



# Roles of electrode material and geometry in liquid sampling-atmospheric pressure glow discharge (LS-APGD) microplasma emission spectroscopy<sup>☆</sup>

C. Derrick Quarles Jr., Benjamin T. Manard, Carolyn Q. Burdette, R. Kenneth Marcus<sup>\*</sup>

Department of Chemistry, Biosystems Research Complex, Clemson University, Clemson, South Carolina 29634-0973, United States

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## ABSTRACT

The roles of the electrode material and geometry on the performance of the liquid sampling-atmospheric pressure glow discharge (LS-APGD) optical emission spectroscopy source are described. The LS-APGD source has been interfaced to a high resolution JY RF-5000 polychromator allowing for simultaneous multiple element detection. This LS-APGD source operates at currents of 20–60 mA and solution flow rates of 0.1–0.4 mL min<sup>-1</sup>. A glow discharge is generated between the surface of the electrolyte test solution exiting a glass capillary and the end of a metallic counterelectrode. Described here is an evaluation of how the counterelectrode material identity (copper, nickel, and stainless steel) and the electrode configuration (geometry) influence the analyte emission responses for a test solution containing Ag, Cr, Cu, Mg, Ni, and Zn in 1 M HNO<sub>3</sub>. Studies of the effect of liquid flow rates reveal that 0.3 mL min<sup>-1</sup> provides optimal analyte emission responses as it relates to peak intensity, peak area, and peak widths. Use of nickel as the counterelectrode material provided the best reproducibility for analyte emission responses with 8.9–13.0%RSDs for 50 μL injections of 100 μg mL<sup>-1</sup> test solutions, while copper and stainless steel electrodes had %RSDs of 3–5 times higher than the nickel electrode. The role of the electrode geometries were evaluated previously-used 180° (co-linear) arrangement as well as for different configurations with the electrodes mounted at 90° with respect to each other, with the most intense optical emission responses found for the 180° geometry. Solution-based limits of detection (LOD) were found to be in the range of 0.44–0.93 μg mL<sup>-1</sup> for Ag, Cu, Mg, Ni, and Zn using the nickel electrode at the 180° geometry. Based on the use of 50 μL injections, this represents absolute detection limits of 22–46 ng. LODs were approximately an order of magnitude higher for the copper and stainless steel electrodes.

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## 1. Introduction

The work towards the development of miniaturized sources for elemental analysis and speciation has grown over the past decade [1]. Microplasmas operating at atmospheric pressure offer advantages such as smaller footprints, lower power consumption, smaller sample and reagent/waste volumes, and the potential to be used as a portable instrumentation for analytical detection [1]. There are a number of approaches (e.g., filaments, electrothermal atomizers, etc.) for the introduction of discrete, dried solution residues into standard spectrochemical sources [2–4]. A much larger challenge, though, is the case of flowing streams introduced via liquid chromatography. Here, the state conversions between solvated metal ions through to gas phase excited state atoms is energy-expensive. The same situation results for cases where rapid analysis of solution aliquots (e.g. flow injection) is required. A family of atmospheric pressure glow discharge devices

shows promise in this regard. Currently, there are two basic designs that have been reported in the literature offering direct liquid sampling capabilities with multielement optical emission spectroscopy (OES) detection [5].

Cserfalvi and co-workers first introduced the electrolyte-cathode discharge (ELCAD) for OES analysis in the 1990's [6–9]. This device operates by striking a glow discharge at atmospheric pressure between an anode (metal rod) and an electrolyte solution (pH 1–3, containing the analyte) acting as the cathode. Typical sample introduction flow rates are in the range of 2–10 mL min<sup>-1</sup>, with the solution flowing vertically upward through a glass capillary, forming a fountain. The solution overflow enters a pool in contact with the electrode potential; as such, only a very small fraction of the test solution is actually vaporized for subsequent plasma desolvation/dissociation/excitation processes. Kim et al. reported limits of detection for various elements to be in the range of 0.01–0.03 ppm for the ELCAD device operating at 10 mL min<sup>-1</sup>, using unspecified analyte volumes [10]. A miniaturized version of the ELCAD has been reported by Hieftje and co-workers [5,11–13] for high-throughput sampling in which limits of detection were found for Li (0.2 ppb) and Hg (270 ppb) for 25 μL samples [11]. These detection limits are promising, but the high sample introduction

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<sup>\*</sup> Corresponding author. Tel.: +1 864 656 5011; fax: +1 864 656 0567.

flow rates ( $2.5\text{--}3.5\text{ mL min}^{-1}$ ) required for optimal operation make it difficult to couple the ELCAD instrument to many chromatographic systems and result in large volumes of chemical waste (predominately acidic aqueous solutions).

Marcus and Davis introduced a liquid sampling-atmospheric pressure glow discharge (LS-APGD) device that operates at sample introduction rates of  $0.1\text{--}3.0\text{ mL min}^{-1}$  [14–16]. The LS-APGD was designed with liquid chromatography in mind, allowing speciation-types of information to be obtained via OES monitoring. More recently, the device has been used as an ionization source for elemental mass spectrometry [17,18]. The LS-APGD source is different from the ELCAD source in that the electrolytic liquid (i.e.  $\sim 1\text{ M HNO}_3$ ) flows out of a small glass capillary tube acting as one electrode. The electrical connection here is applied to the solution in its passage through a metallic fitting. The glass capillary is mounted inside of a metal capillary, such that a cooling/sheath gas (e.g., He, Ar, and  $\text{N}_2$ ) can be passed over the glass capillary and solution tip. A counterelectrode is placed  $\sim 0.5\text{--}3.0\text{ mm}$  from the capillary electrode allowing the glow discharge plasma to be sustained at the liquid surface. To be clear, no plasma can be sustained in the absence of the electrolytic solution flow. The plasma can be operated up to  $1000\text{ V dc}$  and  $5\text{--}80\text{ mA}$  with current–voltage ( $i\text{--}V$ ) plots that are characteristic of the abnormal glow discharge regime [14]. The operating parameters are dependent on the distance between the electrodes and the conductivity of the solution. The passage of electrical current (electrons or positive ions) across the liquid solution causes local heating and thus volatilization of the analyte species [14]. At discharge currents of  $> 30\text{ mA}$  and flow rates of as much as  $0.5\text{ mL min}^{-1}$ , the plasma operates in a total consumption mode, such that no solution goes to waste. The same is achieved at lower currents for correspondingly lower solution flow rates. The sustaining potential (positive or negative) can be applied to either electrode, although it was found that the LS-APGD operates best for OES (greater analyte intensities) when the solution electrode is grounded and a positive potential is placed on the counterelectrode [16], referred to as the solution grounded cathode (SGC) mode. The spatial profile of the plasma emission was captured for both the solution-as-cathode and -as-anode geometry, at a flow rate of  $1.0\text{ mL min}^{-1}$ , revealing that the plasma was of similar size and the total photon flux was identical (equal power supplied to the excitation region of the plasma) in both cases [15]. This spatial map also showed that the negative glow of the plasma is anchored at the respective cathode in each case [15].

Initially, the LS-APGD was operated at stable plasma conditions with flow rates of  $0.5\text{--}1.5\text{ mL min}^{-1}$  [14]. In an effort to stabilize the plasma operation at lower flow rates,  $\text{N}_2$  and He were evaluated as a sheath gas. The gas flows ( $\sim 15\text{ mL min}^{-1}$ ) out of a metal capillary that encases the glass capillary (solution delivery), helping stabilize the plasma at low flow rates ( $< 0.5\text{ mL min}^{-1}$ ) and regulating the temperatures of the electrode materials [15]. It was found that the use of a helium sheath gas resulted in  $\sim 10\%$  increase in gas ( $3000\text{ K}$ ) and excitation ( $3600\text{ K}$ ) temperatures as compared to nitrogen sheath gas [16].

A practical concern in developing instrumentation for spectrochemical analysis is the effect that complex matrices and/or the presence of easily ionizable elements (EIEs) have on analyte signal responses. This issue was addressed for the EIEs Na and Ca, studying their influence across a range of salt concentration as well as changes in electrolyte pH ( $\text{HNO}_3$ ) [19]. Stable operation of the plasma and consistent analyte emission responses were found for electrolyte solutions having a  $\text{pH} \leq 2.0$ . There were no significant changes in the analyte emission responses for Sc, Cu, Mo, and Hg due to increasing concentrations of Ca or Na ( $0\text{--}0.1\%$ ), therefore the LS-APGD source appears to be fairly immune to EIEs present in sample matrices [19].

Two potentially important parameters that have yet to be evaluated are the roles of the composition of the metallic counterelectrode and the spatial geometry of the two electrodes. In previous LS-APGD

works the counterelectrode has been copper or nickel, but no detailed study has been undertaken to determine if the identity of the counterelectrode plays a part in analytical responses. The identity of metal electrode may affect the electrical characteristics of the microplasma via their work function and propensity to form surface oxides when exposed to the discharge and acidic test solutions. Vaporized atoms from the counterelectrode could also contribute to the derived optical spectra. The role of the identity of the counterelectrode (copper, nickel, and stainless steel) is studied here using a multielement test solution (Ag, Cr, Cu, Ni, Mg, and Zn) to monitor the effects of discharge current on analyte response and analytical characteristics (reproducibility and limits of detection). All previous work had been undertaken with photon sampling perpendicular to the interelectrode axis. Recently, preliminary MS experiments have revealed that mounting the electrodes at a  $90^\circ$  angle was most beneficial in terms of ion signal levels and showing very good temporal stability [17,18]. Therefore, this geometry was evaluated for OES here as well to see if there would be substantive advantages. The presented evaluation of liquid flow rate, electrode identity, and source geometry for the LS-APGD-OES system provides a more complete understanding of the operation of the APGD source for optical emission spectroscopy applications.

## 2. Experimental

### 2.1. LS-APGD source

Fig. 1 displays the basic system components of the APGD source, which are relatively unchanged from previous works [14–16,19–21], with slight modifications made to the mounting platform allowing it to fit onto the front of the JY RF-5000 polychromator. A syringe pump is employed for these studies, providing chromatographically-important stability at low flow rates not achievable in past experiments involving the LS-APGD source. The liquid flow (electrolyte solution and test aliquots) was introduced through a glass capillary ( $125\text{ }\mu\text{m o.d.}$ ,  $75\text{ }\mu\text{m i.d.}$ ) housed inside of a stainless steel capillary ( $700\text{ }\mu\text{m o.d.}$ ,  $500\text{ }\mu\text{m i.d.}$ ). A helium cooling/sheath gas ( $\sim 1.2\text{ mL min}^{-1}$ ) was passed through the intercapillary gap across the end of the glass capillary [15]. Commercially available vacuum high voltage feedthroughs (CeramTec Corporation) having  $1.27\text{ mm}$  diameter electrodes (copper, nickel, or stainless steel) were mounted opposite the solution electrode with  $\sim 2\text{ mm}$  gap between the two electrodes. Power was provided by a Bertan Model 915 series power supply (Hicksville, NY) that is operated in constant current mode with a  $10\text{ k}\Omega$  ballast resistor mounted in series between the power supply and the counterelectrode.

### 2.2. Optical spectrometer

The majority of the previous LS-APGD studies were conducted using a monochromator, requiring that each element be analyzed separately. The background optical emission spectra extract from the microplasma are much like a combustion flame with water aspiration, composed of band structure attributable to OH in the region of  $310\text{ nm}$ , NH in the region of  $335\text{ nm}$ , and a variety of  $\text{N}_2^+$  bands across the visible portion of the spectrum [14]. The current apparatus included the use of a high-resolution polychromator as the detector, allowing for simultaneous multielement detection. A JY RF-5000 (Jobin-Yvon, Horiba Group, Longjumeau, France) polychromator has been modified (by removing the supplied rf-GD source) and applied as the detector for the LS-APGD source. The RF-5000 is a  $0.5\text{-m}$  Paschen–Runge polychromator with an ion-etched holographic grating with  $2400\text{ grooves mm}^{-1}$ , providing a practical resolution of  $\sim 0.01\text{ nm}$ . The JY RF-5000 is equipped with 26 photo multiplier tubes (PMTs) allowing for simultaneous detection of all available optical lines at a sampling rate of  $\sim 2\text{ kHz}$ . The optical lines monitored

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