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Effects of Focal Volume on Uncertainty in Single-Aerosol Laser-Induced Breakdown Spectroscopy Measurements

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Particle location with respect to the plasma volume and the focal volume of the collection optics is identified as an important source of uncertainty in single-aerosol Laser-Induced Breakdown Spectroscopy (LIBS) measurements. Two sets of optics were used to image different regions of a LIBS plasma and simultaneously collect spectra from single particles. Strong variation and lack of correlation between the two measurement channels suggests that emission from a single particle is localized within the plasma. Measurement precision and detection efficiency were improved by imaging a larger plasma region, thus integrating the spatially distributed signal.

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Laser-induced breakdown spectroscopy (LIBS) is emerging as a useful analytical technique for measuring the size and composition of individual aerosol particles. Recent studies have indicated that LIBS is suitable for a variety of applications including atmospheric pollution measurements, [1,2] thermal process exhaust monitoring, [3] and biological aerosol detection. [4-8] With the potential ability to measure the size and composition of submicron particles, LIBS is a promising new tool for aerosol science.

In some applications, LIBS can provide highly quantitative results. Calibration curves for laboratory measurements of aerosols have been found linear over a large range of analyte concentration, with small uncertainties. Such curves are typically obtained by sampling a particle-laden gas flow of known mass concentration, and averaging spectra collected from many laser shots. However, many applications require information about single particles, measured with a single laser shot, which significantly reduces the measurement precision. Hahn [9] quantified the uncertainty of single particle measurements by sampling monodisperse aerosols, illustrating both the potential of single particle LIBS measurements and the limitations due to precision in standard implementations of LIBS.

Consequently, a number of recent studies have focused on investigating sources of uncertainty in single-particle LIBS measurements. Nearly all of these studies have focused on shot-to-shot fluctuations of bulk plasma parameters such as temperature and electron density. Fluctuations in laser pulse characteristics and variations in laser-plasma interactions influence the plasma formation, and have been identified as sources of uncertainty in the LIBS signal. [10-13] It has also been observed that if a particle is too large, or if it is located at the boundary of the plasma, there will be insufficient energy transfer

to completely vaporize the particle, resulting in an artificially low signal. [14] However, it has generally been assumed that species diffusion within the plasma is sufficiently fast that, once vaporized, the initial location of the particle relative to the plasma volume and the focal volume of the spectrometer collection optics is irrelevant. In this Letter, the influence of the particle location is identified as an important source of uncertainty in single-particle LIBS measurements.

In these experiments, two separate sets of optics were used to collect two simultaneous spectra from single laser-plasmas. One set collected emissions at a right angle to the incident laser beam ("side-collection"), while the other set collected emissions backwards along the axis of the beam ("back-collection"). The side collection optics consisted of two 50 mm diameter, 75 mm focal length plano-convex UV fused silica lenses. For back-collection, plasma emission was first collimated with a lens, diverted from the laser beam path with a pierced mirror, and focused with a second lens, each identical to the side-collection optics. The two legs of a bifurcated optical fiber bundle, each leg containing 7 fused silica fibers (200 μm core diameter, 700 μm bundle diameter), were positioned at the focal points of the collection optics to guide the light from both side- and back-collection to an imaging spectrometer for simultaneous measurement. The spectrometer (Acton Research, SpectraPro) utilized a 1200 G/mm grating, and was mated to a time-gated ICCD camera (Roper Scientific, PI-MAX). Light from each leg of the fiber bundle was dispersed separately onto two regions of the CCD array, each 85 pixels high. The plasma excitation source is a Q-switched Nd:YAG laser operating at the fundamental wavelength (1064 nm), and at 10 Hz, with a nominal pulse width of 10 ns, average pulse energy of 275 mJ, and beam diameter of 10 mm. The laser

was focused with the same lens that collimated the plasma emission in the back-collection optics. The gate delay of the detector was 15 μs with respect to the laser Q-switch, and the gate width was 20 μs.

Measurements were performed in a dilute stream of magnesium chloride aerosols in air. The particles were size selected by electric mobility diameter using a differential mobility analyzer (TSI model 3080) to a mean diameter of 500 μm. The signal used to quantify the analyte present in the plasma is defined as the integrated atomic line normalized by the continuum baseline value, and termed the peak-to-base (P/B) ratio. A two-line conditional test [15] was used to determine the presence of a particle signal within each collected spectrum. With no analyte present and signal due only to noise, the detection criteria resulted in false hit rates of 0.01% or less. The particle stream was diluted so that particle hits occurred on approximately 1% of the laser shots. Under these conditions, the vast majority of the collected "hit" spectra can be considered to be from plasmas containing single particles, with a small fraction containing more than one particle, and a negligible fraction of false hits. Approximately 1% of the recorded hits contained large outlying values, which were assumed to be multiple-particle hits, and were excluded from calculations of sample mean and standard distribution values.

In the experiment, spectra were recorded from 50,000 laser shots. On each shot, both spectra were recorded. Particle hits were detected in at least one of the two spectra on 522 of the laser shots, however three different cases were observed. Signal was present in both spectra on only 220 shots (42% of the total hits, termed Case 1). Signal was present only in the side-collected spectrum on 125 laser shots (24%, Case 2), and in 177 shots, signal was present only in the back-collected spectrum (34%, Case 3). This

means that 58% of the time when a particle was detected in one spectrum, it was not visible in the other spectrum. Additionally, the side-collected signal tended to be both stronger and show more variation than the back collected signal. The mean values and standard deviations of the signals for each case are given in Table I.

For each pair of spectra, parameters such as the particle size and bulk plasma properties were identical. The only factor contributing to the difference between the two sets of spectra was the collection optics employed with each method. Specifically, each set of optics imaged a different region of the plasma; these experiments show that emissions are not uniform across the plasma volume. The variation between the side- and back-collection spectra illustrate that the region of strongest emission changes with each particle hit. This suggests that the ablated particle material diffuses a limited distance within the plasma, and will not be detected if it is not initially located within, or near the focal volume of the optics. The enhanced particle detection efficiency of the back-collection method is likely due to the fact that the plasma volume is elongated and the focal volume of the back-collection optics is aligned with the major axis of the plasma, making it more likely that an ablated particle will lie within the focal volume than in the side-collection measurement. The mean values of the signals in Cases 2 and 3 are roughly a factor of four larger than the detection threshold, and each case contains spectral signals greater than ten times the detection threshold. Hence it is not true that only the very small particles with weak signals populate Case 2 and Case 3, it is common for a large particle to go undetected on one channel but be detected on the other.

Further illustrating the effects of particle location, the 220 shots from Case 1 are plotted in Figure 1. In this plot, each point represents a single laser shot, with the side-

collected signal plotted on the x-axis, and the back-collected signal plotted on the y-axis. Ideally, the two methods would be well correlated, but the actual measurements show no correlation. The amount of scatter illustrates the measurement uncertainty due to particle location.

The signal values from the set of side-collected measurements, S_i, and back-collected measurements, B_i, along with the standard deviations, σ_S and σ_B respectively, can be used to obtain an estimate of the uncertainty of each method. Additionally, we define the difference $D_i = S_i - KB_i$, where K is the ratio of the mean value of S_i to the mean value of B_i, and calculate σ_D, the standard deviation of D_i. By assuming that the uncertainty due to particle location is independent of particle size, it is possible to eliminate the particle size and shot-to-shot uncertainty from the equations relating the observed variance in the signals, yielding the uncertainty due to particle location with respect to the optics. The variances due to the particle location for each collection method σ_L are given by

$$\sigma_{L,B}^2 = (\sigma_D^2 + K^2\sigma_B^2 + \sigma_S^2)/ 2K^2, \text{ and} \quad (1)$$

$$\sigma_{L,S}^2 = \sigma_D^2 - K^2\sigma_{L,B}^2. \quad (2)$$

From these equations, the uncertainty of the side-collected method is found to be $\sigma_{L,S}$ = 4.69, and for the back-collected method, $\sigma_{L,B}$ = 2.82. These correspond to relative standard deviations of 59% and 46% for the side- and back-collection methods respectively.

These results demonstrate that variation in particle location relative to the focal volume of the optics has strong influence on the resulting LIBS signal. The enhanced precision of the back-collection method over the side-collection method indicates that imaging a larger region of the plasma integrates spatial variations and reduces the uncertainty. Therefore, one approach to improving the measurements is to simply image a larger region of the plasma. It is important to note that the fiber bundles used in this study are smaller than the 19-fiber bundles commonly used in LIBS, resulting in a smaller imaged region than is typical. This is consistent with the fact that the results of Hahn [9] apparently show superior precision to those presented here.

However, these results suggest a second approach to improving the precision of aerosol measurements with LIBS. The observation of spatial variations in the plasma emission suggests that more information would be available with spatially resolved measurements. Specifically, spatially resolved measurements would give insight into the transport processes occurring within the plasma. With knowledge of the distribution of the analyte material, the relative efficiency of the collection optics could be accounted for. Furthermore, it has been demonstrated that the plasma properties vary across the plasma volume, and that analyte emission varies with plasma properties. With spatially resolved measurements, proper integration of the signal would incorporate these spatial variations. Finally, a more sophisticated hit detection threshold could be developed to exclude particles located at the edge of the plasma, which may not be fully vaporized, or to determine whether multiple particles are present. The results presented here suggest that there is significant room for improving the precision of single-particle LIBS measurements. Properly accounting for spatial gradients by employing spatially resolved

measurements could be an important step towards fulfilling the potential of LIBS for single-particle composition measurements in real applications.

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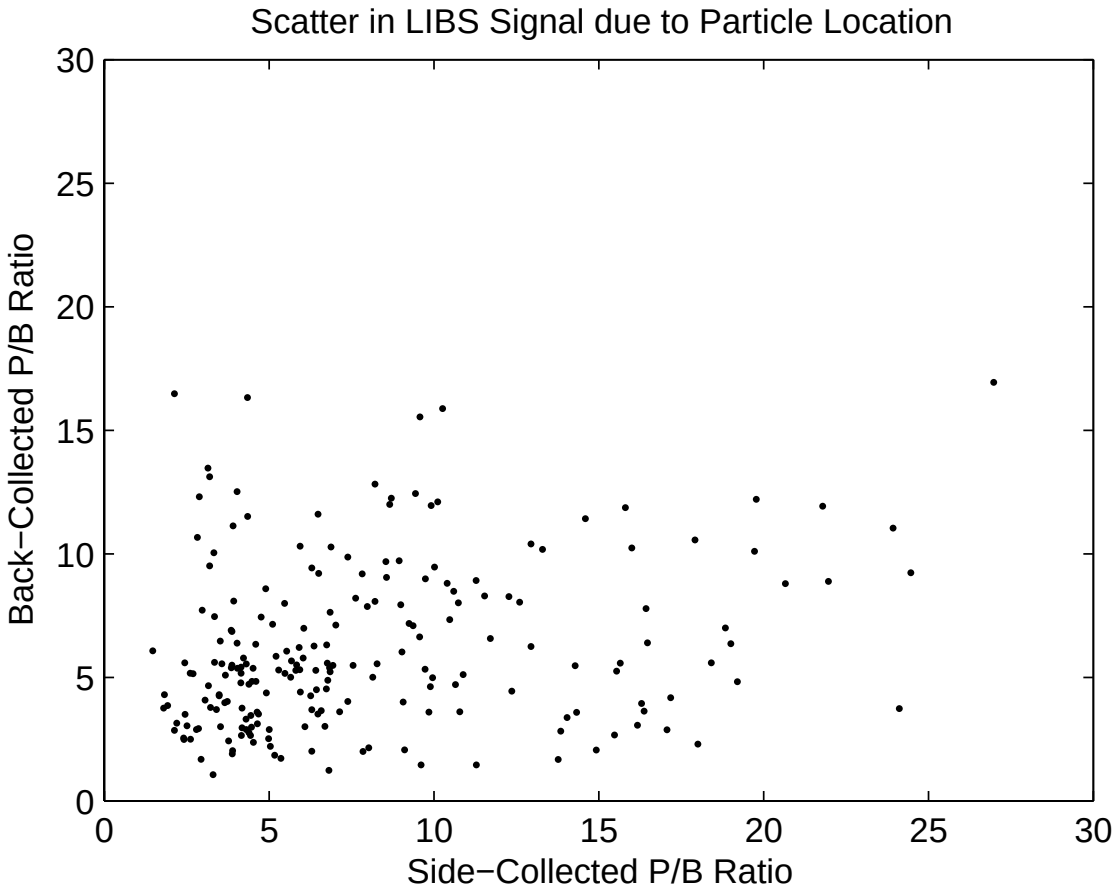
Table I. Mean values and standard deviations of the side-collected and back-collected Peak-to-Base ratios for the data sets in which a particle was detected by both methods (Case 1), or by only one method (Cases 2 and 3).

	Case 1		Case 2	Case 3
	Side	Back	Side	Back
Mean	7.96	6.15	4.94	3.64
Std. Dev.	5.23	3.34	2.89	2.12

Figure Captions

Figure 1. Side- and back-collected particles signals show no correlation. Each point represents a single particle with the side-collected signal on the x-axis and the back-collected signal on the y-axis.


Scatter in LIBS Signal due to Particle Location
Back−Collected P/B Ratio
Side−Collected P/B Ratio
0
5
10
15
20
25
30