



The use of multi-element aerosol particles for determining temporal variations in temperature and electron density in laser-induced plasmas in support of quantitative laser-induced breakdown spectroscopy[☆]



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ABSTRACT

Quantitative laser-induced breakdown spectroscopy (LIBS) analysis operates on the assumption that the sample is completely dissociated and diffused within the highly energetic plasma on time-scales of analyte analysis, resulting in analyte emission ideally at the bulk plasma temperature and a signal that is linear with analyte mass concentration. However, recent studies focusing on aerosol analysis have found the heat and mass diffusion rates within laser-induced plasmas to be finite, resulting in particle-rich, locally perturbed areas within the hot bulk plasma. The goal of this study is to observe any related plasma differences, by calculating the bulk and local (i.e. analyte rich regions) plasma temperatures and electron density, to better understand the time frame of equilibrium between the local and bulk plasma properties. This study also seeks to determine whether the presence of large quantities of a matrix element can significantly alter the local plasma conditions, thereby generating matrix effects. We report the temporal profiles of particle-derived species, adding additional insight into the effect of local perturbation of plasma properties, with the conclusion that significant plasma residence (tens of microseconds) is necessary to minimize such effects.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique that uses atomic emission to identify and quantify the elemental composition of a sample. LIBS enjoys several advantages, including the ability to make in situ and remote measurements, little or no need for sample preparation, applicability to solid, liquid, gaseous, and aerosol samples, simultaneous measurement of multiple elements, and very short processing times. This makes LIBS the measurement system of choice in many applications, such as process monitoring [1], remote sensing [2], biomedical applications [3], and detection in hostile environments, [4] with many other relevant issues and applications reported recently. [5,6].

The LIBS process involves focusing a laser beam to a small focal volume. Within this volume, the sample is rapidly heated, vaporized, and ionized, creating a luminescent plasma characterized by atomic and continuum emission. As the plasma cools, the atoms and molecules within emit light at wavelengths unique to the species present; this light is the source of the LIBS analytical signal. Quantitative LIBS

analysis operates on the assumption that the sample is rapidly and completely dissociated and diffused within the highly energetic plasma, resulting in analyte emission at the representative bulk plasma temperature and a signal linear with increased mass concentration. However, many studies have shown that these assumptions do not always hold [7–12]. As explained in previous work, [8] the validity of those assumptions is dependent on process rates of heat and mass transfer.

To that end, Hohreiter and Hahn [13] used quantitative plasma imaging of particle-derived calcium atoms to measure the diffusion timescales. Their results show that the diffusion timescale is on the same order of magnitude as plasma emission, namely about 15 μ s for the vaporization of 2 μ m glass particles. During the early residence time, calcium emission originated exclusively from an area surrounding the location of the original particle and slowly diffused outward during the analysis. This result is in agreement with Lithgow and Buckley [14], who found spatially inhomogeneous atomic emission in magnesium containing aerosols, and beyond LIBS, by Hieftje et al. [15] who previously proposed a diffusion process in analytical flames and plasmas.

In aggregate, these previous studies suggest that the rate of heat transfer from the plasma to the particle (dissociation), the mass transfer rate of the atomic species (mass diffusion), and the radiative decay rate of the plasma (plasma cooling) are all on the same time-

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scale as typical LIBS atomic emission analysis; as such, the idealized near-instantaneous behavior, as described earlier, cannot be assumed in a LIBS plasma. Indeed, Dalyandar et al. [16] calculated the dimensionless Lewis number, $Le = \frac{\alpha}{D}$ relating thermal diffusivity, α , to the mass diffusivity, D , during a numerical simulation and found it to be on the order of unity, corroborating the comparable time-scales of heat and mass transfer in laser-induced plasmas.

In light of these results, Diwakar et al. [17] used magnesium–cadmium particles to calculate the emission temperature of atoms versus delay time, and found the temperature to increase with time over a certain early time regime. Given the localized nature of aerosol particle-derived emissions, as stated above, and the fact that bulk plasma temperatures decrease rapidly with time, it was concluded that the temperatures measured were local plasma temperatures immediately surrounding the particle (i.e. μm to mm length scales). The authors theorize that in order to dissociate, the particle draws a large amount of energy from the immediately surrounding plasma. Since the rate of heat transfer within the plasma is on the same timescale as the particle dissociation, the heat lost by the plasma to the particle is not rapidly replaced, creating a localized perturbation of the plasma around the dissociated atoms and causing the analyte atoms to emit at an altered effective temperature. As the atoms diffuse to the hotter parts of the plasma and energy is transferred to the locally-perturbed plasma region from the bulk, the emitting temperature of the atoms begins to change until the particles reach an equilibrium temperature with the bulk plasma.

These results are consistent with measurements done by Diwakar et al. [18] who found inflections in the slopes of the temperature curve of Lu and the ion-to-neutral ratio of Mg at around the 15–20 μs point of plasma evolution. Miclea et al. [19] and Groh et al. [20] found similar results in an inductively-coupled plasma, demonstrating the importance of mass transfer in ICP systems.

The goal of the current study is to further explore the bulk and local plasma temperature and electron density, using gaseous analytes and particulate metals as possible within the plasma, respectively, in order to observe any temperature differences and locate the point of equilibrium within the plasma. An additional goal is the further understanding of the presence of large quantities of a matrix element within the aerosol particles and whether the presence additionally alters the local plasma conditions.

2. Experimental methods

The system used for this experiment is similar to that reported previously [21] and is shown in Fig. 1. Briefly, a 1064-nm Q-switched Nd:YAG laser operating with 300-mJ pulse energy, 10-ns pulse width, and 5-Hz pulse repetition rate was used as the plasma source. An expanded, 12-mm diameter beam was focused inside a six-way vacuum cross using a 75-mm UV grade plano-convex lens. The plasma emission was collected along the incident beam in a backward direction and separated using a 50-mm elliptical pierced mirror. The collected plasma emission was launched into an optical fiber bundle, coupled to a spectrometer (2400-groove/mm grating, 0.12-nm optical resolution) and recorded with an intensified charge-coupled device (iCCD) array. Neutral density (ND) filters were used as necessary to prevent saturation of the detector.

Argon, nitrogen, and water vapor (i.e. source of hydrogen) were used for the bulk plasma analysis. For water, ultra-purified deionized water was nebulized with 5 lpm of purified, dry air. This hydrogen nebulization stream was mixed in a co-flow of argon and purified, dry air at a rate of 21 lpm each. For the aerosol particle generation, the nebulized water was replaced with an aqueous solution of aluminum, manganese and lutetium (SPEX CertiPrep ICP-grade). Specifically, 10,000 $\mu\text{g}/\text{mL}$ solutions of aluminum and manganese were each diluted down to 2000 $\mu\text{g}/\text{mL}$ with deionized water and mixed, in equal amounts, with 1000 $\mu\text{g}/\text{mL}$ of lutetium, resulting in the final mixture with concentrations of 667 $\mu\text{g}/\text{mL}$ of both aluminum and manganese, and 333 $\mu\text{g}/\text{mL}$ of lutetium. In the sodium matrix experiments, 10,000 $\mu\text{g}/\text{mL}$ of ICP-grade sodium was added in equal amounts to the above mentioned solutions, resulting in a mixture containing 500 $\mu\text{g}/\text{mL}$ aluminum and manganese, 250 $\mu\text{g}/\text{mL}$ lutetium, and 2500 $\mu\text{g}/\text{mL}$ sodium.

Transmission electron microscopy (TEM) was performed on a sample of aerosol particles gathered from the sample chamber. The presence of roughly spherical particles between approximately 50 nm and 1 μm was confirmed, as seen in Fig. 2. Energy-Dispersive X-ray Spectroscopy (EDS) confirmed the presence of Al, Lu, Mn, and Na within individual particles; a representative EDS spectrum is shown in Fig. 2. These tests confirm that the aerosol stream, and by extension the plasma, contains sub-micron, multi-element aerosol particles; it is also noted that the particle sizes are well below published limits for complete dissociation in laser-induced plasmas [8–10].

Eight different spectral windows were used throughout the study to capture the emission lines of the various elements. For the purely gaseous plasma, four windows were used, centered about 415, 480, 500, and 656 nm. For the aerosol measurements, including aerosol in the sodium matrix, four additional windows were used, centered about 260, 310, 350, and 400 nm. In each window, spectra were collected in a range of temporal delays between 0.1 and 250 μs ; however, not all delays were used in each window (see Table 1). Specifically, the delays used were 0.1, 0.2, 0.3, 0.4, 0.5, 0.75, 1.0, 1.5, 2.0, 3.0, 5.0, 7.5, 10, 15, 25, 40, 65, 100, 150, and 250 μs . At each delay, six sets of data were collected, over multiple days, with each set comprising the average of 600 different plasma events (i.e. laser shots).

2.1. Intensity normalization

A calibrated lamp source (1000-W tungsten halogen, 250–2400 nm) was used to correct for the relative spectrometer spectral response. At each wavelength used, the ratio of the measured signal from the lamp (in arbitrary units) to the actual irradiance, as given by the calibration equation, was calculated and used as a correction factor. This resulted in an irradiance correction factor at each wavelength that was then applied to all the spectra gathered, thereby providing a common intensity scale across all wavelengths.

Because the spectral intensity of the calibrated lamp source was much weaker at lower wavelengths, a stray light correction was

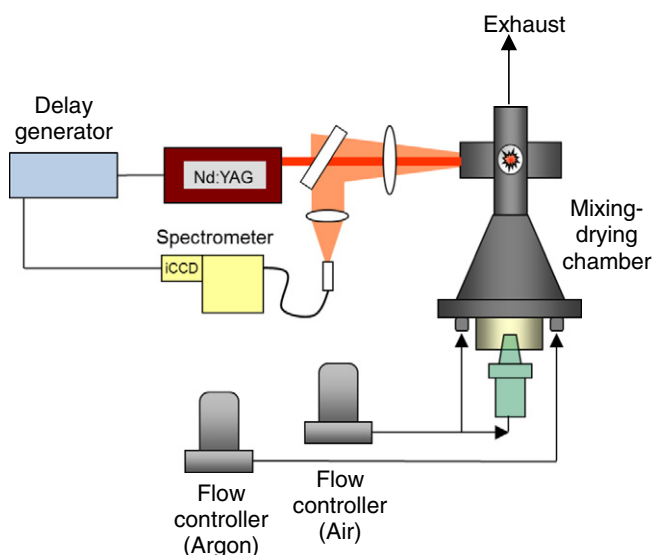


Fig. 1. Experimental apparatus used for present work (not to scale).

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