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Preliminary characterization of a low-powered microwave induced flame plasma for direct organic solvent nebulization

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A low powered (<90 W) microwave-induced plasma has been generated at atmospheric pressure by using a Beenakker cavity, a laboratory constructed torch, and a gas mixture of argon (400 ml/min), hydrogen (100 ml/min), and air (130 ml/min). This plasma has an excitation temperature of 3300–3500 K, electron number density of $7 \times 10^{14} \text{ cm}^{-3}$, and easily accepts direct methanol and ethanol introduction with a 1 ml/min solution nebulization rate. Detection limits (3σ) obtained from the atomic emission signals of Li, Sr, and Cr in water are 15, 120, and 290 ng/ml, respectively. Similarly, detection limits for the metals in methanol are 15, 120, and 260 ng/ml, respectively, and in ethanol they are 25, 360, and 330 ng/ml, respectively. The linear dynamic range is greater than three orders of magnitude. © 2011 American Institute of Physics. [doi:10.1063/1.3664618]

I. INTRODUCTION

Plasmas are used extensively in atomic spectroscopy^{1,2}—as atom sources in absorption, emission, and fluorescence spectroscopy, and as ion sources in mass spectroscopy. Common analytical plasmas are the direct current plasma, the inductively coupled plasma, and the microwave induced plasma (MIP)—with the MIP operating at lowest power levels (<100 W) and gas-consumption rates (<1 l/min). These attractive MIP features also limit the MIP's capability and its use mainly as a detector in gas chromatography applications.³ Introduction of liquid into the low-powered MIP is challenging since the available power is insufficient for simultaneously performing de-solvation and excitation. The liquid feeding rate must be low enough for sustaining the plasma. A direct injection nebulizer has been coupled with a low powered argon-MIP (Ref. 4) and He-MIP.⁵ Direct nebulization of pure methanol and acetonitrile was successful with the argon-MIP, but the solution uptake rate must be less than 20 $\mu\text{L}/\text{min}$.⁴ The He-MIP was tolerant to 10% methanol solutions.⁵

It is desirable to have a low-power MIP capable of handling solutions of aqueous and non-aqueous solvents. In addition, the solution nebulization uptake rate should be $\sim 1 \text{ ml}/\text{min}$. These capabilities will then make the MIP compatible for coupling as a detector with conventional high-performance liquid chromatograph, implementing the wealth of applications already developed in high-performance liquid chromatography (HPLC). The direct nebulization of aqueous solutions into a low-powered MIP has been achieved to a certain extent,⁶ however, the direct nebulization of organic solvents remains difficult.^{1,2} Some of the difficulties arrive from vapor-loading and insufficient power for maintaining the plasma state.

We have employed a Beenakker TM_{010} cavity^{2,7} and a gas mixture of argon, hydrogen, and air, and achieved $\sim 1 \text{ ml}/\text{min}$ solution nebulization rate with pure methanol and ethanol. This paper describes the development and analytical evaluations.

II. EXPERIMENTAL

A. The pre-mix chamber and torch-base-adapter

Hydrogen and air were pre-mixed in a laboratory built chamber, and directed into a laboratory-built torch-base-adapter. The design and construction of the chamber-torch assembly is shown in Fig. 1.

The mixing chamber (MC) and torch base was used to combine combustion and argon gases before entering the alumina discharge tube. The mixing chamber was made from a 2-in. tapered brass nipple that was bored on the bottom to accommodate the sample introduction tube (0.0625 in. outside diameter and 0.0312 in. inside diameter). The top of the MC was tapped and beveled to allow for leak proof seal attached to both of the MC ends to allow the gases to flow into the chamber. Approximately 6 in. before the 1/2 in. compression fitting, 50 psi pressure release valves were installed in case of a sudden increase in pressure making certain safety would be maintained. The torch-base was machined from 1.5 in. brass rod stock and was threaded to a diameter of 9/16 in. to allow for the accommodation of the alumina discharge tube adapter. The bottom of the base was threaded and machined precisely for the insertion of the modified flame ionization detector mini torch. The mini brass torch was precision bored to ensure proper flow geometry and a diameter of 2 mm for accommodating the sample introduction tube. The alumina discharge tube adapter was machined from 9/16 in. brass rod stock and threaded for direct insertion into the torch base. A 1/4 in. hole was bored completely through this adapter to allow for the placement of the alumina discharge tube.

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TABLE II. Instrumental settings and operation parameters using the microwave induced flame plasma.

Microwave frequency and power	2.45 GHz at 90 W (max. value)
Plasma viewing mode	Axial
Entrance and exit spectrometer slit widths	10 μm except for chromium 15 μm
PMT bias	800 V
TM ₀₁₀ resonator cavity dimensions	
Depth	1 cm
Diameter	92.5 mm
Concentric glass nebulizer	
Pressure	20 psi argon
Flow rate	~400 ml/min
Sample uptake rate	~1 ml/min
Combustion gases	
Hydrogen	
Pressure	10 psi
Flow rate aqueous solvent	~120 ml/min
Flow rate organic solvent	~100 ml/min
Air	
Pressure	20 psi
Flow rate aqueous solvent	~100 ml/min
Flow rate organic solvent	~130 ml/min

dihydrate, chromium acetylacetonate, and strontium acetate were used for non-aqueous solutions.

D. Operation procedure

A pure argon plasma was first ignited (with a Tesla coil) with a forward power of 60 W and a nebulizer argon flow rate of ~500 ml/min and ~300 ml argon support gas through the mixing chamber. The hydrogen and air were then turned on, and the flow rates were gradually increasing while slowly decreasing the support argon flow rate to zero. During this time, continuous tuning was required to prevent extinguishment of the discharge. After about 30 s, the plasma reached a state of equilibrium. This was noted by a color change from a pink plasma and yellow tail flame to one of a pure yellow flame emanating from the discharge tube. The experimental settings were adjusted to those listed in Table II for operation.

III. DISCUSSION OF RESULTS

The MIP was generated by tuning the power applied to the modified Beenakker cavity at a lowest reflected power (<2 W) while maximizing the forward power. If this procedure was not followed, intense Joule heating of the discharge cavity and coaxial cables could occur, thereby damaging the magnetron. When the MIP was properly tuned, alumina tube lifetime was on the order of 1 h of continuous operation otherwise discharge tube lifetime was less than 1 min. If the MIP was extinguished, the whole ignition process must be reinitiated usually with the loss of the discharge tube. A 2 mm inside diameter (ID) alumina torch was chosen to prevent plasma wander and decrease signal noise due to plasma flicker. If the hydrogen flow rate was above 170 ml/min, with an air flow rate of 130 ml/min, discharge tube lifetime was less than 30 s.

FIG. 3. Background emission regional spectra of the microwave induced flame plasma: (a) 200–280 nm; (b) 280–340 nm; (c) 340–450 nm; (d) 450–490 nm; (e) 490–700 nm.

During the operation of the MIP, with organic solvent loading (serving as fuel), the flame was allowed to run slightly less hydrogen. It was observed, with organic solvent loading, that if the plasma was allowed to run slightly rich in hydrogen, a green plasma and tail flame occurred. This may be attributed to the green C_2 molecular band emission. The intensity of the C_2 emission was inversely proportion to the air flow rate. The sample was self-aspirating through the concentric glass nebulizer. Sample blanks were run between each working standard. The signals of the blanks between samples runs were relatively constant throughout the run. Approximately 30 s between sample and blank runs was required for signal to return to baseline value. There was no plasma instability observed while the sample was aspirated into the MIP. Figure 3 shows the spectral background emission from the microwave induced flame plasma (MIFP).

A. Analytical figures of merit

A representative atomic emission tracing is shown in Fig. 4. Multiple runs for the elements in the solvents resulted in a signal precision of 5%–6% relative standard deviation. Other experimental figures of merit for the MIFP are given in Table III. Excellent linearity ($R > 0.997$) was obtained from the concentrations (0.5, 1, 5, 10, and 50 ppm) evaluated. The linear dynamic range (signal versus concentrations) was found to cover three orders of magnitude. There is a general decrease in sensitivity for elements run in ethanol ver-

FIG. 4. Typical signal tracing of atomic emission using the microwave induced flame plasma.

sus aqueous solution. Li, Sr, and Cr exhibit a 47%, 15%, and 1% reduction, respectively, in sensitivity versus samples run in aqueous solution. There is also a general decrease in sensitivity for elements run in ethanol versus methanol. A reduction of 34%, 10%, and 30%, respectively, versus samples run in methanol. The above-mentioned effects may be attributed to the difference in sample viscosity, surface tension between the two solvents, and background emissions. Accompanying the decrease in sensitivity is an augmentation in detection limits (DLs, defined as a corresponding signal equal to three times the standard deviation of the background fluctuation). In general, there is a global decrease in detection limits for elements run in aqueous solution versus samples run in organic solvents. The above described effect may be attributed to differences in physical sample characteristics (e.g., viscosity, surface tension, etc.) and/or the plasma background when a sample is introduced. For example, the analytical signal for Cr, measured at 425.24 nm, was overlapped by the OH molecular emission band. The DL for lithium run in both methanol and ethanol, measured at 670.76 nm, is the same. There was no spectral background interference found in this region of the electromagnetic spectrum. Therefore, difference in DL

TABLE IV. Data used to generate the Boltzmann plot and to determine the excitation temperature.

Ar (I) line (Å)	Intensity	Energy (cm ⁻¹) ^{a,b}	A (10 ⁸ s ⁻¹) ^{a,b}	gk ^{a,b}
4200.6	21.1	116 943	0.0801	7
4198.3	13.7	117 563	0.242	1
4510.7	4.3	117 563	0.102	1
5558.5	2.6	122 087	0.148	5
5572.5	1.2	123 557	0.069	7

^aReference 9.

^bReference 10.

between aqueous and organic samples must be attributed to physical sample characteristics that affect the droplet diameter. The larger the droplet that is produced by the nebulizer, the more energy is required for de-solvation and the proceeding processes leading to excitation of the analyte.

B. Excitation temperature

The excitation temperature was determined by two methods.⁹ The first is by way of measuring the slope of the line from a Boltzmann plot and the second is the line pair intensity ratio method (LPIRM). Table IV gives the information used to generate the Boltzmann plot. Table V gives the information used for the line-pair method. From the Boltzmann plot, a linear least squares line was put through the data and a resultant slope of 0.0019 was obtained. The slope (m) of this line has the following relationship in Eq. (1):

$$\text{slope} = m = \frac{-0.625}{T_{\text{exc}}}, \quad (1)$$

solving for the excitation temperature (T_{exc}) gives a value of 3300 K. The Boltzmann plot showed good linearity with a correlation coefficient of 0.98. Note that the Einstein coefficients (A) for spontaneous emission are known to about $\pm 10\%$. The flame temperature of a hydrogen/air chemical flame is on the order of 2000 K, while a pure plasma is on the order of 4000–12 000 K. The excitation temperature of

TABLE III. Experimental figures of merit for the microwave induced flame plasma.

Element	λ (Å) ^a	Solvent ^b	Air/H ₂ (ml/min)	Power (W)	Sensitivity ^c (mV/ppm)	DL ^d (ng/ml)	LDR ^e (10 $\times$)	LCC ^f
Li	6707.7	Water	100/120	90	34.7	15.2	3	0.999
Li	6707.7	MeOH	130/100	90	27.7	24.8	3	0.999
Li	6707.7	EtOH	130/100	90	18.3	24.7	3	0.997
Sr	4607.3	Water	100/120	90	21.8	122	3	0.999
Sr	4607.3	MeOH	130/100	90	16.5	481	3	0.999
Sr	4607.3	EtOH	130/100	90	18.5	363	3	0.997
Cr	4252.4	Water	100/120	90	21.5	286	3	0.999
Cr	4252.4	MeOH	130/100	90	30.5	260	3	0.999
Cr	4252.4	EtOH	130/100	90	21.2	333	3	0.999

^a λ is wavelength in units of angstroms (Å).

^bSolvent used (methanol = MeOH, ethanol = EtOH).

^cSensitivity in units of millivolts (mV) per part-per-million solution concentration.

^dDetection limit (DL) in units of nanograms per milliliter.

^eLinear dynamic range (LDR) in powers of ten of solution concentrations.

^fLinearity coefficient correlation (LCC).

TABLE V. Data used to calculate the excitation temperature using line-pair-intensity-ratio method.

Sr (I) line (Å)	Intensity	Energy (cm ⁻¹) ^a	<i>g</i> ^a	<i>A</i> ^a
4607.3	806.45	21 698	0.27	0.85×10^8
4962.3	113.31	35 045	1.8	4.8×10^8

^aReference 11.

the MIP lies between that of a pure hydrogen/air flame and a pure plasma.

The excitation temperature (T_{exc}) calculated from the line-pair intensity-ratio method was 3500 K by using Eq. (2) as follows:

$$T_{\text{exc}} = \frac{0.625(E_1 - E_2)}{\log(g_1 A_1 \lambda_2 / g_2 A_2 \lambda_1) - \log(I_1 / I_2)}, \quad (2)$$

where g is the degeneracy, E is the excitation energy, λ is the wavelength, and I is the signal intensity. An error of at least 20% in excitation temperatures, calculated from Boltzmann plot and the line-pair method, must be allowed.¹¹ The excitation temperatures obtained in this work agree within 10% of each other. The excitation temperature serves as a guide to the ability for the atom source to excite electronic transitions.

C. Degree of ionization and electron density in plasma

The degree of ionization provides information on the excitation source's ability to atomize and ionize atoms and can be calculated from Eq. (3)

$$\frac{N^+}{N^o} = \frac{(I\lambda^3)^+ u^+ (gf)^o}{(I\lambda^3)^o u^o (gf)^+} \exp\left[\frac{E^+ - E^o}{kT}\right], \quad (3)$$

where I is the intensity of the spectral line, N is the particle density, g is a statistical weighting factor, f is the Ladenburg's oscillator strength for the emitted line, λ is the wavelength, E is the energy of transition, k is the Boltzmann constant, T is the absolute thermodynamic temperature, and u is the partition function. In the equation, the variables associated with the atomic species is denoted with a superscript o and similarly a superscript $+$ denotes variables belonging to the ionic species. Table VI gives the data used to calculate the N^+/N^o ratio of 3.3. The energy units given in Table VI are in kilo-Kaisers (kK), the wavelength is in angstroms, and the absolute thermodynamic temperature in units of Kelvin.

TABLE VI. Data used to calculate the ion density to atom density ratio using the Sr(I) atomic line centered at 4607.3 angstroms and the Sr(II) emission centered at 4077.7 Å.

	<i>I</i>	λ	<i>gf</i> ^a	<i>E</i> (kK) ^a	<i>T</i>	<i>u</i> ^a
Atom	697.93	4607.3	0.27	21 698	3500	1.3
Ion	369.69	4077.7	0.17	24 517	3500	0.17

^aReference 11.

The ion/atom density ratio may be used to obtain the electron density (N_e), via the Saha equation (4), given by

$$\log N_e = 21.245 - 0.988 V - \log(N^+ / N^o) - \log(u^+ / u^o), \quad (4)$$

where V is the ionization potential in volt. In this work, an electron density of $7 \times 10^{14} \text{ cm}^{-3}$ was calculated. This number was calculated by assuming an excitation temperature of 3500 K and an ionization potential of 5.629 V. A conventional electrical discharge has an electron density on the order of 10^{13} – 10^{16} cm^{-3} . The MIP system described in this paper is well within this range.

IV. CONCLUSIONS

The results of the physical measurements characterize this atom excitation source to be a plasma, with an excitation temperature of 3500 K, an electron number density of $7 \times 10^{14} \text{ cm}^{-3}$, and an ion-to-atom ratio of 3.3. This plasma gives good analytical figures of merit, can tolerate 100% organic solvent with a solution nebulization rate of 1 ml/min, and therefore, is amenable as a detector for conventional HPLC operations. An improvement in the torch design should reduce the detection limit and prolong the lifetime of the discharge tube.

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