The influence of ns- and fs-LA plume local conditions on the performance of a combined LIBS/LA-ICP-MS sensor

Nicole L. LaHaye, Mark C. Phillips, Andrew M. Duffin, Gregory C. Eiden and Sivanandan S. Harilal

Both laser-induced breakdown spectroscopy (LIBS) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) are well-established analytical techniques with their own unique advantages and disadvantages. The combination of the two analytical methods is a very promising way to overcome the challenges faced by each method individually. We made a comprehensive comparison of local plasma conditions between nanosecond (ns) and femtosecond (fs) laser ablation (LA) sources in a combined LIBS and LA-ICP-MS system. The optical emission spectra and ICP-MS signal were recorded simultaneously for both ns- and fs-LA and figures of merit of the system were analyzed. Characterization of the plasma was conducted by evaluating excitation temperature and electron density of the plume under various irradiation conditions using optical emission spectroscopy, and correlations to ns- and fs-LIBS and LA-ICP-MS signal were made. The present study is very useful for providing conditions for a multimodal system as well as giving insight into how laser ablation plume parameters are related to LA-ICP-MS and LIBS results for both ns- and fs-LA.

Introduction

Laser-induced breakdown spectroscopy (LIBS) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) are well-established analytical techniques that are routinely used for various applications. Even though laser ablation (LA) is employed in both techniques, the detection schemes for each method are entirely different. In LIBS, the characteristic light emitted due to species excitation and de-excitation during the LA process is used to obtain the elemental composition, while in LA-ICP-MS, the particles emitted from the LA zone are introduced into the ICP torch for dissociation/ionization and elemental information is gathered using a mass spectrometer. Light and particle emission from the LA plume are driven by different processes and occur on very different timescales; consequently, the optimal LA conditions for these analytical techniques may be different. The common factor in both processes, LA, involves generation of a complex and transient plasma, and subsequent plasma evolution characteristics are governed by many different parameters such as laser properties (pulse duration, wavelength, energy), ambient conditions (nature and pressure of the gas, gas flow rate), and sample composition; all of these parameters affect both LIBS and LA-ICP-MS results.

The techniques of LIBS and LA-ICP-MS each have their own advantages and disadvantages. LIBS can yield very accurate compositional results for bulk elements and is especially strong for the analysis of low-Z materials. It is also possible to detect the concentration of atmospheric elements such as H, He, N, and O. LIBS provides stand-off and rapid analysis capabilities compared to other analytic techniques, and can measure multiple elements simultaneously. Challenges for LIBS include measurement of high-Z species, which can be difficult to discriminate due to their high density of atomic lines, though multiple lines can be employed using chemometrics to improve the accuracy of the analysis. Isotopic analysis can also be challenging for LIBS, as spectral isotope line splitting occurs with differences in the pm range, which requires a spectograph capable of greater dispersion than is commonly found in laser labs. Spectral line broadening can also make isotopic resolution challenging, even with a high-resolution spectograph. Poor atomic isotope resolution can in some cases be overcome by using molecular emission bands instead of atomic line emission due to the much larger (100’s of pm) isotope shifts exhibited, but these methods do not have the high dynamic range of mass spectrometry required for quantifying low abundance isotopes.

LA-ICP-MS is able to easily obtain isotopic data and has detection limits in the sub-ppb range, making it a respectable method for analysis of trace and ultra-trace components. It also works very well for analysis of mid- to high-Z elements. Due to their natural abundance in the atmosphere, LA-ICP-MS is not...
able to easily detect H, He, N, and O and also faces uncertainties from potential molecular interferences. The downsides of each method can be mitigated by the other method, which makes the combination of the two analytical techniques complementary.

A major question that has arisen recently in laser-based analytical chemistry is whether the combination of the two LA techniques (specifically, LIBS and LA-ICP-MS) is justified with the added cost and complexity and whether this combination can yield better analytical results. Several groups have successfully employed the simultaneous technique. Chirinos et al. performed spatial mapping of major elements using LIBS and trace elements using LA-ICP-MS. Lakoczky and Ghislain performed similar elemental mapping and developed a new calibration approach using the LA-ICP-MS signal for standardization of the LIBS spectra. However, a better understanding of the fundamental processes that are occurring is necessary; the specific influences of the above parameters are not well understood. Our comprehensive, in situ study of the plasma conditions during LA before aerosol transport to the ICP-MS significantly improves upon previous work.

One of the most important parameters to consider for LIBS and LA-ICP-MS is laser pulse duration. A change in pulse duration can drastically change the results obtained from ICP-MS and from LIBS. In general, two main pulse duration regimes are considered for LA-based analytical chemistry: nanosecond (ns) pulses, obtained from Q-switched Nd:YAG or excimer lasers; and ultrafast femtosecond to picosecond (fs-ps) pulses, obtained using Ti:Sapphire lasers. The difference of up to six orders of magnitude in pulse duration results in a vast change in ablation mechanisms. In ns-LA, the leading edge of the laser pulse initiates ablation and creates a plasma, while the rest of the pulse heats the plasma. Ablation in the ns regime is dominated by thermal effects through heating and melting of the sample. While the heating from ns-LA can improve LIBS results due to enhanced emission, it can also cause spatial migration of elements within the sample and redeposition on the sample, degrading LA-ICP-MS results. In contrast, fs-LA has such a short time scale that the laser pulse ends before the start of ablation and thermal effects are negligible; the pulse duration $t_p$ is much shorter than both the electron-ion relaxation time ($\tau_{ei}$), which is of the order of 1–10’s of ps, and the heat conduction time ($\tau_{heat}$): $t_p \ll \tau_{ei} \sim \tau_{heat}$. As a result, fs-LA leads to generation of a cooler atomic plume, reduced continuum emission, decreased matrix effects, etc.

Since laser pulse duration has such a strong influence on LA-ICP-MS and LIBS results, both ns- and fs-LA have been addressed in this study. An investigation into the fundamental ns-LA properties is of interest to understand better how they affect the ICP-MS results, while fs-LA has been previously shown to yield more precise and accurate ICP-MS results.

The optimal conditions for both LIBS and LA-ICP-MS are governed by conditions in the LA plume. Both ns and fs lasers are routinely used for LIBS and LA-ICP-MS; however, the optimal LA conditions are different for both analytical systems considering the differences in pulse widths as well as differences in detection method: emission from plume vs. mass analysis of generated particles. We recently reported the fundamentals (plume hydrodynamics and plume parameters) of fs-LA and the influence of various parameters on each technique when used together. The purpose of the present paper is to make a comprehensive comparison between the local plasma conditions in ns- and fs-LA plumes in a combined LIBS/LA-ICP-MS system; such a study is non-existent in the literature to the best of our knowledge. To perform this comparison, the emission spectra and ICP-MS signal were recorded simultaneously and figures of merit of the system were analyzed. Signal intensity from the LIBS plume spectra and ICP-MS aerosol detection are compared for both ns- and fs-LA. Additionally, excitation temperature ($T_{exc}$) and electron density ($N_e$) were calculated under different ablation conditions; laser pulse energy was varied, and a comparison is also made between rastering and single spot ablation. The excitation temperature and electron density of LA plumes under various irradiation conditions were measured using emission spectroscopy and correlated to ns- and fs-LIBS and LA-ICP-MS signal behaviour. We find that the observable differences in signal strength, both for LIBS and for LA-ICP-MS, are due to heating effects and crater formation. The present results also indicate that within the fluence regimes generally employed for LA-ICP-MS, ns-LA exhibits higher excitation temperatures and plasma densities than fs-LA. Combined LIBS/LA-ICP-MS is demonstrated as a viable technique using both ns-LA and fs-LA, and active monitoring of plasma conditions through emission spectroscopy can potentially provide insight into optimal plume conditions for fusion of these sensors.

**Experimental details**

A schematic of the experimental setup employed for the present studies can be found elsewhere. Experimental parameters are summarized in Table 1. Two different laser systems were used for these experiments—a Ti:sapphire system for fs-LA and a Nd:YAG laser for ns-LA. The fs Ti:Sapphire laser operates based on chirped-pulse amplification (CPA) principles, with fundamental wavelength $\sim$800 nm and pulse duration $\sim$40 fs FWHM. The ns Nd:YAG laser was frequency-quadrupled from 1064 nm to 266 nm with pulse duration $\sim$4 ns FWHM. Energy was varied for both lasers using a combination of half-wave plate and thin film polarizer; for the purposes of these experiments the fs laser energy was varied from 25 μJ to 800 μJ and ns laser energy from 1 mJ to 5 mJ. The respective laser fluences for these experiments were $\sim$3–16 J cm$^{-2}$ and $\sim$0.5–16 J cm$^{-2}$ for ns and fs LA respectively. The selection of ns and fs laser fluence range for this study is based on the fact that these are characteristic fluences typically used in LA-ICP-MS.

The laser beam was transported to the LA chamber using a series of mirrors and focused down into the chamber using an objective lens (NA = 0.13). Laser spot size at the sample surface was $\sim$80 μm for fs-LA and $\sim$200 μm for ns-LA. The ablation chamber was mounted on an XYZ translation stage, allowing for single spot as well as rastering ablation. A CCD camera above the ablation chamber allowed for visualization of the sample for movement to new target spots for ablation. Sample velocity was maintained at 0.1 mm s$^{-1}$ for rastering experiments. Ar carrier
Table 1  Summary of important laser, LIBS, and ICP-MS experimental parameters

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th>ns</th>
<th>fs</th>
</tr>
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<tbody>
<tr>
<td>Laser system/beam delivery</td>
<td></td>
<td></td>
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<tr>
<td>Wavelength</td>
<td>~266 nm</td>
<td>~800 nm</td>
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<tr>
<td>Pulse duration</td>
<td>~4 ns FWHM</td>
<td>~40 fs FWHM</td>
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<tr>
<td>Energy</td>
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<td>Repetition rate</td>
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<tr>
<td>Beam diameter</td>
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<td>10 mm</td>
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<tr>
<td>Spot size</td>
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<td>~80 μm</td>
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<tr>
<td>Fluence</td>
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<td>~0.5–16 J cm⁻²</td>
</tr>
<tr>
<td>Angle of incidence</td>
<td>Normal to the target</td>
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<tr>
<td>Objective lens NA</td>
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<td></td>
</tr>
<tr>
<td>Raster speed</td>
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</tr>
<tr>
<td>LIBS</td>
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<td></td>
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<tr>
<td>Gate delay</td>
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</tr>
<tr>
<td>Integration time</td>
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<tr>
<td>ICP-MS</td>
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<tr>
<td>Torch RF power</td>
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<tr>
<td>Carrier gas</td>
<td>1.0 L per min Ar</td>
<td></td>
</tr>
<tr>
<td>Gas through torch</td>
<td>15 L per min Ar</td>
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<td>Integration time per isotope</td>
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<tr>
<td>Isotopes analyzed</td>
<td>⁶⁵Cu, ⁶⁵Cu, ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn, ⁶⁸Zn</td>
<td></td>
</tr>
</tbody>
</table>

gas through the chamber flowed at 1.0 L min⁻¹ for all experiments. Brass was selected as the target for this study. Owing to huge differences in the thermal properties of Cu and Zn, brass exhibits interesting behavior in laser plasmas; this results in matrix effects and elemental fractionation that affect LIBS and LA-ICP-MS quantitative measurements, thus making it a useful sample for comparing the techniques.

A fiber optic cable was attached to the ablation chamber to transmit the emitted spectra to a 0.750 m Czerny–Turner spectrograph to perform LIBS as well as characterization of the plasma plume. Two different gratings were used for these experiments: 1200 grooves per mm to have higher resolution for electron density measurements and 150 grooves per mm to capture a wider wavelength range instantaneously for spectra acquisition and excitation temperature measurements. Emission spectra were obtained from single laser pulses with a gate delay of 200 ns and an integration time of 1 μs. It’s important to note that, due to the collection scheme, all spectra are spatially and temporally integrated. The aerosol produced by LA was transported from the ablation chamber to the ICP-MS via Tygon tubing. The aerosol was analysed using a quadrupole-based ICP-MS with RF power 1550 W. ⁶³Cu, ⁶⁵Cu, ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn, and ⁶⁸Zn were detected due to the choice of brass as the sample, each with 10 ms integration time. Aerosol from several laser pulses is mixed during transport to the ICP torch so that the ICP signal at any given time represents a mixture of sample material from many pulses.

Results

The present work explores the fundamental capabilities of combining two analytical techniques, namely LIBS and LA-ICP-MS, and compares the differences in local plasma conditions for ns- and fs-LA sources used for the combined system. Not only does this combination expand the capabilities over each technique alone, the use of optical emission spectroscopy (OES) during simultaneous LIBS and LA-ICP-MS allows for in situ monitoring of plasma conditions during laser ablation, which can provide information on the conditions influencing emission intensity in LIBS as well as particle formation for sample introduction in LA-ICP-MS. Different ablation modes (single spot vs. rastering) are employed in different applications, i.e., single spot for depth analysis and rastering for spatial profiling of samples, so it is important to understand how the LA properties are changing the LIBS and ICP-MS signals as a function of ablation mode. One hundred spectra were acquired and analysed during the first ten seconds of ablation in single spot and raster modes (a spectrum was acquired for each laser shot, with the laser firing at 10 Hz). Fig. 1 gives ns and fs spectra for single spot ablation, with the spectra baseline-subtracted for improved comparison. The ablation energies used were 2 mJ for ns-LA and 200 μJ for fs-LA. The spectral features appear similar for both ns- and fs-LA, with the same major lines observed for both pulse durations. While ns-LA provides higher signal intensity, fs-LA results in narrower lines: ~0.8 nm for ns-LA and ~0.6 nm for fs-LA, as calculated from Fig. 1. The differences in spectral line intensity and linewidth between ns and fs LA also highlight the changes in the local conditions (fundamental plasma parameters such as excitation temperature and electron density).

A comparison of signal intensity for both single spot and raster ablation modes is given in Fig. 2, with Fig. 2(a and b) showing the ⁶⁴Zn ICP-MS signal, and Fig. 2(c and d) showing the Zn I 481.05 nm line emission intensity. Since the behavior of Cu signal was comparable to that of Zn for both ICP-MS and LIBS, the results have been excluded here. The laser fluence was 6 J cm⁻² and 4 J cm⁻² for ns- and fs-LA, respectively. For ns-LA, the ICP-MS and LIBS intensity follow the same general shape for the same ablation mode; raster signal increases with time, while...
single spot intensity is approximately constant for the first ~10 seconds of acquisition. For fs-LA, ICP-MS signal intensity increases slightly for single spot ablation, while it remains constant for rastering with increased signal standard deviation due to surface effects. If data acquisition was continued for a longer period of time, crater formation would cause a large reduction in signal for single spot ablation regardless of pulse duration. A constant intensity is also observed for fs-LIBS in rastering ablation mode. Unlike fs-LA-ICP-MS signal, the single spot fs-LIBS signal is found to decrease rapidly with time.

The changes in signal intensity for both LIBS and LA-ICP-MS could be related to LA plasma plume conditions. A LA plasma can be characterized by two fundamental parameters: temperature and density. Hence we estimated electron density and excitation temperature using OES. The Stark broadened profiles of Zn I 481.05 nm line were used for electron density calculations, while intensities of Cu I lines (427.51 nm, 465.11 nm, 510.55 nm, 515.32 nm, and 521.82 nm) were used for excitation temperature calculations, assuming the plasma is in local thermal equilibrium (LTE). The spectroscopic parameters of the Cu I lines used are given in LaHaye et al., with the values obtained from the NIST spectral line database.

The electron density and excitation temperature for both single spot and rastering LA are given in Fig. 3 for both ns and fs LA. As can be seen in Fig. 3(a and b), for both ns- and fs-LA, the electron density is slightly higher for rastering than it is for single spot ablation. While density is approximately constant for both ablation modes employing ns-LA and for fs rastering ablation, the electron density decreases for fs single spot ablation, correlating with the decrease in signal intensity shown on Fig. 2(c). The excitation temperature is approximately the same for rastering versus single spot ablation (Fig. 3(c and d)).

It could be argued that some of the changes in plasma fundamental properties and signal intensities for both LIBS and LA-ICP-MS could be due to a difference in the laser fluences used for ns- and fs-LA. To that end, we investigated the role of laser energy on LIBS and ICP-MS signal intensity and its correlation to plasma fundamental properties by employing similar fluences. Laser energy was varied from 1 mJ to 5 mJ for ns-LA and from 25 μJ to 800 μJ for fs-LA. The respective fluence ranges at the target surface are 3–16 J cm⁻² and 0.5–16 J cm⁻² for ns- and fs-LA, respectively. The LA-ICP-MS integrated intensity for ⁶⁴Zn is given alongside the LIBS Zn I 481.05 nm line spectral intensity (integrated over the peak area) in Fig. 4. Both ICP-MS and LIBS intensity increase with fluence; however, the ICP-MS signal increases ~1 order of magnitude over the range of energies used, while the LIBS signal increases by over 3 orders of magnitude. Signal intensity increases with increasing fluence, with higher values for ns- vs. fs-LIBS at similar fluence levels. This higher value for ns-LIBS is due to the greater line width compared to fs-LIBS; since peak area is correlated to species population, this indicates that a greater number of excited Zn atoms are present in the ns plasma. This does not, however, necessarily indicate that more material is ablated for ns-LA; temporal and spatial integration play a role here, as well as spectral acquisition delay. The LIBS signal only indicates the
population that is excited to the particular energy state transition represented by the observed emission line.

The electron density and excitation temperature of the plasma were calculated at the same fluences used to measure signal intensity. An increase in electron density and excitation temperature is also observed with increasing fluence (Fig. 5). However, electron density is distinctly higher for ns-LA than fs-LA, in contrast to the behavior observed in the LA-ICP-MS signal intensity but agreeing with the LIBS emission. The excitation temperature, though within error bars, is also higher for ns-LA than fs-LA except at the lowest fluences near the ns-LA threshold for measurable emission.

**Discussion**

Even though the only difference between the conventional ns-LA and fs-LA is the variation in pulse duration, the ablation mechanisms leading to plasma formation are drastically different due to the significant differences in how the relevant physical processes are driven when energy is delivered at these different timescales.\(^{18-19}\) Because of this, ultrafast LA offers greatly reduced thermal damage and heat affected zone (HAZ) in the target due to negligible heat conduction and hydrodynamic motion during the laser pulse duration. Moreover there are several advantages in using fs-LA for LIBS and LA-ICP-MS over ns-LA, which include reduced continuum emission, better

**Fig. 3** Electron density (a) fs-LA and (b) ns-LA and excitation temperature (c) fs-LA and (d) ns-LA using single spot and rastering modes.

**Fig. 4** Signal intensity as a function of fluence for (a) \(^{64}\)Zn ICP-MS signal, and (b) Zn I 481 nm line emission, integrated over the peak area.
control of ablation efficiency, particle distribution, elemental fractionation and matrix dependence. The differences in ns- and fs-LA are documented in the literature for both LIBS\textsuperscript{19,20,26} and LA-ICP-MS\textsuperscript{18,27,28} applications.

The signal intensity variation noticed for both single spot and rastering cases (ns- and fs-LA, Fig. 2) and its correlation to plume fundamental properties (Fig. 3) are intriguing. Among them the highest ICP-MS signal intensity is noticed for fs single spot ablation. The emission intensity $I_{nm}$ of a transition is related to excitation temperature ($kT$), number density ($N$) and transition probability for spontaneous emission ($A_{nm}$) through $I_{nm} = A_{nm}N^2\pi\hbar c\lambda_{nm}^{-3}e^{-E_{nm}/kT}$ where $\hbar$ is Planck’s constant, $g_m$ is the statistical weight, $c$ is the speed of light, $\lambda_{nm}$ is the wavelength of the emission, and $E_{nm}$ is the excitation energy. The enhancements in excitation temperature and number density (Fig. 3) lead to improvements in LIBS signal, however, they do not necessarily result in more ions reaching the ICP-MS detector. The whole process is two-fold: particles generated in the LA zone are flushed to the ICP torch for atomization and ionization, but only a fraction of the ions generated in the ICP will reach the MS detector through the sampling cones and mass analyzer. The trade-offs between processes leading to improved LIBS signals and processes leading to improved ICP-MS signals are exactly what we want to understand better. A two-fold increase in electron density and 10% rise in excitation temperature noticed for ns-LA could be partly due to the use of larger spot size as well as 50% higher laser fluence used in comparison with fs-LA.

The laser fluence dependence on signal intensities (Fig. 4) showed that both ns- and fs-LA provided similar signal levels at higher fluence levels for LA-ICP-MS though their local plasma conditions are different (Fig. 5). However, the LIBS signal is higher for ns-LIBS than fs-LIBS, which matches the behavior of the excitation temperature and density. The density of the ns-LA plume is found to be higher compared to fs-LA in the range of laser fluence used in the present study though the excitation temperature showed approximately similar values at lower fluence levels while marginally higher at higher fluence for ns-LA. Since the reflectivity of brass increases with increased wavelength,\textsuperscript{29} this difference can be partially explained by a variation in absorbed laser energy for ns- vs. fs-LA under similar fluence conditions. Additionally, the higher LIBS signal observed for ns-LA (Fig. 4(b)) indicates that there is a greater population of excited atomic Zn present in the ns plasma. However, it has to be mentioned that both excitation temperature and density measurements are spatially and temporally integrated, and hence the reported measurements are considered to be averaged considering LA plumes are highly dynamic systems and their properties change significantly with space and time. There is a direct correlation between excitation temperature and LIBS signal with respect to laser fluence. The LIBS signal intensity is found to increase with laser fluence for both ns- and fs-LA; however, signal saturation tendency is apparent for ns-LA which could be caused by laser screening by the plasma. So even though there are noticeable differences in recorded excitation temperature values at higher laser fluences, similar levels of LIBS signal recorded for both ns- and fs-LA are attributed to differences in laser-target and laser-plasma coupling with varying fluence levels for ns- compared to fs-LA. Mass loading in the ICP-MS is also possible at higher fluences,\textsuperscript{21} which can cause a change in observed ICP-MS signal (i.e., efficiency of atomization and ionization within the ICP can decrease with increased mass).

Apart from plume fundamental properties, the other main mechanism affecting the observed results is the formation of the laser ablation crater. The crater formation effect is much more evident for fs-LA than it is for ns-LA; more material is removed during fs-LA as compared to ns-LA,\textsuperscript{18,20,21} resulting in a deeper crater and therefore more plasma confinement. This effect is also much more pronounced in the LIBS signal than ICP-MS. With repeated laser pulses in the same location, the plasma becomes more contained within the crater, resulting in less light emission captured by the fiber optic cable as the collection optics were optimized for plasmas at the original target surface. Since plasma is most dense close to the target near the ablation spot, the electron density appears to decrease artificially as the crater forms during fs-LA (see Fig. 3(a)). However, the observation of a flat ICP-MS signal during single spot ablation means that an approximately constant amount of aerosol is reaching the ICP throughout single spot fs-LA, indicating that while the optical emission is contained within the crater, the particles are still being swept out to the ICP.

Thermal effects are also evident during ns-LA. This can be observed in the difference between single spot and rastering ns-LA in both the LIBS and LA-ICP-MS signal (see Fig. 2(b and d)).
The heat deposited on the target by the ns laser assists ablation of the target; however, during single spot ablation the crater that is produced confines the plasma and therefore aerosol, reducing or negating the increased ablation due to heating and resulting in a flat signal. Since the rastering speed is 0.1 mm s$^{-1}$, spot size $\sim$ 200 $\mu$m for ns-LA, and laser repetition rate 10 Hz, multiple laser shots will overlap during rastering ablation, taking advantage of the target heating while avoiding crater effects. This results in the increasing signal intensity. Additionally, since ns-LA forms a much more ionized plume due to heating from laser-plasma coupling, while the fs-LA plume is more atomic, ns-LA will result in a higher early excitation temperature and electron density. This can be seen in the excitation temperature and electron density measurements in Fig. 5. The higher excitation temperature and electron density compensate for the ablation of less mass, resulting in signal intensities that are approximately equal for ns- and fs-LA.

Despite having different electron densities and excitation temperatures at the same fluences, ns- and fs-LA exhibited similar LA-ICP-MS signal strengths and higher LIBS signal for ns-LA than fs-LA. Therefore, to further elucidate the cause of this similarity, the LA-ICP-MS signal was plotted together with the LIBS peak area, normalized for excitation temperature through dividing by the Boltzmann factor ($e^{-E/kT}$), as a function of fluence (Fig. 6). By normalizing for any excitation temperature differences, a better comparison can be made between the mass ablated by two different laser pulse durations. As can be seen in the figure, the ICP-MS intensity and LIBS signals follow the same general trend and match well, with fs-LIBS peak area diverting at higher fluence. The thermal effects of ns-LA that cause an increased excitation temperature and electron density, as mentioned above, are also responsible for increasing the LIBS signal up to levels higher than for fs-LA. The figure demonstrates the importance of excitation temperature on the emission properties; at lower fluence, most of the laser energy is used for ablation and with increasing fluence most of the energy is used for heating.

**Conclusions**

In this article we made a comprehensive comparison of local plasma conditions between ns and fs LA sources in a combined LIBS and LA-ICP-MS system. Characterization of the plasma was conducted by evaluating excitation temperature and electron density of the plume under various irradiation conditions using optical emission spectroscopy. The ability to actively monitor fundamental parameters of the plasma provided interesting insights into the effect of various parameters on plasma conditions and its correlations to ns- and fs-LIBS and LA-ICP-MS signals.

The present results indicate that within the fluence regimes generally employed for LA-ICP-MS, plasmas under the conditions employed here will exhibit similar excitation temperatures and electron densities, with ns-LA exhibiting higher excitation temperatures and electron densities than fs-LA. Signal intensity behaviors are also similar for ns- and fs-LA, excluding comparisons of single shot ablation to rastering. The difference observed in single shot vs. rastering is due purely to increased sample heating and crater depth from ns-LA. Limited heating during fs-LA ensures that signal will be approximately constant under rastering due to similar ablation conditions, while the large amount of material removal (i.e., deeper crater) helps to emphasize the crater effects that are observed during single spot fs-LA, especially as compared to ns-LA.

The measured density of the ns-LA plume is found to be higher compared to fs-LA in the range of laser fluence used in the present studies though the excitation temperature showed approximately similar values at lower fluence levels while marginally higher at higher fluence for ns-LA. However, both LA-ICP-MS and LIBS showed similar signal levels with respect to laser fluence for ns and fs excitation despite differences in ns and fs fundamental properties. The emission signal showed good correspondence with excitation temperature with increasing laser fluence. Increased particle density with increased energy (as can be deduced from increasing LIBS/ICP-MS signals and increasing electron density) for both ns- and fs-LA leads to a greater number of collisions within the plasma, which may have an influence on particle condensation; however, further studies are necessary. It is important to note that the spectral investigation was spatially and temporally integrated; more analysis is necessary to fully elucidate the spatial and temporal evolution of laser-produced plasmas in the context of LA-ICP-MS sample introduction. Though the combined LIBS/LA-ICP-MS is demonstrated as a viable technique for both ns- and fs-LA, further research is also essential to investigate the efficacy of analysis for different samples, including those with low elemental concentrations of interest.

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