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## **Advanced Notice Turbine Component Wear Monitor**

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# **Advanced Notice Turbine Component Wear Monitor**

**Advanced Committee Concept Contract # 400**

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## **Final Report**

### **ABSTRACT**

A 5 – 30 kHz, high voltage atmospheric pressure discharge device is being investigated as an excitation source for atomic emission spectroscopy. Electron excitation energy and molecular rotational temperature of nitrogen have been measured in this plasma at voltages of approximately 2 kV and average power levels of 130 - 300 Watts with a 2 mm gap between electrodes. Iron and titanium lines have been used for the electron excitation temperature measurements. These measurements show that the electron excitation energy is about 0.5 eV and does not vary with frequency or power over the ranges studied. The rotational temperature of the second negative system of nitrogen molecule ion ( $N_2^+$ ) was found to be 1840 K (0.16 eV) showing that this discharge is a non-equilibrium plasma.

## I. INTRODUCTION

A very low radio frequency, high voltage, and low current electric discharge device called a plasmatron had been developed at the Massachusetts Institute of Technology Plasma Science and Fusion Center for fuel reforming<sup>1</sup>. This device uses a high voltage electric discharge in the range of 1 - 3 kV at about one hundred milliamps of current and at frequencies between 5 kHz and 30 kHz. Originally developed for fuel reforming to produce syngas (carbon monoxide and hydrogen) from liquid fuels such as gasoline, diesel and bio-oils, it is now being investigated as a low cost excitation source for atomic emission spectroscopy. The Advanced Concept Committee at MIT Lincoln Laboratory has funded this project to investigate the use of this device as an Advanced Notice Turbine Component Wear Monitor by detecting the materials of thermal barrier coatings in the exhaust gas of a turbine. Also, detecting minute amounts of hazardous metals in gas streams has been of interest to many researchers in the last decade. Of particular interest is the detection of mercury, lead, and arsenic emitted from coal power plants. Several plasma technologies are being researched as excitation sources to perform atomic emissions spectroscopy of these pollutant metals. Among these technologies are thermal plasmas such as electric arc discharges that use DC voltage<sup>2</sup>, radio frequency plasmas such as inductively coupled plasma (ICP)<sup>3</sup>, microwave plasma torch (MPT)<sup>4</sup>, and laser induced breakdown<sup>5</sup> atomic spectroscopy. All these technologies have been well characterized, but have not achieved a cost effective solution to the monitoring need.

The two major goals of this study were to determine the electron excitation temperature of the electric discharge and the minimum detection limit of this method for zirconium, yttrium, and nickel.

The very low radio frequency, high voltage atmospheric pressure discharge device as described here may offer a solution for atmospheric trace metals pollution monitoring. The excitation probability of atomic species in a discharge is a sensitive function of the electron energy. In previous experiments with thermal atmospheric plasmas the electron excitation temperature has been much lower than the peak of the excitation cross-section for many of the metals of interest. For example, the electron impact excitation cross-section for the detection of mercury at 253.6 nm is maximized at an electron energy of 5.5 eV<sup>6</sup>, but the electron excitation temperature is only about 0.5 eV or less in an atmospheric pressure air MPT<sup>7</sup> and in an air ICP<sup>8</sup>. A contributing factor to the low electron excitation energy in MPTs and ICPs may be that the induced electric field in the waveguide or induction coil is much less than 1 kV cm<sup>-1</sup> even at several kilowatts of input power<sup>9, 10</sup>. The low radio frequency plasmatron tested here has an average applied electric field of over 10 kV cm<sup>-1</sup> in the 2 mm gap discharge region. It is therefore possible that higher energy electrons may be generated in the plasmatron due to its inherent higher electric field. This paper tests this hypothesis by spectroscopic measurements of the high voltage, very low radio frequency plasmatron to determine the electron excitation temperature. Rotational temperature of the plasma gas (nitrogen) was also measured to determine the degree of local thermodynamic equilibrium (LTE). These parameters have been measured over a range of power levels and frequencies.

## II. EXPERIMENTAL SETUP

The overall schematic of the experiment is given in Figure 1.

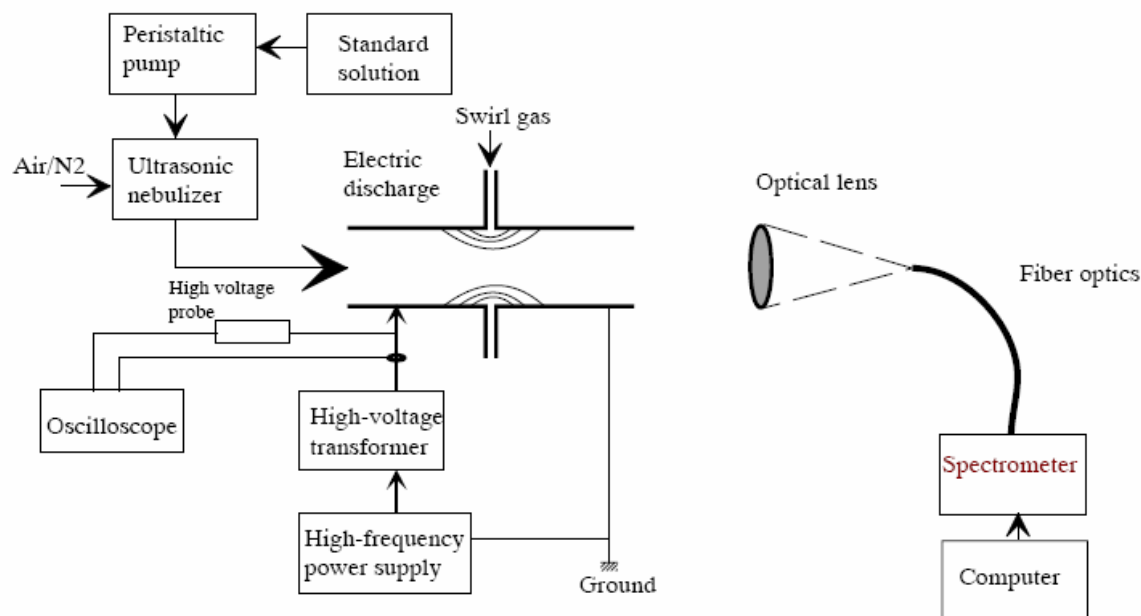


Figure 1. Schematic of experimental setup

It consists of a very low radio frequency, high voltage electric discharge device that is powered by a high voltage power supply, an ultrasonic nebulizer that produces aerosols from a standard solution, and an optical/UV spectrometer to analyze the light from the discharge. This plasma device was originally described in Rabinovich et al.<sup>11</sup>. It consists of two stainless steel cylindrical electrodes that face each other, separated by a 2 mm gap. The two electrodes have an axial cylindrical channel of 20 mm diameter through which the sample gas is passed. In addition, compressed gas at a rate of 25 liters per minute is supplied between the two electrodes through the 2 mm gap by small jets to form a swirl flow. This swirl flow keeps the electric discharge from attaching to a single point on the electrodes.

One electrode is connected to a current limited high voltage power supply and the other electrode is grounded. The power supply delivers a maximum of 300 volts that is frequency modulated from 5 to 30 kHz to a high voltage step up transformer with a maximum rating of 15 kV. A Cetac 5000 ultrasonic nebulizer is connected to the plasmatron to aerosolize a standard solution containing iron or titanium. The aerosol is carried into the plasmatron channel by a gas flow through the nebulizer at a rate of 1.45 liters per minute. A 5 cm diameter, 10 cm focal length quartz lens located 10 centimeter from the exhaust of the plasmatron collects the axially emitted light of the discharge and focuses it into a 2-meter long, UV-grade fiber optic, which in turn is connected to an optical spectrometer. The fiber optic is made of 19 fibers that are bundled together at the lens focus and stacked linearly along the slit at the spectrometer.

The spectrometer is an Instruments S.A. Model THR-640 spectrometer. It has a 2400 groove/mm grating, adjustable slit, and a Princeton Instruments Model IRY-512W intensified 512-element detector array. The spectral resolution is about 0.05 nm with an instantaneous spectral range of about 6.5 nm that can be tuned from 180 to 600 nm.

A high voltage probe and a current probe are connected to the high voltage lead on the plasmatron. They in turn are connected to a Tektronix TDS 3032B oscilloscope to monitor the frequency and power injected into the plasmatron.

Two standard solutions of 1000  $\mu\text{g/ml}$  of iron and 1000  $\mu\text{g/ml}$  of titanium dissolved in 5% nitric acid were used to generate the atomic emission spectra for electron excitation temperature measurements. Calibration of the ultrasonic nebulizer showed that 10% of the metal dissolved in the acid reaches the exhaust of the nebulizer and is carried out by the carrying gas into the plasmatron discharge channel.

For all experiments nitrogen gas was used as a carrier gas for the aerosol and as a swirl gas for the electric discharge. Also, an aerosol of clean de-ionized water vapor was first injected into the plasma through the nebulizer to acquire a background spectrum. An aerosol of the solution containing either iron or titanium was then introduced into the plasma. The water spectrum was used to subtract the effect of moisture on the discharge spectrum. It is assumed that the water spectrum is representative of the dilute  $\text{HNO}_3$  acid spectrum.

The ISA spectrometer sequentially takes 100 instantaneous spectrums at 1 s/spectrum at each of the different frequencies and power levels tested. The data analysis consists of averaging the 100 spectrums for the background and for the signal with iron or titanium injected into the plasma, then subtracting the averaged background signal from the averaged signal with the metals.

Experiments as a function of frequency consisted of changing the frequency of the power supply and maintaining the power level constant by adjusting the voltage.

### III. RESULTS AND DISCUSSION

The visual aspect of the plasma discharge presented by the plasmatron is shown in Figure 2 with an axial view through the cylindrical channel of the electrodes.

The plasma appears to be volumetric, filling the entire cylindrical channel. However, fast camera movies<sup>12</sup> reveal a single plasma filament at any one instant that is moving around the circumference of the central channel gap. This filament is elongated and moved by the swirl flow in a way similar to a plasma filament rising up a Jacob's ladder discharge. It appears that the filament extinguishes when its elongation length reaches a certain limit and then restarts at different points on the electrodes.



Figure 2. Electric discharge

A typical voltage/current trace for two rf cycles at a frequency of 23 kHz is shown in Figure 3. The discharge voltage rapidly reaches a maximum of about 2.5 kV and then gradually decreases to about 1 kV before rapidly reversing polarity.

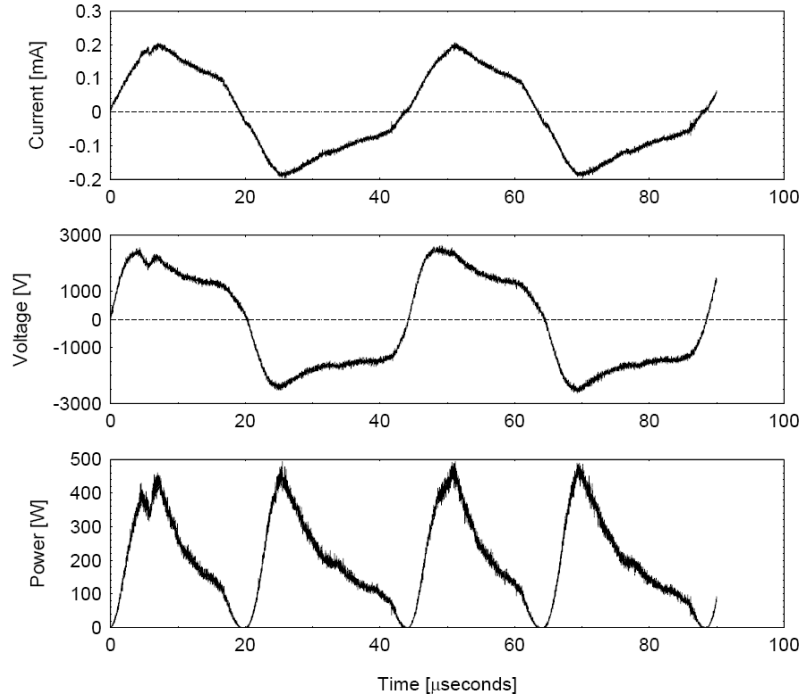


Figure 3. Oscilloscope image of the voltage/current trace at a frequency of 23 kHz.

The maximum current is much lower than what is described by Akishev et al.<sup>13</sup> for a transition from a streamer to a spark in a similar discharge. The discharge appears to be an aborted spark that does not evolve entirely into an arc. This is due to a combination of two factors: the current-limited power supply and the swirl flow that pushes and elongates the streamer/spark away from the electrodes to a point where the electric field cannot sustain the discharge. The electric field to density ratio ( $E/N$ ) here decreases due to a decreasing  $E$  field in the streamer due to space charge and streamer elongation effects overcoming a decrease in gas density due to temperature increase in the streamer<sup>14</sup>. It appears that the decrease in the electric field occurs much faster than the decrease in density, causing the streamer filament to frequently extinguish and then restart with a short length.

### 3.1. Electron excitation temperature

The atomic excitation temperature was calculated from the measured emission line intensities by assuming a local thermal equilibrium. The calculation assumed a Maxwell-Boltzmann distribution of the excited electronic energy levels. The slope of a log plot of the normalized emission intensity ( $I\lambda/gf$ ) versus the energy of the excited level ( $E_{exc}$ ) gives the temperature, where  $I$  is the emission signal intensity,  $\lambda$  is the wavelength of the

transition,  $g$  is the statistical weight, and  $f$  the oscillator strength. The slope is related to the excitation temperature by the following equation:

$$T_{\text{exc}} = \frac{-0.625}{\log \frac{I\lambda^3}{gf}} \cdot E_{\text{exc}}$$

Because iron lines between 370 and 380 nm were too weak to use for temperature measurements in pure nitrogen plasma, we used titanium lines from 321.7 nm to 324.2 nm, covering an energy range from 30,359 to 43,781  $\text{cm}^{-1}$  to measure the excitation temperature. The values of  $gf$  parameters are taken from Boumans<sup>15</sup>. Figure 4 gives titanium spectrum at 220 watts power level and 10 kHz.

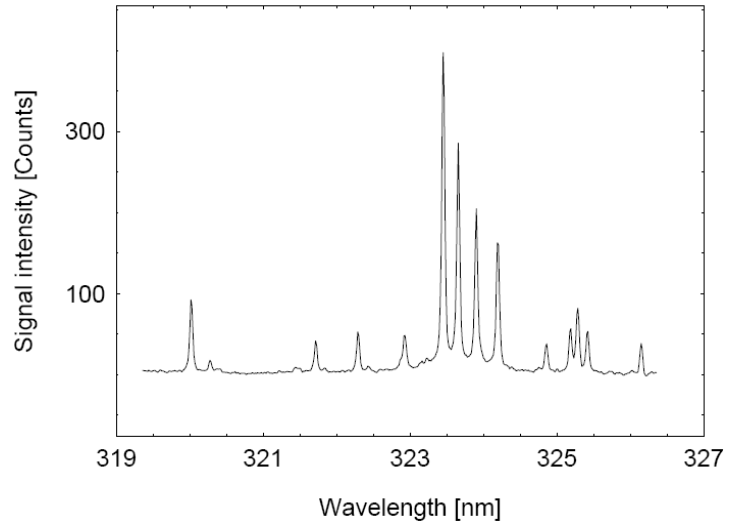


Figure 4. Ti Spectrum in nitrogen plasmatron discharge

Figure 5 gives the excitation temperature for frequencies from 5 to 25 kHz at a plasma power level of 212 watts.

As it is shown on Figure 5, the excitation temperature stays relatively constant over the range of frequencies studied. This temperature was found to be  $0.57 \pm 0.01$  eV, similar to the excitation energies found in air MPT<sup>4</sup> and ICP<sup>8</sup>.

Contrary to our original assumption, the order of magnitude higher induced electric field in the plasmatron did not translate into a higher electron excitation temperature.

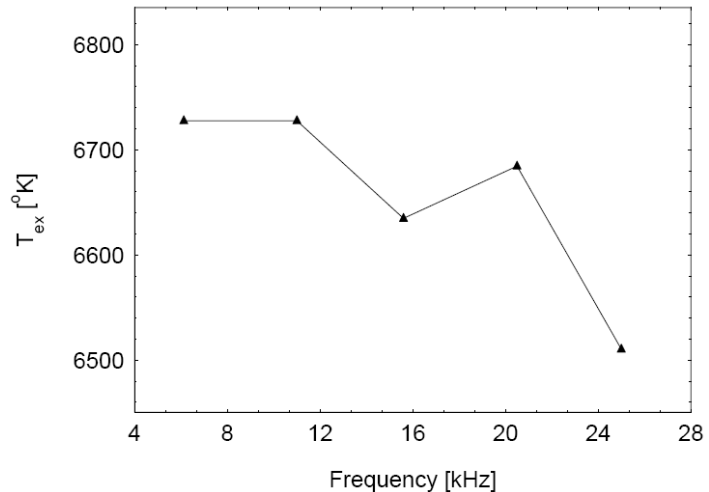


Figure 5. Excitation temperature versus high voltage frequency at 212 Watts

Apparently, the space charge effect in the elongated filament streamer of the plasmatron shields the majority of the electron distribution from the higher E-fields.

### 3.2. Molecular rotational temperature measurement

The first negative system of the nitrogen ion  $N_2^+$  was used to measure the rotational temperature<sup>16, 17</sup>. Figure 6 gives the nitrogen spectrum that includes the first negative system of the nitrogen ion  $N_2^+$  spectrum and the second positive system of the nitrogen molecule  $N_2$ .

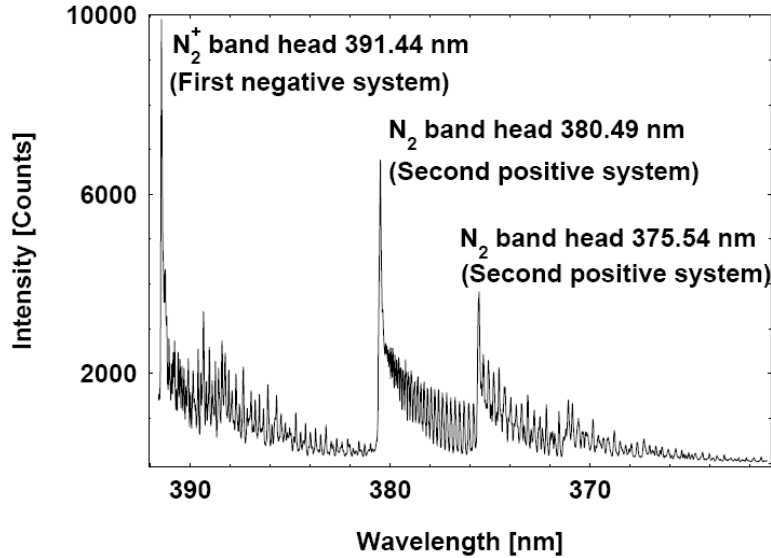
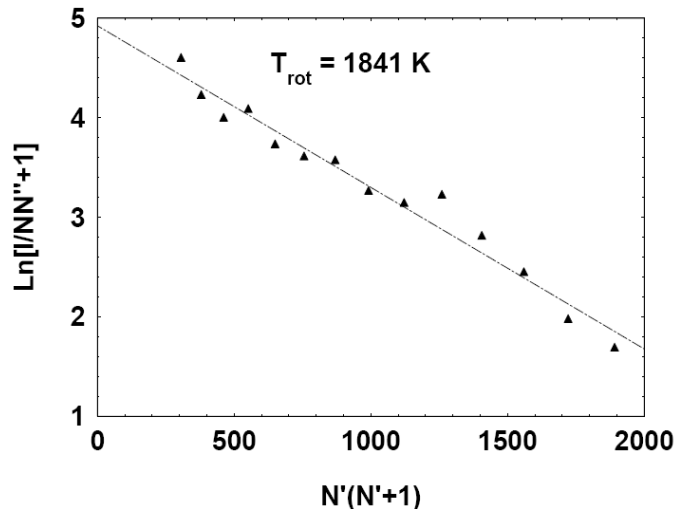


Figure 6. Nitrogen spectrum using plasmatron discharge at atmospheric pressure 215 Watts, 20 kHz

The rotational temperature was calculated by plotting  $\ln[I/(N'+N''+1)]$  versus  $N'(N''+1)$  as shown in Figure 7; where  $I$  is the line intensity,  $N'$  is the lower energy level and  $N''$  is the upper energy level. The slope of the curve is equal to  $2.983/T$ ; where  $T$  is the rotational temperature in Kelvin<sup>16</sup>.

The rotational temperature fitted to the data was found to be equal to 1840 K. This is only about one third of that for the electron excitation temperature determined above, showing that the plasma in this low radio frequency discharge is not in local thermodynamic equilibrium. It is further from equilibrium than the plasmas found in the MPT and ICP, but the plasmatron rotational temperature is high enough to suggest that the gas temperature would be sufficient to volatilize and





decompose trace species for atomic emission spectroscopy.

### 3.3 Minimum Detection Limits

The minimum detection limit for yttrium has been measured for different power levels at different frequencies using the plasmatron device. The minimum detection limit (MDL) is calculated as 3 times the standard deviation of the noise of the resulting signal and is given by the following formula:

$$MDL = \varepsilon \frac{3\sigma XR}{SF}$$

where  $\varepsilon$  is the nebulizer efficiency,  $\sigma$  is the standard deviation of the noise taken on a background detector pixel as close as possible to the spectral signal peak, X is the standard solution concentration in  $\mu\text{g/ml}$ , R is the rate of solution in ml/min pumped into the nebulizer, S is the signal intensity in counts, and F is the volume flow rate of gas in the sample line in  $\text{m}^3/\text{min}$ .

Figure 8 gives the minimum detection limit for the yttrium transition line 437.49 nm for three different frequencies and at different power levels. The experiments were performed in a complete nitrogen environment.

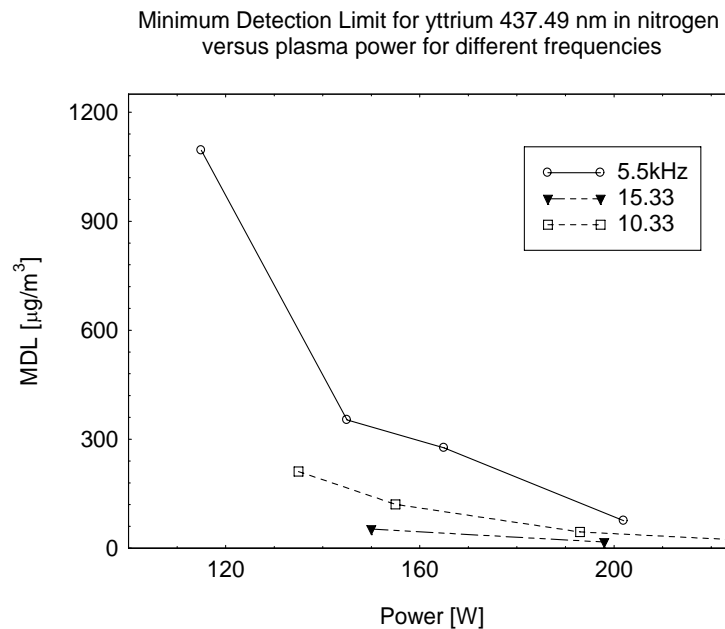


Figure 8. Minimum detection limit for yttrium

Also, the microwave plasma torch has been used to investigate the MDL for yttrium, zirconium and nickel. We also performed tests with gold, platinum and aluminum. Table 1. summarizes this work.

Table 1. Minimum detection limits for different elements using plasmatron and microwave generated plasma

Microwave Plasma Torch			Plasmatron Discharge		
Element	Minimum Detection Limit [ $\mu\text{g}/\text{m}^3$ ]	Wavelength [nm]	Element	Minimum Detection Limit [ $\mu\text{g}/\text{m}^3$ ]	Wavelength [nm]
Nickel	30.6	341.47	Nickel	97.6	301.2
Yttrium	178	437.49	Yttrium	64	437.49
Zirconium	3909	339.5	Zirconium	13750	339.1975
			Platinum	207	306.4711
			Gold	317	267.597
			Aluminum	1055	396.15

Also, it appears that the minimum detection limit depends on a combination of factors. Two of these factors are the energy level of the excited transition and the boiling point of the metal. Table 2 gives these two factors for the metals analyzed using the plasmatron discharge.

Table 2. Minimum detection limit, excitation energy and boiling temperature for specific metals.

Plasmatron Discharge				
Element	Minimum Detection Limit [ $\mu\text{g}/\text{m}^3$ ]	Wavelength [nm]	Energy [eV]	Boiling Temperature C
Zirconium	13750	339.1975	3.81	4377
Platinum	207	306.4711	4.04	3827
Yttrium	64	437.49	3.24	3337
Gold	317	267.597	4.63	2807
Nickel	97.6	301.2	4.53	2732
Aluminum	1055	396.15	3.14	2467

The nebulizer produces very fine metal particles (~ 1 micron) from standard metal solutions. If the particle is completely volatilized, then there would be more atoms to be excited, which lead to a higher signal. Metals with high boiling temperatures are more difficult to volatilize, leading to the excitation only of the atoms on the surface of the particle.

#### IV. CONCLUSION

This study has shown that the mean excitation temperature of a very low radio frequency, high voltage electric discharge in air at atmospheric pressure is about 0.5 eV, which is comparable to the mean excitation temperature of a microwave generated atmospheric plasma at 2.45 GHz and to an air ICP. Despite the order of magnitude higher initial electric field in the plasmatron device tested here, the resulting electron excitation

temperature is not significantly different from the lower field MPT and ICP. This may be due to a combination of the stretch of the discharge channel by the swirl flow to a point where the local electric field is no longer strong enough to propagate the streamer and to the fact that the discharge current density is sufficiently high enough for space charge effects to effectively shield the higher electric field from the majority of the plasma. Therefore significant improvement for using the plasmatron as an excitation source for atomic emission spectroscopy of metals with high electron excitation energies such as mercury would not be expected. Alternative ways for increasing the mean electron excitation temperature in atmospheric pressure air plasmas need to be explored. This could include shorter pulse, higher voltage and lower current discharges to minimize space charge and maximize high voltage transient effects.

Furthermore, the rotational temperature of the nitrogen ion molecule in the plasmatron was found to be 1840 K, which is much lower than the thermal plasma air MPT and ICP devices. Yet this temperature, which is generally characteristic of the gas temperature, should be high enough to volatilize any chemical compound for elemental spectroscopic analysis. However, because the character of the plasmatron discharge is that at any one instantaneous moment it is a thin, discrete filament rotated by the swirl flow, the instantaneous excitation volume is small. Most of the atoms that go through the discharge channel would not pass through the thin streamer and would therefore not be excited. This can dramatically reduce the sensitivity of an atomic emission spectroscopy instrument based on the plasmatron. Possible ways to increase the instantaneous excitation volume would need to be explored to improve the prospects of using the plasmatron as an atomic emission excitation source for trace metals monitoring.

The minimum detection limit for nickel and zirconium has been found to be higher for the plasmatron than for the microwave plasma torch. The minimum detection limit for the three metals of interest has been found to be much higher than the required sensitivity needed to detect erosion and spallation of thermal barrier coating materials in a gas turbine. Therefore, this technology would need a much further development in order to increase its sensitivity.

#### **ACKNOWLEDGMENTS**

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