

Laser-induced breakdown spectroscopy for sizing and elemental analysis of discrete aerosol particles

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The laser-induced breakdown spectroscopy technique has been extended to provide quantitative analysis of the mass and elemental composition of individual, submicrometer to micrometer-sized aerosol particles. A two-part approach was used for calibration of the overall mass concentration response, and of the characteristic plasma volume, equal to $2.5 \times 10^{-4} \text{ cm}^3$. Laboratory results are presented for submicrometer-sized particles containing a known concentration of magnetite. Additional data are presented for fine particulate matter measured in ambient air, including magnesium-containing particles with an average size of 313 nm. © 1998 American Institute of Physics. [S0003-6951(98)04723-8]

The analysis of small particles (i.e., submicrometer to several micrometers in diameter) using *in situ*, real-time techniques has a wide range of applications. Areas of interest include atmospheric sciences, process monitoring and control, and effluent waste stream monitoring. In addition, considerable attention has been focused recently on ambient fine particulate matter, including source characterization, related health effects, and data for modeling validation.^{1,2} For particle analysis, parameters of interest include size distributions, number densities, and species composition. Simultaneous measurements of these parameters are not readily available using most conventional sizing instruments, although a recently reported technique can provide aerodynamic size and chemical composition of individual particles.³ In this letter, a new technique is described for real-time sizing and elemental analysis of single particles that is based on laser-induced breakdown spectroscopy (LIBS).

With the LIBS technique, a pulsed laser beam is tightly focused in a particle source flow. The resulting optical breakdown, also referred to as a laser-induced plasma, decomposes and excites all species within the ensuing plasma volume, and is characterized by a continuum spectrum containing discrete atomic emission lines. The atomic emission lines, both neutral (I) and ionic (II), and the continuum emission decay with time, but persist strongly on the order of tens of microseconds. The LIBS technique has been applied to the analysis of aerosols, vapors, and combustion particulates.⁴⁻⁸ LIBS has also been applied to the analysis of aqueous particle suspensions and droplets,^{9,10} and more recently to discrete particle detection in gaseous waste streams.¹¹

The excitation source for all experiments in the current work was a Q-switched Nd:yttrium-aluminum-garnet (YAG) laser ($\lambda = 1064 \text{ nm}$) operating with a nominal pulse width of 10 ns, pulse energy of 400 mJ, and 5 Hz repetition rate. After beam expansion to 12 mm, the plasma was created using a 75-mm-focal length, 50-mm-diam UV grade lens. The parameters were such that breakdown was initiated with each laser pulse. Plasma excitation temperatures were on the order of 15 000 K, based on the Boltzmann relation evaluated for a series of Fe II lines. The focusing lens also

collected the plasma emission, as described previously,¹¹ which was launched into a fiber optic bundle and coupled to a 0.25 m spectrometer and time-gated, intensified CCD detector array. Detection delay times ranged from 3.5 to 14.0 μs with respect to the initial laser pulse ($t=0$), and integration times ranged from 6.0 to 14.0 μs .

Particle source streams were generated using a commercial nebulizer designed for inductively coupled plasma systems. Standard aqueous solutions of metals including beryllium, chromium, iron, and magnesium, were nebulized and introduced into a bulk nitrogen flow, where the droplets subsequently dried, producing a fine dispersion of particulate metallic salts. The resulting particle diameters ranged from 50 to 350 nm, as measured using a differential mobility analyzer, a technique that is based on the characteristic particle mobility.¹² Precise calibration flows were generated with known mass concentrations ranging from 100 to 2000 micrograms per cubic meter of sample gas ($\mu\text{g}/\text{m}^3$).

For quantitative particle sizing and elemental analysis, a novel two-part calibration scheme was developed that involved establishing the LIBS system response to (i) a known mass concentration, (ii) and a known discrete particle mass. The LIBS response to a known mass concentration was established using the particle source flow described above. The average LIBS signal response for thousands of laser pulses was calculated for a range of known mass concentrations for iron and for magnesium. The LIBS signal, defined as the integrated atomic emission line intensity normalized by the plasma continuum emission intensity in the region near the line, was correlated to the known mass concentration using a linear least-squares fit. Regression coefficients were 0.99 or higher. The ratio of the integrated line intensity to the continuum emission intensity provided a more robust signal, due to the variation in absolute plasma emission, as compared to the absolute peak intensity alone. A typical calibration spectrum corresponding to an iron mass concentration of 1920 $\mu\text{g}/\text{m}^3$ is presented in Fig. 1(a), with the identified Fe II lines at 249.3, 256.3, 258.6, 259.9, 260.7, 261.2, and 263.1 nm noted.

The second part of the calibration scheme involved replacing the stream of known mass concentration with a particle laden stream of known particle size, mass, and compo-

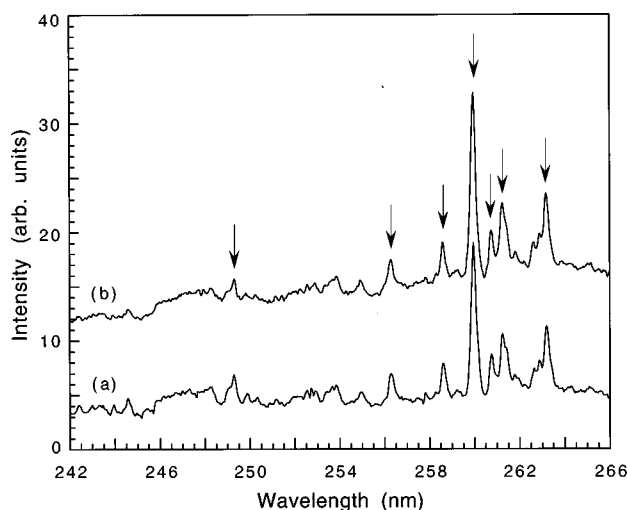


FIG. 1. LIBS spectra for iron corresponding to (a) known mass concentration of $1920 \mu\text{g}/\text{m}^3$, and (b) polymer/iron particles of known particle size and composition. Fe II atomic emission lines are noted.

sition. Monodisperse ($0.940 \mu\text{m}$ diameter) polymer (polystyrene/divinylbenzene) particles were used that contained 65% by mass of Fe_3O_4 , equivalent to $4.4 \times 10^{-13} \text{ g}$ of iron per particle. A dilute flow of the polymer/iron particles was established by nebulizing and drying an aqueous suspension of particles in an overall bulk flow, similar to the process described above. The resulting particle concentration was adjusted, such that a particle signal (i.e., iron emission lines) was recorded for about 1% of the laser shots, to promote single-particle sampling. The sampling rate varied linearly with the particle concentration of the aqueous solution. Single-shot LIBS spectra were recorded for individual polymer/iron particles, which were identified as particle hits using a real-time processing scheme. Specifically, particle discrimination was achieved by comparing the emission intensity about the expected Fe II line (259.9 nm) to the intensity of the adjacent continuum emission, as described previously.¹¹ It is noted that about 5% of the recorded particle hits were attributed to two- or three-particle agglomerates based on their significantly higher mass concentration values (greater than 3σ above mean value). These spectra are not included in the final sets of 182 and 190 spectra discussed below.

Using the dilute particle flow, 182 individual polymer/iron particle spectra were identified. The average spectrum of these discrete particle hits ($n=182$) is presented in Fig. 1(b), and is identical in structure to the spectrum corresponding to the known iron mass concentration [Fig. 1(a)]. The defined LIBS signal (i.e., integrated peak area normalized to continuum as described above) was calculated for the average spectrum of the polymer/iron particles using the iron emission lines. The signal was combined with the least-squares calibration fit determined for iron to yield an equivalent mass concentration of $1745 \mu\text{g}/\text{m}^3$. Using the equivalent mass concentration of the 182 recorded particle hits ($1745 \mu\text{g}/\text{m}^3$) and the known particle mass of iron ($4.4 \times 10^{-13} \text{ g}$), the characteristic plasma volume was calculated to be $2.5 \times 10^{-4} \text{ cm}^3$, which corresponds to an equivalent spherical diameter of $725 \mu\text{m}$. The measured plasma volume is characteristic of the effective plasma sample volume.

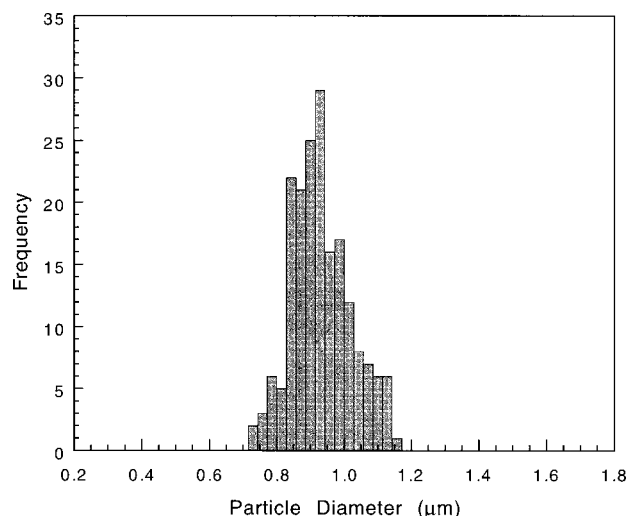


FIG. 2. Size distribution of polymer/iron particles measured using the LIBS technique. Mean diameter= $0.93 \mu\text{m}$, $\sigma=0.090 \mu\text{m}$.

Using this calibrated plasma volume, a new LIBS-based particle sizing and elemental composition scheme may be defined for an individual particle hit. For each element of interest, the emission line signal response is evaluated and the equivalent mass concentration is calculated using the corresponding linear calibration response function. The elemental mass component of the particle is then calculated from the product of the equivalent mass concentration and the characteristic plasma volume. This is simply the reverse of the plasma volume calibration procedure presented above. The particle size is subsequently calculated from the total mass of all identified elements, using an effective particle shape and mass density. The overall elemental composition of a particle may be inferred from the LIBS data, however, some *a priori* information may be required. For example, differentiation between FeO and Fe_3O_4 is limited due to the ubiquitous nature of oxygen, while other elements may exist within a given particle but their atomic emissions lines might not be within the measured spectral bandwidth.

To demonstrate the LIBS-based sizing scheme, experiments were conducted using the same polymer/iron particles utilized for calibration. As described above, spectra corresponding to individual particles were identified and the particle size was calculated based on the measured mass of iron, the defined percentage of Fe_3O_4 (65%), and the defined particle density ($2.17 \text{ g}/\text{cm}^3$). A histogram of 190 individual particle size measurements is presented in Fig. 2. The mean diameter of the measured distribution is $0.932 \mu\text{m}$, with a standard deviation of $0.090 \mu\text{m}$, and is in excellent agreement with the specified value ($0.940 \mu\text{m}$). The relatively narrow standard deviation provides a quantitative assessment of the system response of the LIBS-based sizing scheme, as implemented here. Because the LIBS technique actually measures the mass of constituent elements, experimental uncertainty in the calculated particle diameter is minimized due to the cube-root dependence. For example, the average mass concentration of the 190 individual particles of Fig. 2 was $1730 \mu\text{g}/\text{m}^3$, with a standard deviation of $575 \mu\text{g}/\text{m}^3$. The range for all particles was from 810 to $3245 \mu\text{g}/\text{m}^3$, nominally within a factor of two of the mean value, which corresponds to a deviation in particle size of less than 26%.

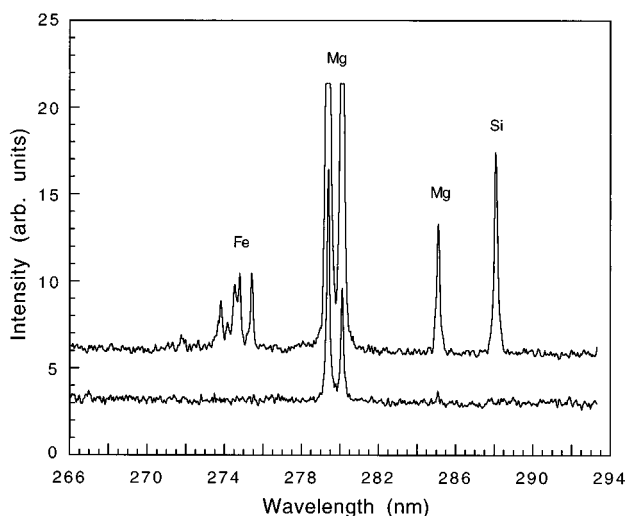


FIG. 3. LIBS spectra for two Mg-containing particles recorded in ambient air. Both spectra have same scale, and have been shifted vertically for clarity.

In addition to the laboratory work described above, a series of measurements were taken in ambient air in central California in November 1997 to assess the LIBS-based sizing technique for the analysis of fine particulate matter. The plasma was created in open air using the experimental parameters described above, and measurements were recorded utilizing the air inlet stream of a gas-turbine cogeneration facility. LIBS spectra corresponding to individual particles were identified by triggering on various atomic emission lines, including emission lines for Ca, Fe, Mg, Si, and Na. Two single-shot spectra are presented in Fig. 3 that correspond to individual particles recorded when triggering with the 279.55 nm Mg II line. The signal-to-noise ratio of the two spectra is excellent, demonstrating a combination of high analyte sensitivity and signal discrimination.

The spectra in Fig. 3 are representative of the two types of magnesium-containing particles observed. The upper spectrum contains the prominent Mg II lines at 279.55 and 280.27 nm, the 285.21 nm Mg I line, a series of Fe II lines at 274.0, 274.6, 274.9, and 275.6 nm, and the 288.16 nm Si I line. This spectrum is expected for a typical soil-derived particle, and corresponds to about 5% of the total Mg-containing particles detected. The lower spectrum is representative of the remaining 95% of the Mg-containing particles detected, and is characterized by the lack of detectable Si or Fe signals. Over a 72 min period, 63 individual particles corresponding to this latter particle type (i.e., no Si or Fe) were identified. For the 63 particles, the individual particle size was calculated based on an equivalent spherical diameter of magnesium carbonate, MgCO_3 (density = 3.1 g/cm^3). The corresponding histogram is presented in Fig. 4. The mean particle size is 313 nm (standard deviation of 110 nm) with a range from 175 to 660 nm. The calculated ambient concentration level of magnesium during this period was 280 ng/m^3 , approximately 230 parts per trillion by mass. As an alternative to the MgCO_3 analysis, the calculations were repeated for a particle composition of MgO , MgCl_2 , or MgSO_4 , which yielded mean particle diameters of 232, 356, and 370 nm, respectively. For this data set, a wider spectral bandwidth (e.g., including Al, Ca, Cl, Fe, Mg, Na, S, and Si

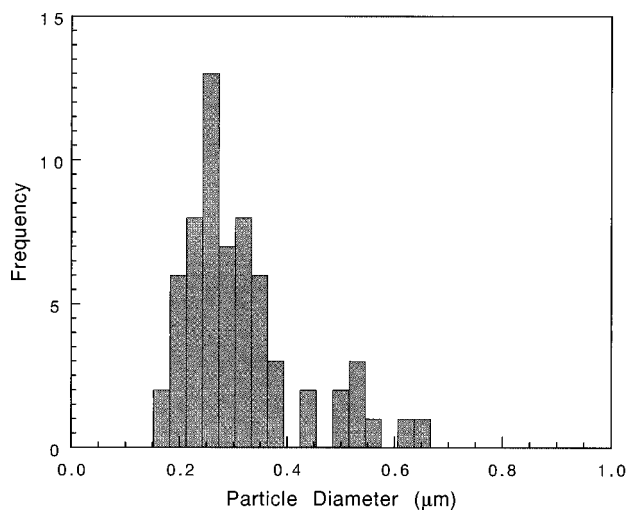


FIG. 4. Size distribution of magnesium-containing particles measured in ambient air using the LIBS technique. Mean diameter = 313 nm, $\sigma = 110$ nm.

emission lines) would enable a more accurate determination of the particle composition.

In summary, the LIBS technique has been extended to provide quantitative analysis of the elemental mass and composition of individual, submicrometer to micrometer-sized aerosol particles. The technique yielded excellent results in laboratory tests, and proved to be both robust and highly sensitive during initial field experiments for the detection of ambient fine particulate matter. Future work will better quantify the plasma-particle interactions, including a spatial response effects and plasma homogeneity issues, gas matrix effects, particle size limits, and the application to systems with high particle loadings which may require data deconvolution.

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