

# Real-Time Measurement of Combustion Generated Particles with Photofragmentation-Fluorescence

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Excimer laser fragmentation-fluorescence spectroscopy (ELFFS) is a viable technique for real-time monitoring of carbonaceous particles in combustion exhausts. The exhaust from a single-cylinder two-stroke engine is diluted and diverted into the laser interrogation region, resulting in a particle concentration of approximately  $1 \times 10^7/\text{cm}^3$ . Light from a 193 nm ArF laser photofragments the particles and then produces fluorescence from the atomic carbon fragments at 248 nm, CH fragments at 431 nm, and  $\text{C}_2$  fragments at 468 nm. The atomic carbon fluorescence signal is proportional to the number concentration of particles in the laser interrogation region. The 100-shot (1 s) detection limit for particles in the exhaust is  $1 \text{ mg}/\text{m}^3$ , expressed as a mass concentration of particulate matter. Interferences from carbon monoxide and carbon dioxide are negligible. The relative fluorescence yield at 248 nm is four times greater from particles than from the gas phase hydrocarbons present in the exhaust. This high yield suggests that the gas phase hydrocarbon interference would not be problematic for measurements of diesel exhaust, where the ratio of particulate carbon to gas phase hydrocarbon is high.

Index Headings: **Particulate monitoring; Laser diagnostics; Aerosol; Excimer; Combustion.**

## INTRODUCTION

The detection of carbonaceous, combustion-generated particles is an area of research that has received considerable attention over the last several years, driven by suspected human health effects of exposure to airborne particulate matter.<sup>1</sup> Most nucleation mode particles ( $d_p < 0.1 \mu\text{m}$ ) in the atmosphere are generated from combustion, and combustion-generated particles often contain, or are coated by, toxic compounds. Combustion-generated particles also serve as nucleation sites for condensation growth to the accumulation mode ( $0.1 \mu\text{m} < d_p < 1 \mu\text{m}$ ). Because accumulation mode particles are slowly removed from the atmosphere by gravitational settling and diffusion to surfaces, they have long atmospheric lifetimes and can travel long distances. These particles can impact the air quality of places far removed from the original emission sources, can impair visibility, and can impact the global energy balance.

Real-time particle measurement techniques are needed to better understand particle formation and growth in combustion processes, as well as in the atmosphere. While several different techniques have been developed to measure particles, no single technique can meet all the requirements necessary to completely understand particles in these complex environments. A recent study by

Moosmuller et al. compared five real-time diesel PM measurement techniques to the standard code of federal regulations (CFR) filter collection method.<sup>2</sup> They found that the tapered element oscillating microbalance (TEOM) and a nephelometer correlated well with the CFR method. An aethalometer, a photoacoustic instrument, and a smoke meter did not compare favorably to the CFR method. The two-color method, which measures the ratio of thermal radiation from particles at two different wavelengths, has been used to measure diesel combustion temperature since the 1940s. If some assumptions are made, the particle concentration can also be determined with the two-color method.<sup>3</sup> Light scattering has long been used for particle sizing measurements and is often used in conjunction with other techniques that provide additional information about the particles.<sup>4</sup> Ottesen et al. used Mie scattering with laser spark spectroscopy (LSS) to measure the size and composition of coal particles.<sup>5</sup> Light extinction, which is a measure of the sum of scattering and absorption from particles, is widely used for particle measurements in a variety of environments. Van de Hulst first proposed using the ratio of scattering to extinction to infer soot particle size.<sup>6</sup> Hentschel and Richter applied the technique in a high-speed direct-injection diesel engine.<sup>7</sup> Laser-induced incandescence (LII) is a powerful tool for two-dimensional soot concentration measurements, and provides information about primary particle size under certain conditions. It was first noticed by Eckbreth as an interference in coherent anti-Stokes Raman scattering measurements.<sup>8</sup> Several researchers have developed LII as a diagnostic.<sup>9-14</sup> Vander Wal et al. recently used cavity ringdown (CRD) to calibrate LII measurements.<sup>15</sup> Cavity ringdown has also been used to measure atmospheric particulate matter.<sup>16</sup> Aerosol time-of-flight mass spectrometry (ATOFMS) measures the chemical composition and size of single particles; Silva and Prather recently used the technique to characterize particles from automobile emissions.<sup>17</sup> Photoelectric charging of aerosols by irradiation with ultraviolet light has been used for the determination of particle size and concentration.<sup>18</sup> This method was recently used in conjunction with diffusion charging and condensation particle counting to measure submicron particles from diesel engines.<sup>19</sup> Optical emission studies have been performed on particulate carbon from a laser vaporization cluster source.<sup>20</sup> The author suggests that the technique could be used to study soot formation in combustion. The only application of photofragmentation-fluorescence to measure particulate matter is the work of Bengtsson and Al-

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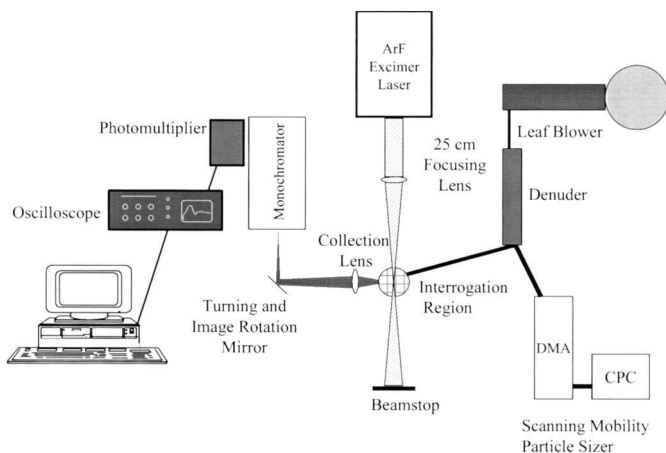


FIG. 1. Experimental setup.

den that combined photofragmentation followed by laser-induced fluorescence of  $C_2$  with LII to make soot measurements in laboratory flames.<sup>11</sup> For more details on optical diagnostics for soot measurements in engines, the reader is referred to the recent review of Zhao and Laddomatos.<sup>3</sup>

## EXCIMER LASER FRAGMENTATION-FLUORESCENCE SPECTROSCOPY

Photofragmentation-fluorescence (PFF) has been used for measurements of trace gas species in a variety of environments.<sup>21–26</sup> The technique employs photofragmentation of larger molecules to form less complex, fluorescent species. These fluorescent species act as signature fragments for the larger non-fluorescing species. Our laboratory has recently applied the technique to the measurement of inorganic particulate matter in flames and in post-flame environments.<sup>27,28</sup> Sausa et al. used photofragmentation and fragment excitation to explore the interaction of an ArF laser pulse with simple hydrocarbons.<sup>29</sup> McDonald et al. explored the photochemistry of acetylene following photofragmentation by an ArF laser.<sup>30</sup> Other researchers have used PFF for photochemical studies of gas phase hydrocarbons; the reader is referred to the review of Simeonsson and Sausa<sup>21</sup> for details.

In our study, an ArF laser pulse interacts with solid carbonaceous particles, generating excited atomic carbon fragments that fluoresce at 248 nm ( $^1P_1^0 \rightarrow ^1S_0$ ). If hydrocarbons are present in the gas phase or condensed on the particles, CH ( $A^2\Delta \rightarrow X^2\Pi$ ) and  $C_2$  ( $d^3\Pi_g \rightarrow a^3\Pi_u$ ) fluorescence is also observed at 431 nm and 468 nm, respectively.

## EXPERIMENTAL

The experimental arrangement for these experiments is similar to our earlier ELFFS work (Fig. 1).<sup>22,23,27,28</sup> A single cylinder, two-stroke, 25-cm<sup>3</sup> leaf blower engine (Homelite) generates carbonaceous particles and other combustion products. The exhaust from the engine mixes with the blower air, resulting in an air to exhaust dilution ratio of 100:1. A portion of the diluted flow (5 Lpm) is directed either to the laser interrogation region for fragmentation-fluorescence measurements, or to a TSI scanning mobility particle sizer (SMPS) (model 3071A with

a 3025A counter) for measurements of the particle size distribution (PSD). For some measurements, the exhaust passes through a multi-channel diffusion denuder,<sup>31</sup> which removes gas phase hydrocarbons from the diluted exhaust, before fluorescence and SMPS measurements are made. The denuder is composed of an array of carbon impregnated filter sheets (Schleicher and Schuell, Inc). A quartz filter removes the particulate fraction for other measurements. Hence, there are four different measurement arrangements. Comparisons are made among the measurements of the diluted exhaust (all species), diluted-denuded exhaust (particles and background gases), diluted-filtered exhaust (hydrocarbons and background gases), and diluted-filtered-denuded exhaust (background gases). Measurements of gas phase hydrocarbons were made with a flame ionization hydrocarbon analyzer (Horiba) and with a Fourier transform infrared (FT-IR) spectrometer (Nicolet Magna IR 760).

The ArF excimer laser (Lambda Physik EMG 102 MSC) develops 120-mJ pulses of 193-nm light, which are focused into the interrogation region using a 25-cm focal-length UV-grade fused-silica lens. This creates a detection region with a minimum cross-section of 2 by 0.5 mm. The peak fluence at the focal region is  $1.2 \times 10^5$  J/m<sup>2</sup>. This fluence is not sufficient to cause air breakdown, which would create unwanted chemical effects, but does assure that a large number of the molecules in the detection region will interact with the laser light. Laser energy is measured using a Gentec ED-500 joulemeter.

The detection region is imaged onto the entrance slit of a 0.3 m McPherson scanning monochromator with a single plano-convex lens. The measurements are made using a 7.5-cm-focal-length, 2.5-cm-diameter fused-silica lens positioned roughly 9 cm from the detection region to focus the detection region through the monochromator slit. All spectra presented here were collected with a horizontal slitwidth of 0.4 mm, which corresponds to a bandpass of 1.1 nm.

The light passed by the monochromator enters a Hamamatsu R928 photomultiplier tube; the signal generated is digitized by a LeCroy 9410 digital oscilloscope and is sent to an IBM-compatible PC for storage and processing. ELFFS spectra are obtained coincident with the laser pulse (pulse width = 20 ns). Atomic carbon fluorescence is observed at 248 nm; CH and  $C_2$  fluorescence are observed at 431 nm and 468 nm, respectively.

## RESULTS AND DISCUSSION

Figure 2 shows the particle size distribution (PSD) for the diluted exhaust (dilution ratio 100:1), measured by the SMPS system. The particle number concentration is  $1.2 \times 10^7$ /cm<sup>3</sup> with a median diameter of 0.10  $\mu$ m, and a geometric standard deviation of 1.7. The volume concentration is  $1.7 \times 10^{13}$  nm<sup>3</sup>/cm<sup>3</sup>, corresponding to a volume fraction of 17 parts per billion. Assuming a particle mass density for elemental carbon of 2 g/cm<sup>3</sup>,<sup>32</sup> this is a mass concentration of 34 mg/m<sup>3</sup>. The gas phase hydrocarbon concentration in the diluted exhaust is 300 parts per million (ppm), measured as propane with a flame ionization detector and confirmed with an FT-IR spectrometer. The carbon atom mass concentration associated with the gas phase hydrocarbons is 450 mg/m<sup>3</sup>. Note that this

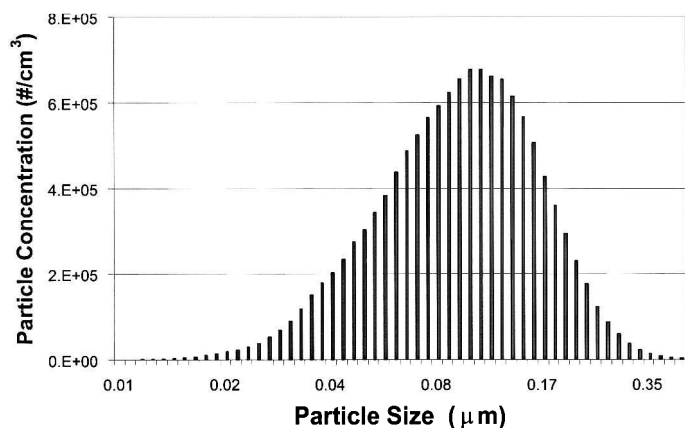


FIG. 2. Particle size distribution of diluted exhaust.

carbon atom mass concentration is 13 times higher than the mass concentration of carbon due to the particles (assuming the particles are entirely elemental carbon). Thus, the gas phase hydrocarbons may dominate the resulting carbon atom fluorescence from the diluted exhaust. For some measurements, the gas phase hydrocarbons are removed with a denuder to accurately measure the fluorescence from particles.

FT-IR measurements show that the removal efficiency of the denuder for gas phase hydrocarbons is approximately 95 percent. However, methane, carbon monoxide, and carbon dioxide concentrations are unchanged by the denuder. These species have a negligible fragmentation-fluorescence signal at 248 nm (this is addressed in more detail later). The denuder has a minimal effect on the PSD. The denuder removes approximately 15% of the particles, but the median diameter (0.11  $\mu\text{m}$ ) and geometric standard deviation (1.7) are virtually unchanged. The mass concentration is 30  $\text{mg}/\text{m}^3$ , corresponding to a particle volume fraction of 15 ppb. These data are used to calculate the relative fluorescence yield for particulate and the detection limit reported later.

Figure 3 shows the fluorescence spectra for the diluted exhaust and the diluted-denuded exhaust. Recall that the diluted exhaust contains both particles and gas phase hydrocarbons while the denuded exhaust contains only particles. There are several prominent features in the spectrum of the diluted exhaust, including the atomic carbon

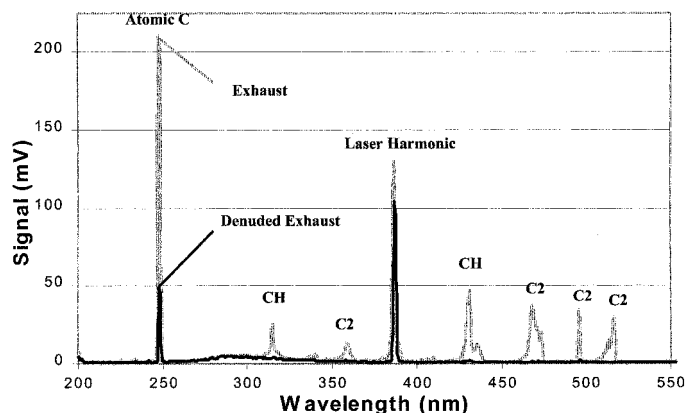


FIG. 3. Fluorescence spectra of diluted exhaust and diluted-denuded exhaust.

fluorescence at 248 nm, several  $\text{C}_2$  fluorescence peaks, two peaks from CH fluorescence, and a scattered signal at 386 nm ( $2 \times$  laser wavelength). When the exhaust is denuded, there is still an atomic carbon peak but the  $\text{C}_2$  and CH features are no longer present. These measurements suggest that fluorescence from the carbonaceous particles can be monitored at 248 nm and that the CH and  $\text{C}_2$  fluorescence are due to gas phase hydrocarbons.

Figure 4 presents the 100-shot averages of the atomic carbon, CH, and  $\text{C}_2$  fluorescence measured at 248, 431, and 468 nm, respectively. The values above the bars are 100-shot averages of the fluorescence measured at 248 nm for the four different experimental arrangements. The values are uncertain by  $\pm 15\%$  (1 standard deviation), and the background (in room air) is 1 mV. This figure illustrates the proportion of fluorescence due to particles in the exhaust at the three monitored wavelengths. The 223 mV atomic carbon signal in the diluted exhaust is from gas phase hydrocarbons and from particles. To determine the fraction of the signal from particles, we remove the particles with a filter and observe a decrease of 42 mV in the fluorescence. When we remove the gas phase hydrocarbons, measure the fluorescence from particles directly, and correct for the gas phase hydrocarbons not removed by the denuder, the result is 52 mV. These results are in reasonable agreement, considering the experimental uncertainty. In the diluted exhaust, the particles thus contribute about 20% to the total atomic carbon signal.

The difference between the exhaust signal and the filtered signal at 430 and 468 nm suggests that the particles account for about 50% of the CH and  $\text{C}_2$  fluorescence. However, when the gas phase hydrocarbons are removed with the denuder, no CH or  $\text{C}_2$  fluorescence is observed from the particles. There are two possible explanations for this apparent discrepancy. If gas phase hydrocarbons condense on the filter, or on particles that have been collected on the filter, the concentration remaining in the exhaust stream would be lower, resulting in a decreased signal. However, FT-IR measurements of the exhaust and the filtered exhaust gave similar gas phase hydrocarbon concentrations. If hydrocarbons condense on the particles, they would presumably exhibit CH and  $\text{C}_2$  fluorescence. When the particles are removed, the CH and  $\text{C}_2$  fluorescence would then decrease, as observed. No CH or  $\text{C}_2$  fluorescence is observed from the denuded particles because the denuder effectively removes the condensed hydrocarbons from the particle surface as well as removing the gas phase hydrocarbons.

In contrast to the CH and  $\text{C}_2$  fluorescence measurements, the atomic carbon fluorescence from particles with hydrocarbons condensed on their surface is approximately equal to the fluorescence from particles without hydrocarbons on their surface (42 mV vs. 52 mV).

The relative atomic carbon fluorescence yields of the major carbon containing species in the exhaust were measured to determine the significance of interference when monitoring fluorescence from particles. To determine the yield for methane and carbon dioxide, fluorescence was measured from prepared methane/air and  $\text{CO}_2$ /air mixtures. The yield is measured by dividing the fluorescence signal from the pollutant of interest by the mass concentration of that pollutant. The mass concentration is mea-

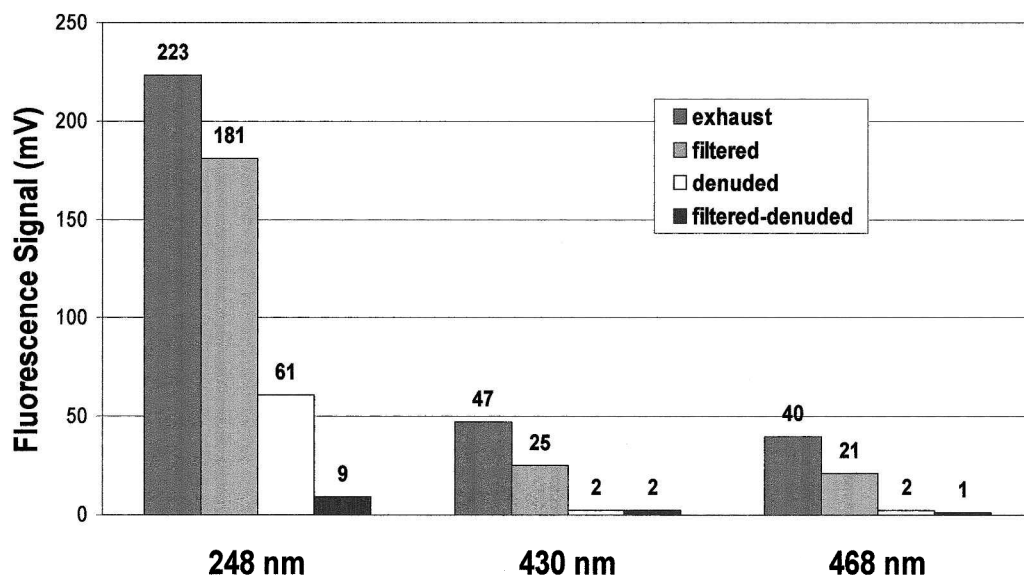


FIG. 4. Atomic carbon, CH, and C<sub>2</sub> fluorescence from diluted exhaust, diluted-denuded exhaust, and diluted-filtered-denuded exhaust.

sured either with the SMPS system (for particles, assuming a particle density of 2 g/cm<sup>3</sup>) or with an FT-IR spectrometer. The yield was measured for all the species listed except carbon monoxide, where we used the value from Sausa et al.<sup>29</sup>

The fluorescence yield for the particles is four times greater than the yield for the gas phase hydrocarbon found in the exhaust. This observation suggests that it would not be necessary to remove the gas phase hydrocarbons when making measurements in many typical combustion exhausts. In a diesel engine, for example, the particle number concentration is typically about 10 to 100 times greater, and the gas phase hydrocarbon concentration is typically a factor of 5 lower than what we observe in the diluted two-stroke exhaust. This, combined with the higher fluorescence yield for the particles, implies that only 1–7% of the atomic carbon fluorescence signal would be from gas phase hydrocarbons in diesel exhaust. From the results presented in Table I, it is also clear that any interference from carbon monoxide and carbon dioxide in the exhaust is negligible.

A second stage of dilution was used so that the atomic carbon fluorescence could be measured for different particle concentrations. The fluorescence signal was found to be proportional to the particle number concentration (Fig. 5). The particle size distribution did not change as the dilution was varied, so it is not possible at this time to determine whether the signal is proportional to particle surface area concentration or particle mass concentration.

Defining the minimum detectable signal as 3 times the standard deviation of the background signal, the 100-shot (1 s) detection limit for the mass concentration of car-

bonaceous particles is 1 mg/m<sup>3</sup>, equivalent to a soot volume fraction of 0.5 ppb. This is comparable to the detection limit achieved by Vander Wal et al. using cavity ringdown detection (CRD) to calibrate laser-induced incandescence (LII) measurements.<sup>15</sup> The corresponding single-shot detection limit, assuming the background noise is random and follows Poisson statistics, is 10 mg/m<sup>3</sup>. These detection limits make the method suitable for monitoring particulate matter in combustion exhausts, but they are not low enough for ambient measurements, where a detection limit on the order of 1 µg/m<sup>3</sup> is needed.

ELFFS allows for the simultaneous measurement of several pollutants in addition to carbonaceous particulate. With the same experimental arrangement, it is possible to measure chlorinated hydrocarbons, many toxic metals, and ammonia, among others. This advantage makes ELFFS more valuable as a continuous emissions monitor. ELFFS is sensitive to both the non-volatile and the volatile fraction of carbonaceous particulate. There is not a lower particle size limit on the technique. In addition, it may be possible to use the ratios of the atomic carbon, C<sub>2</sub>, and CH peaks to obtain information on the molecular

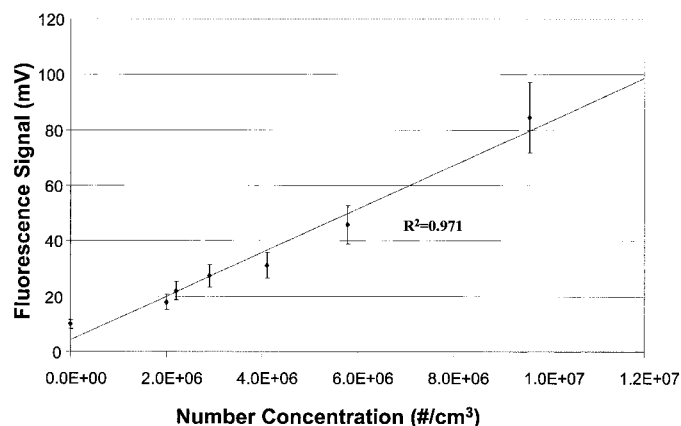


FIG. 5. Atomic carbon fluorescence (248 nm) from diluted-denuded exhaust. A second stage of dilution was used to vary the particle number concentration.

TABLE I. Relative fluorescence yield at 248 nm.

Species	Relative yield
Denuded particulate	1
Gas phase hydrocarbon in exhaust	0.22
Carbon monoxide	5.E-04
Methane	5.E-05
Carbon dioxide	<5.E-05

forms of compounds condensed on or contained within the particles measured. Because gas phase hydrocarbons interfere with the fluorescence from particles, the applicability of the technique for in-cylinder engine studies may be limited. Another limitation is the inability of ELFFS, at this point, to yield information on the particle size distribution of the aerosol.

## CONCLUSION

Excimer laser fragmentation-fluorescence spectroscopy is an effective technique for detecting carbonaceous particles in combustion exhausts. When measuring carbon atom fluorescence from particles there is negligible interference from carbon monoxide and carbon dioxide in the exhaust. The interference from unburned gas phase hydrocarbons is significant here because two-stroke engines emit a relatively large amount of unburned hydrocarbons (~30 000 ppm in the undiluted exhaust). Gas phase hydrocarbon interference is not expected to be a problem when making measurements of diesel engine exhaust because the particle concentration is 10–100 times greater and the gas phase hydrocarbon concentration is considerably lower. The atomic carbon fluorescence signal is proportional to the number concentration of particles in the laser interrogation region, and the single-shot detection limit of ELFFS is low enough to allow for real-time monitoring in combustion systems ranging from diesel engines to industrial boilers.

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