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Liquid sampling-atmospheric pressure glow discharge as a secondary excitation source: Assessment of plasma characteristics

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ABSTRACT

The liquid sampling-atmospheric pressure glow discharge (LS-APGD) has been assessed as a secondary excitation source with a parametric evaluation regarding carrier gas flow rate, applied current, and electrode distance. With this parametric evaluation, plasma optical emission was monitored in order to obtain a fundamental understanding with regards to rotational temperature (T_{rot}), excitation temperature (T_{exc}), electron number density (n_e), and plasma robustness. Incentive for these studies is not only for a greater overall fundamental knowledge of the APGD, but also in instrumenting a secondary excitation/ionization source following laser ablation (LA). Rotational temperatures were determined through experimentally fitting of the N_2 and OH molecular emission bands while atomic excitation temperatures were calculated using a Boltzmann distribution of He and Mg atomic lines. The rotational and excitation temperatures were determined to be ~1000 K and ~2700 K respectively. Electron number density was calculated to be on the order of $\sim 3 \times 10^{15}$ cm^{-3} utilizing Stark broadening effects of the Hα line of the Balmer series and a He I transition. In addition, those diagnostics were performed introducing magnesium (by solution feed and laser ablation) into the plasma in order to determine any perturbation under heavy matrix sampling. The so-called plasma robustness factor, derived by monitoring Mg II/Mg I emission ratios, is also employed as a reflection of potential perturbations in microplasma energetics across the various operation conditions and sample loadings. While truly a miniaturized source (<1 mm^3 volume), the LS-APGD is shown to be quite robust with plasma characteristics and temperatures being unaffected upon introduction of metal species, whether by liquid or laser ablation sample introduction.

1. Introduction

As the trend of miniaturization in analytical chemistry instrumentation has progressed, the development of new atmospheric pressure plasma sources has seen increased interest. Currently, there is a need to design spectrochemical instruments with lower power consumption, reduced sample sizes, compact footprint, low operating costs, and the ability to be operated under ambient conditions [1–3]. Reductions in sampling size have been addressed over the past two decades by laser-ablation (LA), allowing for chemical analysis of solids without sample preparation [4–6]. LA utilizes a short-pulsed, high-power laser beam to remove material for either a direct analysis of the plasma volume by optical emission spectroscopy (OES) or to be transported into a secondary excitation/ionization source such as the inductively coupled plasma (ICP) [7,8]. The former, termed laser-induced breakdown spectroscopy (LIBS), is easily miniaturized for portability with applications expanding to exploration on the surface of Mars [9,10]. By utilizing a secondary source, higher power densities and longer residence times can be utilized for enhanced sensitivity and lower limits of detection (LODs) when compared to LIBS [6,11]. To this end, atto-/femtogram detections limits are readily achieved in ICP-MS [12].

Unfortunately, the conventional ICP is not ideal as a secondary source as minute amounts of ablated mass are introduced into the relatively large plasma volume (~125 mm^3), not to mention the high operating cost and large footprint of the base ICP-OES/MS instrument [6]. Few efforts have addressed miniaturizing the ICP or reducing the operational overhead of LA-ICP instrumentation. Improving designs by incorporating alternative plasmas as the secondary excitation/ionization source of particulates should be explored, especially regarding the miniaturization of the spectrochemical instrumentation. In recent years, a few secondary sources have been proposed for the detection of laser ablated particles such as microwave induced plasmas (MIP) and the flowing atmospheric pressure afterglow (FAPA) [4,13].

Marcus and co-workers developed a liquid sampling-atmospheric pressure glow discharge (LS-APGD), which is sustained between an

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electrolytic liquid (HNO_3) flowing from a glass capillary and a metallic counter electrode placed ~2 mm away [14–16]. The operational space of this excitation/ionization source fits well in terms of the miniaturization characteristics mentioned above. While early LS-APGD works focused on OES monitoring, recent efforts have demonstrated the ability of the source to effectively ionize solution-introduced species by mass spectrometry (MS) [17,18]. The scope of application has been expanded through the introduction of LA-generated particles [19,20]. This combination, LA-LS-APGD, has been shown to be qualitatively similar to LA-ICP, with efficient vaporization/excitation/ionization of particles produced from nanosecond and femtosecond pulsed lasers. Particularly relevant for LA sampling, the LS-APGD operates at much higher power densities (~10 W mm^{-3} versus 0.1 W mm^{-3}) and a much smaller plasma volume (~1 mm^3 versus ~125 mm^3) than the ICP (i.e., less dilution). Finally, simple gas dynamics calculations suggest plasma transit times of 5–30 ms vs. ~1 ms for the ICP, though these must be verified experimentally.

When assessing plasma performance, fundamental properties must be characterized to understand excitation conditions, which may vary with operation parameters or the introduction of sample material [21,22]. Optical emission spectroscopy (OES) is a versatile means of characterization of atmospheric pressure flames and plasmas, typically by the fitting of molecular bands (e.g., N_2, OH) to obtain rotational temperatures (T_{rot}), determinations of excitation temperatures (T_{exc}) by monitoring excited states of various species such as plasma gases or sample species, and measurement of the broadening of emission lines (H, He) to yield plasma electron number densities (n_e) [23–25]. Finally, the ability of an spectrochemical source to be immune to sample-induced perturbations can be assessed through changes in the "robustness" factor determined by the Mg II/Mg I emission intensity ratios [26,27].

The research presented here utilizes OES to evaluate the properties of the LS-APGD to gain fundamental knowledge regarding the source as a means for secondary excitation/ionization of LA-introduced particles. T_{rot}, T_{exc}, and n_e were evaluated across a matrix of plasma operation conditions generated through a central composite, design of experiments (DOE) approach, studying the roles of electrode separation distance, discharge current, and carrier gas (He) flow rate. Molecular bands, OH and the N_2 second positive system [28] were utilized for rotational/vibrational temperatures while the emission of He and Mg lines was utilized for the determination of excitation temperatures and plasma robustness. In addition to baseline values for these quantities determined for aqueous HNO_3 blanks, the plasma was stressed by introduction of large amounts of magnesium, to determine potential deleterious effects due to sample matrix. In one case, Mg^{2+} was added in the nitric acid feed at a concentration of 1000 μg mL^{-1}, and in the other case metal shards were compacted in a paraffin matrix and introduced via laser ablation. Such studies set the stage for applications in the analysis of matrix-laden solutions and LA sampling.

2. Materials and methods

2.1. LS-APGD source

The LS-APGD source is relatively unchanged from previous publications, incorporating the flow of laser-ablated particles into the microplasma through the *hollow* counter electrode [19,20]. The microplasma is sustained between an electrolytic solution (5% HNO_3) and the counter electrode (nickel, 0.3 cm o.d., 0.1 cm i.d.) through which the He carrier gas flows, transporting ablated particles from the ablation cell into the plasma volume. A syringe pump (New Era Pump Systems Inc., model NE-1000 Multi-Phaser, Farmingdale, NY) was used to deliver the electrolytic solution through a fused silica capillary (360 μm o.d., 100 μm i.d. Idex Health and Science, Oak Harbor, WA) which is housed within a metal capillary (nickel, 0.16 cm o.d., 0.06 cm i.d.). Helium was employed as a sheath gas (0.2 L min^{-1}) flowing between the capillaries, as optimized in a previous publication [19]. Power for the microplasma was delivered by a Glassman High Voltage Inc. power supply (0–100 mA, 0–2 kV, High Bridge, NJ) operating positive polarity with a 10 kΩ, 225 W ballast resistor (Ohmite, Arlington Heights, IL) placed in-line with the powered solution electrode (the counter electrode was held at ground potential). It is important to point out that the entirety of the LS-APGD plasma components, power supply, gas metering, and the ablating laser are mounted on a single 30.5 × 30.5 cm^2 optical bread board. Potential plasma perturbations were assessed by introducing 1000 μg mL^{-1} magnesium (CPI International, Santa Rosa, CA) in the electrolytic feed solution and by the ablation of a 2% Mg pellet (2% in paraffin) that was made in-house (LBNL).

2.2. Laser ablation apparatus

For the introduction of laser ablated particles a commercial laser ablation system (J100 Applied Spectra, Inc., Freemont, CA, USA) consisting of a nanosecond laser (Nd:YAG) with a 5-ns pulse duration was used and operated at its fundamental wavelength of 1064 nm, and variable energy (max 50 mJ) and repetition rate (1–10 Hz). Laser ablation was performed in a helium atmosphere. The J-100 ablation system is equipped with an ablation chamber that could accommodate samples up to 100 mm diameter with flexibility in volume and wash-out time.

2.3. Optical emission measurements

Broad wavelength range measurements were performed using an optical fiber-based spectrometer (Aurora, Applied Spectra, Fremont, CA). This spectrometer consists of six channels, each composed of a 2048 pixel CCD detector dedicated to different spectra regions. A fused silica biconvex lens (35 mm focal length, 25.4 mm diameter) was used to focus the entire microplasma image onto the input optic of the fiber bundle connected to the spectrometer. While there are known inhomogeneities in the LS-APGD [29], this approach is the most pragmatic way of sampling the ~1 mm^3 plasma volume, analogous to the case with LIBS analyses. A composite (simultaneous) spectrum is acquired using a 1.05 ms gate over each of the 500 laser shots, with spectral resolution of 0.05–0.12 nm across the 190–1040 nm wavelength range. For the calculation of n_e, Stark broadening of the H (I) 656.3 nm and He (I) 587.6 nm lines was measured employing a 1.25 m focal length, 2400 gr mm^{-1} grating, Czerny–Turner spectrometer (Horiba-JY, Model 1250 M, Longjumeau, France), with an intensified charged-coupled device (ICCD) detector (Princeton Instruments, PI MAX 1024 Gen II, Trenton, NJ 08619, USA). This detection system yields a spectral window of ~13 nm with 0.04 nm resolution. The same optical coupling was used in this case as the analytical (array) spectrometer system. Experimentally-determined line widths were processed under Lorenz fitting to isolate Stark effects from Doppler broadening contributions. Corrections were employed by subtracting the FWHM from the corresponding Hg lines to correct for instrument broadening [30]. The ICCD acquisition was set at a 1 μs delay, a gate width of 150 μs, and a gain set at 200 out of a maximum setting of 256. Due to experimental constraints, laser ablation sample introduction could not be performed in conjunction with the high-resolution optical measurements.

2.4. Experimental design

The various plasma species were optically monitored during the course of varying the electrode gap, He carrier gas flow rate, and applied current of the LS-APGD, with the specific parameters listed in Table 1. A central composite DOE, with three experimental factors, was used to study the effects of the operating parameters on the plasma properties [31]. The experimental design and the surface responses were generated using Statgraphics (Warrenton, VA). The central composite design generates a random sequence of experiments and parameter combinations across a range of parameter values centered among typical operating conditions. A total of n = 16 parameter combinations was