Investigation of Spectrochemical Matrix Effects in the Liquid Sampling-Atmospheric Pressure Glow Discharge Source

Benjamin T. Manard^{1,2}, Jhanis J. Gonzalez², Arnab Sarkar^{2,3}, Xianglei Mao², Lynn X. Zhang¹, Stefanie Konegger-Kappel¹, R. Kenneth Marcus^{1*}, and Richard E. Russo²

1. Department of Chemistry, Clemson University, Clemson, South Carolina 29634
2. Lawrence Berkeley National Laboratory, Berkeley, California 94720
3. Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

* - Author to whom correspondence should be addressed

Abstract:

The liquid sampling-atmospheric pressure glow discharge (LS-APGD) microplasma was evaluated with regards 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.

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 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 improves 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 regards 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, 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 (<50W), small

plasma volume ($\sim 1 \text{ mm}^3$), and small instrument footprint ($< 125 \text{ cm}^2$) 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 ($> 10 \text{ W mm}^{-3}$) 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 $T_{\text{rot}} \approx 1100 \text{ K}$, $T_{\text{exc}} \approx 2700 \text{ K}$, and $n_e \approx 3 \times 10^{15} \text{ cm}^{-3}$, 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 $500 \text{ } \mu\text{g mL}^{-1}$ 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 $\mu\text{g mL}^{-1}$. 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 $\mu\text{g mL}^{-1}$) 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 $\mu\text{g mL}^{-1}$ 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 $\mu\text{g mL}^{-1}$ 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 (HNO_3) 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 k Ω , 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% HNO_3) is delivered through the fused silica capillary at a constant flow rate of 200 $\mu\text{L min}^{-1}$ 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 $\sim 1\text{ mm}$ opposite the electrolytic solution. The footprint of the plasma apparatus is $<125\text{ cm}^2$.

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 2048 pixel CCD detector dedicated to different spectral regions. A composite (simultaneous) spectrum is acquired using a 1.05 ms gate time, with spectral resolution of 0.05–0.12 nm across the 190–1040 nm wavelength range. Data collection and spectral manipulation were performed with the Aurora system software, with calculations and plotting functions performed in Microsoft Excel (Redmond, WA). Statistical analysis was performed employing Statgraphics software (Warrenton, VA). In each analysis data was modeled by the fitting of regression equations. Equations utilized were linear, exponential, reciprocal-Y, reciprocal-X, double reciprocal, logarithmic-X, multiplicative, square root-X, square root-Y, and S-curve in order to determine statistical relevance per relationship of spectrochemical metrics (e.g. T_{exe}) to physicochemical characteristics of probe elements. P-values were determined through the Statgraphics software and statistical significance was demonstrated to be within the 95% confidence level when the P-value was less than 0.05 and 90% when the P-value was less than 0.10.

3. Results and Discussion

The efficiency of successive processes occurring in spectrochemical sources (i.e., nebulization, desolvation, vaporization, dissociation, and excitation/ionization) is a function of the solvent/solute (analyte and matrix) composition and the available energy to affect the aforementioned processes. To a first approximation, the ability to sustain the ICP at 1-2 kW powers (high thermal capacity) with high electron densities differentiates its efficiency and lowered susceptibility to matrix effects versus combustion flames. Until recently, it was the inability to operate MIPs at sufficiently high powers that limited their use to OES detection following gas chromatography separations [38].

In the LS-APGD the feed solution composition, dictated by the sustaining electrolyte and sample make-up, could change the aqueous phase conductivity, changing the discharge i-V characteristics. As such, the heat generated at the solution/air interface would affect the rate of solution evaporation and sample introduction. The viscosity, surface tension, and vapor pressure of the solution would affect vaporization rates, evaporating droplet sizes, and latent internal energy. This is a different situation than combustion flames and ICP/MIPs, where nebulization, and to a great extent desolvation, occurs prior to entering the plasma. The physical characteristics of solutes (e.g., Table 1) might be expected to play complex roles in the LS-APGD as the sample solution is an integral part of the functioning of the device. While all uses of the LS-APGD involve a total-consumption (i.e., total sample vaporization) mode of introduction, any differences in the amounts of energy remaining for the gas phase process could induce spectrochemical matrix effects. Once in the gas phase, potential matrix effects in the LS-APGD would be similar to direct current

plasmas (DCPs) [39] and arc/spark sources [8], as changes in electron number densities could effect the current flow through the plasma. The range of elemental characteristics presented in Table 1 represents a variety of conditions to assess the spectrochemical robustness characteristics of the LS-APGD microplasma.

3.1 Influence of concomitant elements on the plasma excitation temperatures

The most common first-line assessment of a spectrochemical source is the excitation temperature (T_{exc}). T_{exc} reflects the partitioning of energy amongst the excited states of the probe species [9, 40]. Previous studies in this laboratory have used an Fe spike as the spectrochemical probe for different powering modes and sheath gas identities, yielding values from ~2500 – 3600 K [37]. To best monitor the excitation conditions across the range of concomitant elements, He I emission was monitored with the T_{exc} values extracted based on the assumption of a Boltzmann distribution of states. The approach was similar to that employed by Quintero et al. where excitation temperatures were calculated for a microwave induced plasma (MIP) [41]. While only four He I lines (501.6, 587.6, 706.5, and 728.1 nm) were utilized in this determination, the accuracy was sufficient to identify differences between matrix probes, as specific temperatures are not necessarily the overall goal. The majority of the correlation coefficients (R^2) for the derived Boltzmann plots were greater than 0.900, with triplicate determinations under each experimental condition varying by <5 %RSD.

Figures 2 a-e depict the derived He I excitation temperatures plotted as a function of the concomitant element characteristics of first and second ionization potentials, heat of vaporization, boiling point, and metal-oxide bond energy, respectively.

In the first case, the dashed horizontal lines depict a single standard deviation (plus and minus) for all of the measurements. As can be seen, the T_{exc} values remained relatively unchanged across the breadth of concomitant test elements; there were virtually no changes in He I line intensities as the different concomitant elements were introduced into the plasma. Statistical analysis across each of the elemental constituent parameters reveals no level of correlation for the mathematical fits at the 90% confidence level, with all P-values being greater than 0.125. The average excitation temperature across the various species was determined to be 2769 ± 79 K for the LS-APGD; the average temperature of 2672 K was presented in previous work using 5% HNO_3 as the electrolytic solution [35]. The consistency of these values across various elemental species reflects little-to-no perturbations of the excitation environment. Studies in MIPs have illustrated a temperature change (some up to 300 K) upon the introduction of EIEs [14], with the extent of variation significantly decreasing upon increasing the power of the plasma up to 1.5 kW, to eliminate matrix effects. While the LS-APGD is operated at total powers of 36 W, the power density is ~30 times higher than the conventional ICP, thus it is suggested that this microplasma is highly robust (immune to perturbations of excitation temperature) with respect to moderately-high ($500 \mu\text{g mL}^{-1}$) sample loadings.

3.2 Influence of concomitant elements on the plasma ionization temperature

The excitation temperature of a spectrochemical source depicts only a portion of the overall kinetic processes. Beyond the extent of populating atomic states, bulk ionization rates and further population of excited atomic ions must be concerned. Under the assumption of local thermodynamic equilibrium (LTE), the ionization temperature

(T_{ion}) is the fundamental measure of the latter processes. The Saha equation, Eq. 1, is commonly used in deriving the ionization temperature assuming the existence of LTE.

$$\frac{I_{Ionic}}{I_{Atomic}} = \frac{4.83 \times 10^{15}}{n_e} \times \left(\frac{g_q A_{pq}}{\lambda_{pq}} \right)_{Ionic} \times \left(\frac{\lambda_{pq}}{g_q A_{pq}} \right)_{Atomic} \times T^{3/2} e^{\frac{-(E_i^+ + E_q^+ - E_q)}{kT}} [1]$$

As described previously, the ionic-to-atomic line ratio of Mg was used to monitor plasma-related matrix effects by changes in the excitation/ionization conditions within the plasma. This ratio can be utilized under the assumption that the electron number density is known. The ionic:atomic ratio is related in this equation where I is the emission intensity, n_e is the electron number density, g_p and g_q are the statistical weights of the upper and lower state (respectively), A_{pq} is the transition probability, λ_{pq} is the wavelength of the specific transition, k is the Boltzmann constant, E_i^+ is the first ionization potential of magnesium, E_q^+ and E_q are the energy levels of the upper state for the ionic and atomic emissions (respectively), and T is the ionization temperature of the plasma. An electron number density of $3 \times 10^{15} \text{ cm}^{-3}$ was utilized for calculating ionization temperature based on Stark broadening of the hydrogen Balmer alpha line [35]. Calculations of the ionization temperature were performed using Microsoft Excel as well as by a predictive modeling program developed in LabView, with both yielding similar results.

In comparison to the excitation temperatures presented in Fig. 2 (~2800 K), the derived ionization temperatures averaged $6665 \pm 151 \text{ K}$ across the concomitant additive elements. The general difference between ionization and excitation temperatures in the LS-APGD ($T_{ion} > T_{exe}$) follows the observation in non-thermal ICPs, though the two characteristic temperatures are in much closer proximity for the ICP with values of $T_{ion} \approx$

6000-8000 K and $T_{\text{exc}} \approx 5000\text{-}7000$ being typical [42-44]. Large differences between ionization and excitation temperatures have been cited for other microplasmas such as the solution-cathode glow discharge (SCGD) [22, 23]. The discrepancy between ionization temperature and excitation temperature does not change the fact that the LS-APGD might be considered as being at LTE, as a “single” temperature is not a necessarily requirement [40]. More correctly, the individual T_{ion} , T_{exc} , etc. must be uniform across various spectrometric species [45], as has been found in previous LS-APGD works [35, 37, 46].

Statistical evaluation of significant factors across the physical parameter space of Table 1 showed a virtual lack of meaningful correlations. The only parameters effecting the ionization temperature were the 2nd IP and metal-oxide bond strengths of the added elements, showing slight correlations at the 90% confidence levels: a reciprocal trend in the former and a linear dependence in the latter. There is indication of outliers from the norm in Fig. 3, where the derived ionization temperatures are plotted as a function of the 2nd IP of the test elements. Here, it is seen that 500 $\mu\text{g mL}^{-1}$ additions of Ba and Ca impart slight increases in the ionization temperature. Kitagawa and Takeuchi proposed that the introduction of the EIEs into a microwave plasma increased the overall collision rate in the plasma (i.e., more electrons) [47], with the increased collisions correlating with the increased ionization temperatures. In Fig. 3, Sr stands out as an outlier as the T_{ion} determined upon its addition is on the lower end of the range of measured values. As a general measure of potential spectrochemical matrix effects, there are no appreciable perturbations of T_{ion} seen across these test elements.

3.3 Influence of concomitant elements on the plasma robustness parameter

While the ionization temperature is a fundamental parameter of a spectrochemical device, the robustness parameter as described by Mermet [17, 26], provides both a reflection of source excitation/ionization conditions as well as a facile means of assessing changes in those conditions. While measured Mg II:Mg I emission intensity ratio values are part of the calculation of T_{ion} , Eq. 1 is composed of many factors, each of which has a level of uncertainty. For example, a single value of n_e was used in those calculations, which may not be an accurate assumption. Indeed, this further argues toward the practical utility of the robustness parameter. In general, miniaturized plasmas typically have lower ionic:atomic ratios than an ICP, mainly due to the lower power and decreased plasma temperatures. The ICP's high excitation/ionization temperatures (<7000 K) generate ionized species more effectively than that of miniaturized plasmas (~3000 K). As such, robustness parameters for ICPs are much higher (10x) than the LS-APGD and other miniaturized plasmas [46, 48].

As might be expected based on the parametric dependences seen for ionization temperatures, only the 2nd IP and metal-oxide bond strengths of the concomitant elements have any influence on the derived robustness parameters. In fact, both quantities display significant effects at the 95% confidence level, though the overall impact in terms of the range of derived values is not appreciable. It is important to emphasize that the raw intensity values for the Mg II and Mg I transitions vary little across the different concomitant elements; suggestive of minimal analytical matrix effects for the 500 $\mu\text{g mL}^{-1}$ additives. Neither the Mg II or Mg I show a statistical correlation to either factors, but the ratios do. Figure 4a depicts the dependence of the Mg II:Mg I ratios on the 2nd IP of the test elements, revealing a reciprocal dependence

with a P-value of 0.034. The baseline value (i.e. absence of matrix elements) of the ratio was measured by the introduction of the $100\ \mu\text{g mL}^{-1}$ Mg solution in 5% HNO_3 , yielding a value of ~ 1.2 , which is in agreement with previous LS-APGD studies [46]. In this case, Ba and Ca show a stronger (positive) influence on the ratio than seen in Fig. 3, lying farther outside the ± 1 standard deviation boundaries. As in the case of the ionization temperatures, Sr yields a ratio that reflects much lower excitation/ionization efficiency than would be expected based on its 2nd IP. Exclusion of the Sr response from the data set results in an improvement in the statistical P-value to 0.002. While there is a high level of mathematical correlation, again, it must be pointed out that overall, the variation across the suite of elements is predominately within ± 1 standard deviation of the complete experiment set. It must also be pointed out that, the variability in the Mg II:Mg I ratios is driven almost exclusively by the lower-energy Mg I responses, as the Mg II responses are virtually independent of the concomitant element identity. One would expect that the ionic transition, having a much higher total excitation energy, would be more prone to changes in plasma conditions.

Given the relative low total power and low excitation temperatures of the LS-APGD, one might have expected some contribution of the concomitant element's 1st IPs in terms of spectrochemical matrix effects, as in the classical case of EIEs in combustion flames [7, 9]. This is not the case. The lack of impact here may lie in the relatively high electron number densities of the LS-APGD; on the order of $10^{15}\ \text{cm}^{-3}$ [35]. As such, enhanced electron densities by virtue of EIEs are inconsequential. Russo et al. demonstrated that elements with low 2nd IP ($<15\ \text{eV}$) prompt extreme matrix effects in the ICP [11], more so than low first ionization potentials. Further works by Chan and

Hieftje reinforce this relationship, but also point to secondary factors affecting matrix effects across a wide range of elements [18]. Elements of low secondary IP are mainly of the group two elements (Ca, Sr, and Ba), with Ba having the lowest second IP (10.0 eV) of all elements. The introduction of Ba and Ca to the LS-APGD yields increased Mg II:I ratios (and to a lesser extent T_{ion}) implying a more energetic plasma. This trend is opposite that found in ICPs, where elements with low 2nd IPs lead to lower ionic:atomic ratios [11, 18]. In general, low 2nd IP elements have been suggested to be readily ionized via Penning collisions, removing important argon metastables from the overall plasma energy pool and suppressing measured ionic:atomic emission ratios. Chan and Hieftje noted Ca, Sr, and Ba as being anomalies in their relative matrix effects, having less suppressive effects than elements of comparable 2nd IPs [18] due to the lack of a Penning pathway for ionic state population. Russo et al. had found that use of He as the carrier gas in their experiments virtually eliminated the 2nd IP-based suppression effects [11], pointing to the fact that metastable depletion was active in the argon ICP.

Mechanistic explanations for the correlations with 2nd IPs here, which in overall magnitude are rather small, suggest different effects than the ICP. This is reasonable as the LS-APGD is primarily composed of “reactive” water-originating species, versus the ICP that is predominately water vapor diluted in Ar. Differences exist also as He is used as the sheath/cooling gas here. As such, primary energetic species which will affect the overall distribution of energy will be electrons, metastable He atoms and ions, and ionized water molecules and water fragments (e.g., H, H⁺, etc.). If treating Ba, Ca, and Sr as a group, and acknowledging that Sr is somewhat of an anomaly, one must

consider the total energy to create the doubly-charged ions. As listed in Table 1, only these three elements can be created via a Penning collision with 19.8 He metastable atom. Decreasing He^*_m populations via this path would not likely effect the Mg II emission which originates from ~12.05 eV state above the ground Mg atom level. On the other hand, if one supposes the that doubly-charged ions are formed from M^+ precursors, then these may be formed by a charge transfer with H_2O^+ which has an IP (and thus electron affinity) of ~12.7 eV. This process would lessen the energy drain on the plasma as the group II species are more easily formed, and thus leave more energy for the ionization/excitation of the Mg probe species. The relative contributions of sheath gas and water-based species need much further investigation. The use of other ion:atom pairs, such as Zn may be more instructive, as greater sensitivity to changes in plasma conditions have been noted in ICP diagnostics [11, 18].

The second significant factor affecting the plasma robustness parameter is the metal-oxide bond strength of the concomitant element. Metal-oxide ions have been noted in LS-APGD mass spectra [32], though it cannot be said whether or not those ions are plasma-originating or formed in transit from the plasma to the MS sampling orifice. As shown in Fig. 4b, Mg II:I ratios show an overall slight positive trend as a function of the metal-oxide bond energies, yielding a P-value of 0.024 for a linear fit, indicative of a correlation at the 95% confidence. As in the case of the 2nd IP correlations, neither of the individual transitions shows a correlation, but the ratio does. More clearly seen here than in Fig. 4a, Sr seems to be an anomaly among the group II elements. Here again, removal of Sr from the test data results in greatly improved correlations, reducing the P-value to 0.005. This overall trend seems counterintuitive as

the need to dissociate metal oxides to yield free atoms and ions would be an energy drain on the plasma.

3.4 Influence of concomitant element concentration on the plasma robustness parameter

It is not only the identity of concomitant elements, but also their concentration, that contributes to spectrochemical matrix effects. In fact large concentrations of almost any element can “overload” spectroscopic flames and plasmas. In addition to EIE-type effects, problems such as disruption of normal operating conditions exist wherein the energy of the system is not sufficient to affect the gas-phase processes of desolvation, vaporization, and dissociation to create free atoms. While the previously-discussed studies of plasma excitation conditions were undertaken at relatively-high loadings ($500 \mu\text{g mL}^{-1}$), it is important to gain an understanding how the concomitant element loading can effect this microplasma. Because Ba showed the largest effects on the ionization temperature and plasma robustness parameters, it was chosen as the test element to identify potential concentration-based spectrochemical matrix effects. The data in Fig. 4 illustrate the effect of Ba concentration to the Mg II:Mg I emission ratio across a range of $66 - 1000 \mu\text{g mL}^{-1}$. As seen in the derived robustness parameter values, there is essentially no change in the excitation/ionization characteristics from the case of no Ba addition to the point of a 0.1 % loading. The variability seen in the emission ratios, as noted previously, is predominately in the denominator of the calculation (Mg I emission), as the Mg II responses across the range Ba loadings varied by less than 6% RSD, independent of the Ba content. From the point of view of Ba being an analyte, its emission response across this concentration range increased linearly with a slope close

to unity, with no indication of self-absorption. Thus, to this level of loading, with what is the most perturbing element, the plasma exhibits negligible spectrochemical matrix effects.

4. Conclusions

The liquid sampling-atmospheric pressure glow discharge (LS-APGD) has been evaluated for spectrochemical matrix effects using excitation temperature, ionization temperature and the plasma robustness parameter. Eleven elements of diverse atomic weight, 1st and 2nd ionization potential, heat of vaporization, boiling point, and metal-oxide bond energy were added at concentrations of 500 $\mu\text{g mL}^{-1}$. Plasma temperatures (T_{exc} and T_{ion}) remained relatively unchanged throughout the introduction of the various elemental probes, with variations across the entire probe element suite of <3 %RSD. Studies suggest that the high power density ($>10 \text{ W mm}^{-3}$) and high electron density ($>10^{15} \text{ cm}^{-3}$) microplasma can effectively tolerate a wide range of elements without disruption of the plasma, demonstrating a spectrochemically robust plasma. Only in the case of the plasma robustness parameter, the Mg II:Mg I emission intensity ratio are any element-specific differences seen. Overall, the robustness parameter varied by 0.95 ± 0.3 across the concomitant element suite. The absolute values would be considered “non-robust” in comparison to the ICP, but the actual range across many matrices suggests a high level of tolerance not reflected in the absolute value. The only physicochemical aspects of the added elements that had statistically significant correlations were the 2nd ionization potential (a reciprocal dependence) and the metal-oxide bond strengths (a linear dependence). These effects were minimal, making

mechanistic assignments difficult. When looking at the robustness parameter as a function of the total amount of concomitant element introduced, the Mg II:Mg I ratios did not significantly change upon changing the concentration of Ba from 66 - 1000 $\mu\text{g mL}^{-1}$, with the Mg II response changing by less than 3.5 %RSD.

Consistent with previous research, the LS-APGD demonstrates high promise as an elemental excitation/ionization source due to its low operating costs and minimal matrix effects. Questions remain to be answered regarding practical matrix effects across different sample types. Reported here was the extent of spectrochemical perturbations. There may be physical matrix effects related to the ability to generate consistent atom populations from solutions of diverse bulk compositions. As one looks to field-deployable applications, samples of different ionic strength, viscosities, and heats of vaporization will surely be encountered. These effects must be quantified, but the lack of appreciable spectrochemical matrix effects bodes well for development towards these applications.

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Figure Captions:

- Figure 1. Components of the liquid sampling-atmospheric pressure glow discharge optical emission spectroscopy (LS-APGD-OES) source with a photograph of the microplasma taken through the optical coupling lens.
- Figure 2. Correlations of He I-based excitation temperatures with the introduction of 11 matrix elements ($500 \mu\text{g mL}^{-1}$ each) in terms of a) first ionization potential, b) second ionization potential, c) heat of vaporization, d) boiling point, and e) metal-oxide bond dissociation energy.
- Figure 3. Correlation between the measured ionization temperatures and the second ionization potential for each of the 11 matrix elements ($500 \mu\text{g mL}^{-1}$ each).
- Figure 4. Resultant Mg II:Mg I emission intensity ratios correlated with a) second ionization potential and b) metal-oxide bond dissociation energy of the 11 matrix elements ($500 \mu\text{g mL}^{-1}$ each).
- Figure 5. Resultant Mg II:Mg I emission intensity ratios as a function of the added barium concentration.

Fig. 2b

Fig. 2c

Fig. 2d

Fig. 2e

Fig. 3

Fig. 4a

Fig. 4b

Fig. 5

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	10.0	140.3	1897	563