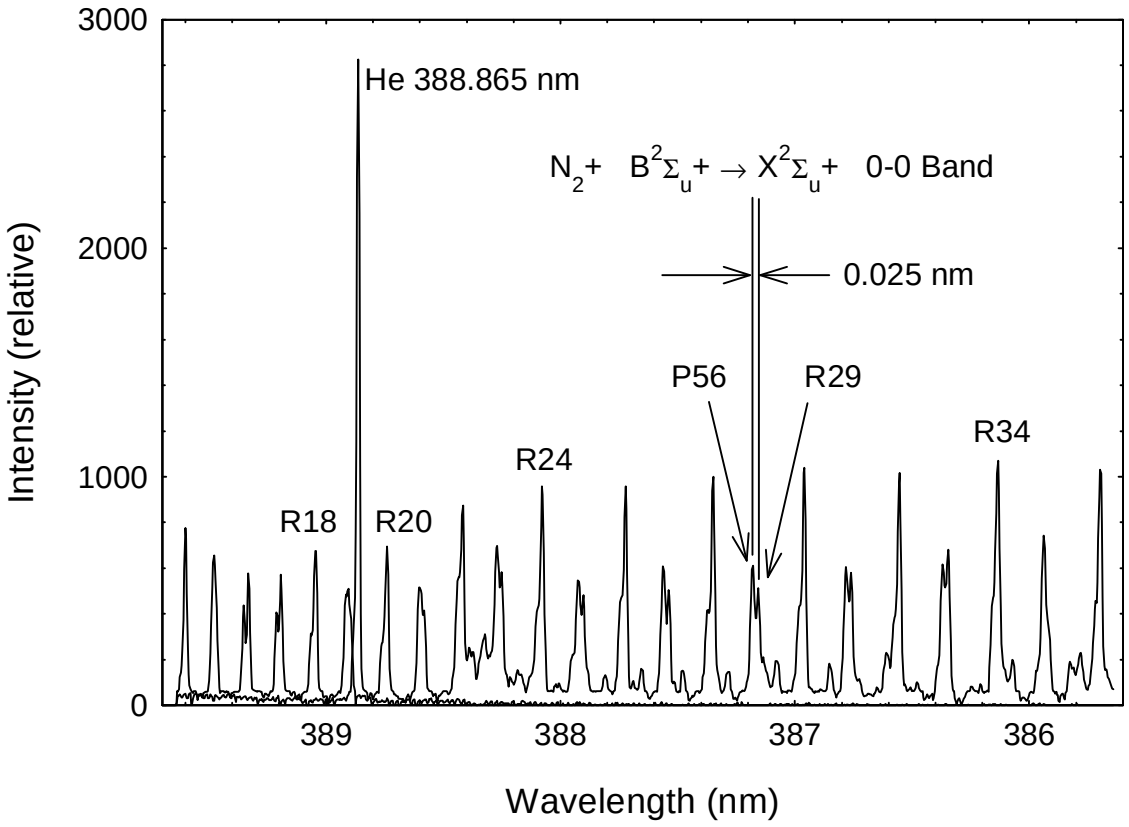

Figure 4. Part of the 0-0 band spectrum of the first negative system of N_2^+ taken with the MIT spectrometer.

This is evident from just being able to resolve the near coincidence of the P branch lines with the odd R branch lines.

The rotational temperature is obtained by plotting log[I/(K'+K"+1)] versus K'(K'+1) where K' and K" are the upper and lower rotational quantum numbers respectively [10]. The slope is equal to $-2.983/T_{rot}$. The relative calibration of the MIT spectrometer has not been tested, so fitting a temperature to the complete spectrum of Figure 4 may not be accurate. Quantitative measurements carried out with the ISA spectrometer with side views through the point view and slit have produced rotational temperatures of approximately 5500 $\pm$ 500 K in pure N_2 plasmas to date. This temperature is also consistent with the observed P56 to R29 intensity ratio in Figure 4.

V. Collimated View Optics

One of the shortcomings of the spectroscopic measurements taken so far is that they are chord averaged with fairly wide field-of-views. The axial view with the lens collects light from most of the plasma cross-section and the side views are by unfocused fiber cable. Some non-linearity to the temperature fits has been observed, with the higher energy levels giving higher temperatures than the lower levels [7]. Peaked plasma

temperature profiles axially and radially could account for these observations. Localized temperature profiles can be obtained by an Abel inversion of a series of many, narrow-beam collimated chord measurements across the plasma diameter. To make such measurements possible a fiber optic collimator from OZ Optics was tested.

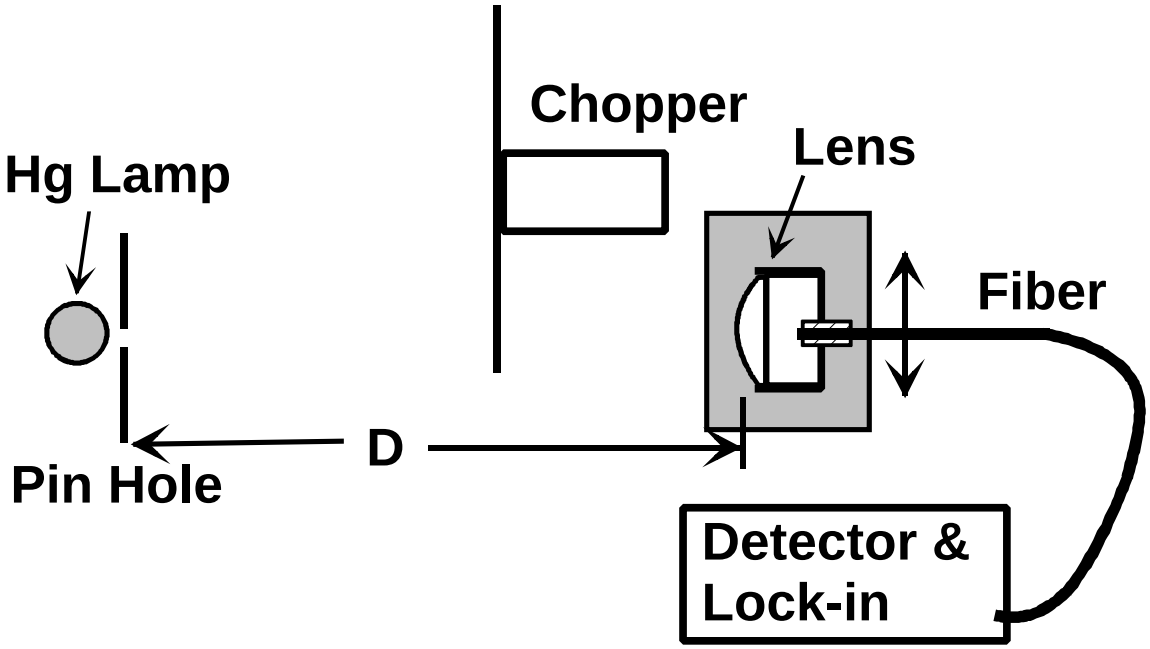

Figure 5. Experimental setup for measurement of the fiber optic collimator field-of-view.

The fiber optic collimator makes use of a 2 mm diameter, 3.5 mm focal length achromatic lens with a 125 μm diameter fiber cable. It was tested with a mercury lamp as shown in Figure 5. The mercury lamp emission was restricted to a point source by a 100 μm pin hole. The fiber cable was of non-UV glass so it was opaque to the 253 nm Hg transition but transmitted the 365 and 404 nm transitions. A blue filter was used to confirm the measurements were restricted to these transitions. The field-of-view was measured by translating the collimator across the pin hole emission at various distances, D, from the collimator. A Nν Optics silicon diode receiver and lock-in amplifier were used to detect the light.

The resulting field-of-view (FOV) profiles are shown Figure 6. At approximately 40 mm distance from the collimator the FOV is 1.6 mm in diameter at half maximum. The far field divergence angle is 2.7°. The plasma is approximately 40 mm distant from the collimator when it is set up for viewing through the side waveguide slit. Initial plasma profile measurements in pure N_2 plasmas show that the

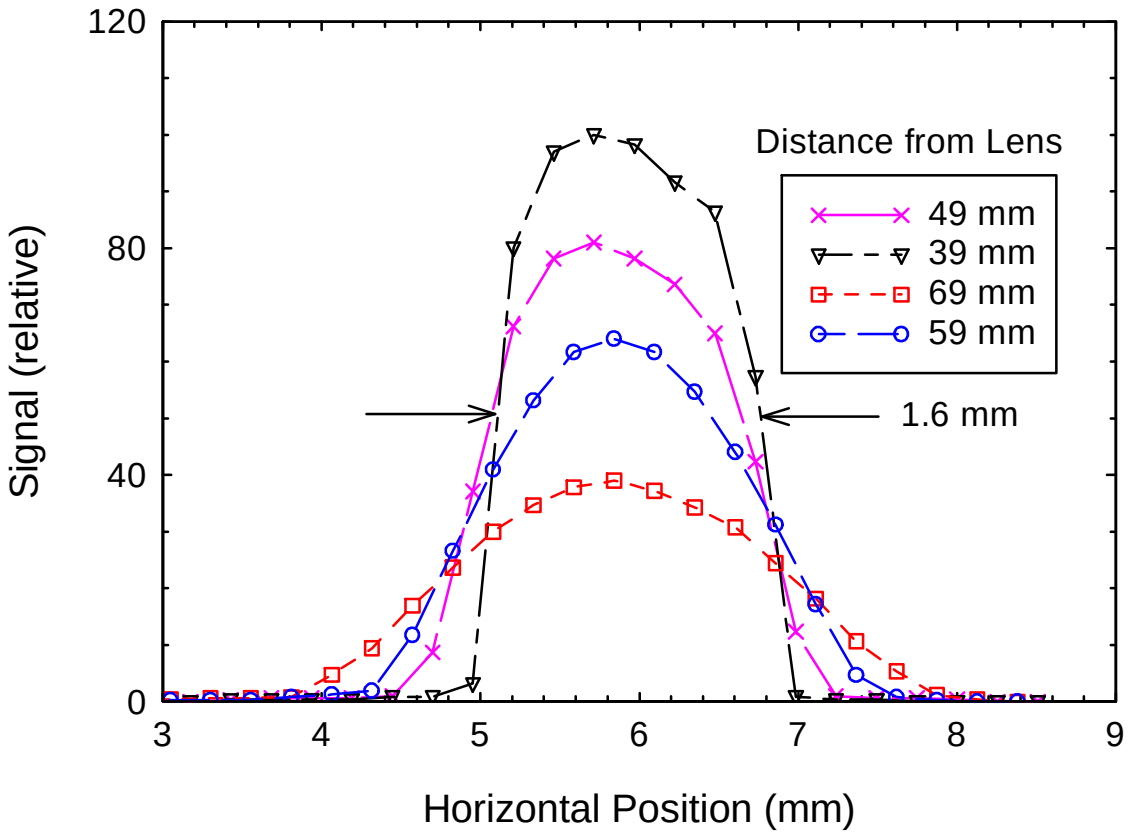

Figure 6. Measured fiber optic collimator field-of-view profiles.

plasma emission is peaked on center and is only 8 –10 mm in diameter to half maximum emission levels. The Abel inverted rotational temperature profile is relatively flat. The initial measurements indicate that better chord resolution is needed, which may be achieved with the use of apertures and additional lenses.

VI. Discussion

The spectroscopic diagnostic instrumentation and techniques described here will provide useful insights into the performance of the high-power atmospheric pressure microwave plasma being developed for the CEM application. Atmospheric pressure microwave plasmas operating in air and gas mixes representative of stack exhaust have not been well studied in the past. The highly collisional, partially ionized plasma with many atomic and molecular species is a very complex medium with many potential mechanisms that can effect the light emission strengths of entrained atomic species. Spectroscopic diagnostics of the light emission are easily implemented in comparison to Langmuir probes, which would not be practical inside a microwave waveguide, or laser scattering, which would require a much greater investment in hardware and effort.

One question to be answered is the existence of local thermodynamic equilibrium (LTE). Measurements of T_{exe} and T_{rot} under identical plasma conditions are required to

determine if they are equal or different. The measurements presented here are inconclusive since the iron and N_2^+ transitions used are not mutually present in the plasmas studied so far. Using another molecular species, such as the OH radical, that is present with iron emission will be investigated in the future. A technique to measure electron density would also be highly desirable. A suitable method for this microwave plasma CEM has not yet been identified. Measurement of the Stark broadening of an atomic transition such as one from hydrogen has been demonstrated in the past as an electron density diagnostic in ICPs [4], but such a transition is difficult to identify in the high background emission levels of air plasmas. Alternatively, if LTE can be established, then the electron density can be inferred from the plasma temperature and ratio of emission strengths between neutral and ionized species through the Saha equation [11].

Another plasma optical parameter that must be examined is the optical depth or self-absorption of the UV-optical radiation. The use of relative intensities of transitions to determine temperatures implicitly assumes that the plasma is optically thin. However, this assumption has not been verified for the present large microwave plasma, which along the axial view can have a light emission path length of 10 cm or more. We plan to test this assumption with a second microwave plasma as a source of probing radiation at frequencies identical to the plasma under study. These planned spectroscopic measurements with the instrumentation described here should make an advance in our understanding of high-power atmospheric microwave plasmas which could lead to improved performance for CEM and other applications.

Acknowledgements

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