



Investigation of spectrochemical matrix effects in the liquid sampling-atmospheric pressure glow discharge source[☆]



Benjamin T. Manard^{a,b}, Jhanis J. Gonzalez^b, Arnab Sarkar^{b,c}, Xianglei Mao^b, Lynn X. Zhang^a, Stefanie Konegger-Kappel^a, R. Kenneth Marcus^{a,*}, Richard E. Russo^b

^a Department of Chemistry, Clemson University, Clemson, SC 29634, United States

^b Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

^c Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

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ABSTRACT

The liquid sampling-atmospheric pressure glow discharge (LS-APGD) microplasma was evaluated with regard to its spectrochemical robustness in its application as a miniaturized optical emission spectroscopy (OES) source for liquid samples. The susceptibility to perturbations in excitation/ionization conditions was probed across a wide range test species, including transition metals, easily ionized elements (group I), and elements with low second ionization potentials (group II). Spectrochemical metrics included the plasma excitation temperature (T_{exc}), ionization temperatures (T_{ion}), and magnesium (Mg) ionic:atomic (Mg II:Mg I) ratios. The introduction of the 11 different matrix elements into the LS-APGD at concentrations of $500 \mu\text{g mL}^{-1}$ yielded no significant changes in the optically-determined plasma characteristics, indicating a relative immunity to spectrochemical matrix effects. T_{exc} values for the plasma, using He I as the spectrometric species averaged $2769 \pm 79 \text{ K}$ across the test matrix, with Mg-based ionization temperature values centered at $6665 \pm 151 \text{ K}$. Typical Mg II:Mg I ratios (the so-called robustness parameter) were 0.95 ± 0.3 . The lack of appreciable perturbation in excitation/ionization conditions observed here is also manifested in virtually no changes in the probe Mg II and I species' intensities, even at matrix loadings of up to $1000 \mu\text{g mL}^{-1}$ of Ba. These observations indicate that the LS-APGD could serve as an OES source for the analysis of diverse aqueous samples without appreciable spectroscopic matrix effects, though potential physical matrix effects including vaporization effects must be evaluated.

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1. Introduction

There recently have been appreciable efforts dedicated towards instrument miniaturization relative to spectrochemical analysis methodologies [1–4]. Decreases in footprint, power requirements, solvent waste, and sample size are all characteristics targeted with the miniaturization of plasma excitation/ionization sources. The driving forces for these investigations involve both not only the economics of performing an analysis, but also the potential for field deployment applications. The low operating powers (<100 W) employed in many of these small-volume devices suggest that they may not have the ability to effectively vaporize/dissociate/excite analyte species in solution for determinations by optical emission spectroscopy (OES). Thus, analogous to the Beenakker-cavity MIPs [5,6], the majority of these sources are dedicated to vapor phase samples. Beyond solvent-loading difficulties, there would seem to be a propensity for matrix effect in the

case of complex samples wherein the introduction of easily ionizable elements (EIEs) or the formation of refractory species could cause plasma disruption and alter the spectrochemical characteristics (e.g., excitation temperature) [7–12]. Changes in excitation conditions and altered energy partitioning are some of the mechanisms contributing to matrix effects in sources employed for elemental analysis. As shown in inductively-coupled and microwave-induced plasmas (ICPs and MIPs), increases in the power delivered to plasmas improve their tolerance to solvent loading, while also reducing the extent of matrix effects [13,14]. However, the operational space for such high power devices is contrary to the driving forces for miniaturized instruments.

A great deal of research has been dedicated to studying the comparatively minor spectrochemical matrix effects in the ICP [10–13,15–18]. Similar detailed studies are scarce in regard to miniaturized plasmas, where the vast majority of fundamental spectrochemical studies are performed under conditions where there is no appreciable sample burden [19–24]. Perturbations of excitation/ionization conditions (i.e., potential matrix effects) must be considered for practical analyses, particularly for the analysis of complex samples with target analytes in low concentrations. In the case of field-deployable instrumentation, there is certainly a need to do as little sample manipulation as possible,

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* Corresponding author.

E-mail address: marcusr@clemson.edu (R.K. Marcus).

and so matrix effects should be well characterized. This would apply to all spectrochemical sources. Based on the projected fields of use for microplasmas, matrix-effect studies are important for the analysis of natural materials such as biosamples (e.g. biofluids) and geological samples (e.g. rocks) that are rich in EIEs. A low power source that is not significantly afflicted by matrix effects would be a valuable part of the spectrochemical instrumentation portfolio, especially in field deployment situations.

The term “robustness” is used generically in analytical chemistry to describe the ability of a method/instrumentation to tolerate the loading of a specific sample matrix or inaccuracies that are the result of poor instrument control. Clearly, there are many steps in the spectrochemical analysis process that could result in matrix effects, including interspecies reactions, changes in sample introduction efficiency, and perturbations of excitation/ionization conditions. The latter we refer to here as “spectrochemical robustness”. Many metrics can be employed for characterizing spectrochemical robustness, including gas rotational temperatures (T_{rot}), excitation temperatures (T_{exc}), ionization temperature (T_{ion}) and the ionic:atomic line ratios of specific elements, most commonly magnesium [10,11,17,25,26]. Potential changes in the first three “temperatures” can reflect whether or not the source can withstand the addition of different sample/matrix/solvent species without affecting the plasma thermal (kinetic), excitation, and ionization conditions, respectively.

The last metric, ionic:atomic line ratios, is particularly employed in ICP spectrochemical analysis as ionic transitions of the “monitor element” should be more sensitive to plasma changes than atomic transitions, with the ratio being independent of the absolute photon yield of analytes under those conditions [26,27]. The Mg II 279.5 nm and Mg I 285.2 nm lines are most commonly used in ICP-OES due to the proximity of the ionic and atomic lines and the similar excited-state energy levels [17,18]. The Mg II:I ratio is a reflection of the ionization temperature of the source on a fundamental level, but the robustness defined by the simple line ratio serves as a convenient monitor of plasma excitation/ionization conditions. There are two ways in which plasma robustness can be used as a metric: 1) the absolute value which reflects the overall ionization conditions and 2) its immunity to change upon matrix introduction. Under robust plasma conditions (ratios for the ICP in the range of 9–11), the Mg II:Mg I ratio remains relatively constant with the introduction of concomitants, implying no change in the plasma excitation/ionization characteristics. Magnesium line ratios allow for real-time assessment of source excitation/ionization conditions with commercial optical spectrometers [28].

Marcus and co-workers have developed the liquid sampling-atmospheric pressure glow discharge (LS-APGD) microplasma as a low power (<50 W), small plasma volume (~1 mm³), and small instrument footprint (<125 cm²) source for detection by OES [29,30]. Differentiating aspects of the LS-APGD versus other liquid electrode devices [3,4,31] are the very high power densities (>10 W mm⁻³) and ability to run in “total consumption” modes at flow rates up to 0.5 mL min⁻¹. The LS-APGD has demonstrated very promising initial performance as an elemental MS source [32,33]. The LS-APGD also is effective for OES and MS analysis of laser-ablated particles [34–36] and direct surface probing for ambient desorption ionization mass spectrometry (ADI-MS) [33]. A parametric evaluation of the LA-LS-APGD-OES implementation was performed with respect to discharge current, gas flow rate, and electrode gap [35], and their effects on rotational temperatures, excitation temperatures, and electron number densities. Those studies yielded average values of $T_{rot} \cong 1100$ K, $T_{exc} \cong 2700$ K, and $n_e \cong 3 \times 10^{15}$ cm⁻³, in line with earlier studies [37], but importantly remaining relatively unperturbed across the range of discharge parameters or by the introduction of LA particulates.

Presented here is an in-depth investigation of the spectrochemical robustness of the LS-APGD microplasma. The influence of 11 different elements at a relatively high concentration of 500 µg mL⁻¹ was investigated as reflected in changes in the fundamental plasma metrics of

excitation temperature, Mg II:Mg I ratio, and ionization temperature. Attention was paid to the potential dependences on the first and second ionization potentials, heats of vaporization, boiling points, and metal-oxide bond dissociation energies. The extent of spectrochemical perturbations and absolute analyte (Mg) responses was evaluated for the case of Ba added at concentrations of 50–1000 µg mL⁻¹. Such studies set the groundwork in moving forward in the development of the LS-APGD as a low cost, low power, small footprint spectrochemical source.

2. Experimental

2.1. Sample preparation

Elemental stock solutions (1000 µg mL⁻¹) of Ba, Ca, Cu, Ga, In, Mg, Sr and Zn prepared in 1 M nitric acid were obtained from CPI International (Santa Rosa, CA). Other stock solutions (Rb, Na, and Li) were prepared from analytical grade salts (Fisher Scientific, Waltham, MA) at a concentration of 1000 µg mL⁻¹ in 1 M nitric acid, each. The test elements, as seen in Table 1, were chosen to achieve a range of atomic masses, first and second ionization potentials, and thermodynamic properties. Magnesium was spiked into each test solution at a concentration of 100 µg mL⁻¹ to each solution as the constant probe element.

2.2. LS-APGD-OES apparatus

The LS-APGD set-up remained relatively unchanged from previous works [34,35]. As depicted in Fig. 1, the microplasma is sustained between the electrolytic liquid (HNO₃) and the counter electrode upon the application of a d.c. potential (Glassman High Voltage Inc.; 0–100 mA, 0–2 kV, High Bridge, NJ). The positive supply output is coupled to the counter electrode through a 10 kΩ, 225 W ballast resistor (Ohmite, Arlington Heights, IL) and the solution electrode is held at ground potential. Throughout this work, the power supply was operated in a constant current mode, set at 60 mA as this provides high OES sensitivity. The electrolytic solution (5% HNO₃) is delivered through the fused silica capillary at a constant flow rate of 200 µL min⁻¹ using a New Era (Farmingdale, NY) Model NE-1000 syringe pump. The glass capillary (360 µm o.d., 100 µm i.d.) is housed within a Ni capillary (0.16 cm o.d., 0.06 cm i.d.), between which the helium sheath gas flows (0.2 L min⁻¹) to assist in plasma stability. The Ni counter electrode (0.3 cm o.d., 0.1 cm i.d.) is placed ~1 mm opposite the electrolytic solution. The footprint of the plasma apparatus is <125 cm².

Plasma optical emission was collected with a fused silica biconvex lens (35 mm focal length, 25.4 mm diameter) focusing the plasma image onto the entrance aperture of an optical fiber coupled to the spectrometer (Aurora, Applied Spectra, Fremont, CA). The insert in Fig. 1 is a photographic image of the microplasma taken through the collection lens. This spectrometer consists of six channels, each composed of a

Table 1
Physicochemical characteristics of spectrochemical probe and concomitant matrix elements.

Element	Atomic mass (Da)	1st ionization potential (eV)	2nd ionization potential (eV)	Heat of vaporization (kJ mol ⁻¹)	Boiling point (K)	Metal-oxide bond dissociation energy (kJ mol ⁻¹)
Li	6.94	5.39	75.64	147.1	1342	284
Na	22.99	5.14	47.35	97.4	883	257
Mg	24.31	7.65	15.04	127.4	1090	394
Ca	40.08	6.11	11.87	154.7	1484	464
Cu	63.54	7.73	20.29	300.4	2562	343
Zn	65.39	9.39	17.96	123.6	907	284
Ga	69.73	5.99	20.51	254.2	2204	285
Rb	85.47	4.18	27.28	75.7	688	255
Sr	87.62	5.70	11.03	136.9	1382	454
In	114.82	5.79	18.87	231.8	2072	360
Ba	137.33	5.21	10.00	140.3	1897	563

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