REAL-TIME SIMULTANEOUS MEASUREMENTS OF SIZE, DENSITY, AND COMPOSITION OF SINGLE ULTRAFINE DIESEL TAILPIPE PARTICLES

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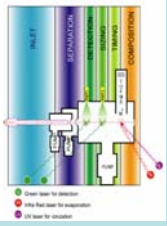
Abstract

We have recently developed Single Particle Laser Ablation Time-of-flight Mass Spectrometer (SPLAT) for the real-time characterization of size, composition and density of individual exhaust particles. The instrument was specifically designed to provide high sensitivity for particles in the 150nm to 50nm range to cover the bulk of the particle mass that is present in the exhaust.
We are presenting results from measurements of particles generated by two very different diesel engines: a Mercedes A-Class and a heavy duty off-road John Deer. A total of approximately 0.5 million individual particles were sized and their composition characterized in real-time. The data were analyzed using SpectraMiner, our data mining and visualization program. The aerodynamic size distribution of the detected particles peaked at 50 – 100nm, depending on engine operating conditions.
We investigated the effects of different load, RPM, fuel and exhaust gas recirculation (EGR) conditions on particle size distributions and composition. Variation of particle composition with injection timing and sequence, the use of oil recirculation and the presence or absence of a catalytic converter were also examined.
The most prevalent particles were composed of almost pure soot. Other types of characterized particles include oxygenated organics, nitrates, engine wear and tear particles, lube detergent particles and particles containing PAHs, partially burned and unburned fuel. Many of these particles were internally mixed with soot. When SPLAT was combined with DMA in addition to particle aerodynamic size and composition it was possible to measure in real-time the density of individual particles and derive the fractal dimension of diesel soot.

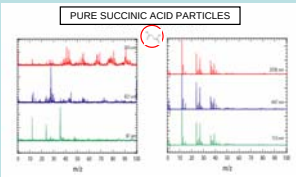
Experimental

Single Particle Laser Ablation Time-of-flight Mass Spectrometer (SPLAT)

The instrument provides size, density and molecular composition of individual aerosol particles obtained by real-time sampling directly from exhaust or ambient air.
An aerodynamic lens is used to focus 90 percent of entrained particles into an extremely narrow beam. Two-stages of optical detection placed along the well-defined particle path provides both velocity and size information for individual particles in the beam. An IR laser pulse timed to arrive coincident with the particle evaporates it and the UV laser pulse generates ions that are subsequently analyzed in the TOF-MS.



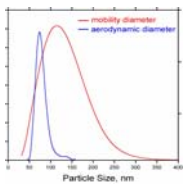
Separating Ablation into Evaporation Followed by Ionization Greatly Improves the Spectra



Two step ion formation using IR laser heating for particle evaporation followed by UV ionization greatly improves reproducibility and the instrument quantitative ability

SPLAT in ORNL engine R&D cell

The Diesel Exhaust Challenge to Single Particle-MS

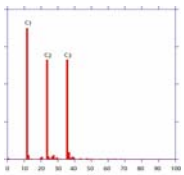


Virtually all the exhaust particles are smaller than 150nm. SPLAT is unique in that it has the sensitivity and detection limit that allow for a study of the most important fraction of the particle population.

SPLAT II

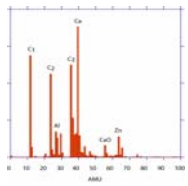
Particle Composition

Soot Particles are Most Prevalent



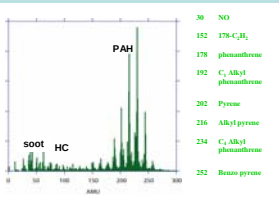
The most prevalent particles are composed of almost pure soot as evident by the carbon progression

At Rated Speed, Oil Components and Engine Wear and Tear Appear Products Appear in Particles



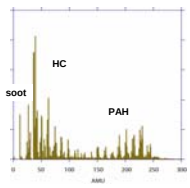
Ca Al and Zn indicate lube oil consumption and engine wear and tear

PAHs Volatilize from Particles using Laser Heating



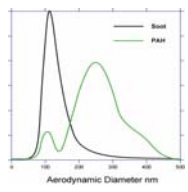
PAH dominated particles are most common under high RPM and low load conditions

Unburned and Partially Oxygenated Fuel Volatilize from Particles using Laser Heating



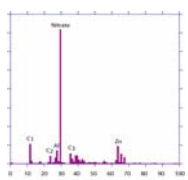
Some PAH containing particles are mixed with partially oxygenated fuel components

Where are the PAHs?



The size distributions above indicate that most of the PAH mass is on PAH dominated particles and not on soot.

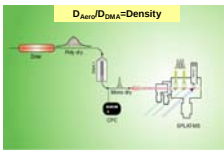
A Small Fraction of Particles Contain Significant Amounts of Nitrates



Nitrate containing particles are mixed with Al and Zn and are most common under high RPM and low load conditions.

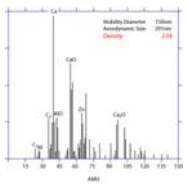
Density and Fractal Dimension

Size, Composition & Density Measurements Using SMPS to Feed Particles to SPLAT



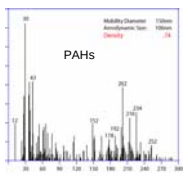
A schematic of a system for measuring particle density, size and composition. A DMA selects single mobility size particles to "feed" to SPLAT where their aerodynamic diameter and composition are measured. The relationship between particle mobility diameter and aerodynamic diameters yield density.

Particle Density Depends on Composition



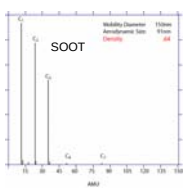
A Ca dominated single 150nm mobility diameter particle containing lube components and engine wear and tear with a density of 2.04 g/cc

Particle Density Depends on Composition



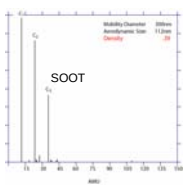
A PAH single 150nm mobility diameter particle containing soot and unburned fuel with a density of 0.74 g/cc

Particle Density Depends on Composition



A soot single 150nm mobility diameter particle with a density of 0.64 g/cc

Particle Density Depends on Composition and Size!!



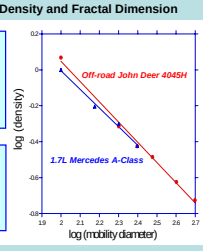
A soot single 300nm mobility diameter particle with a density of 0.39 g/cc

Diesel Soot Density and Fractal Dimension

Density = D_{aero}/D_m
Density = CD_m^{Df-3}

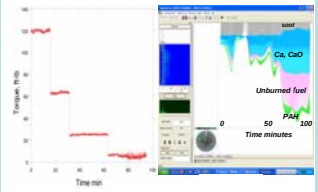
D_f = 1.87
D_f = 1.96

These values are consistent with fractal dimension predicted for diffusion-limited cluster-cluster agglomeration



PM as a Function of Load

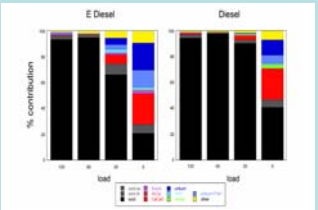
Experiments probing the relationship between PM Composition and Density as a Function of Load @ 3000RPM



Engine load as a function of time

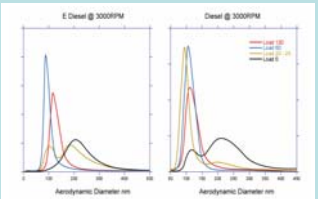
PM composition as a function of time/load

PM composition as a function of load



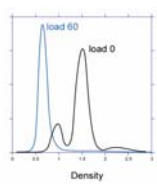
Average particle composition as a function of engine load for two fuel types

PM Aerodynamic Diameter as a Function of Load



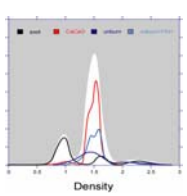
Aerodynamic size distribution as a function of load for two fuel types

PM Density as a Function of Load



The effect of load on particle density

PM Density and Composition as a Function of Load



Particle density as a function of composition

Conclusion

- SPLAT provides in real-time individual particle:
  - Size – 50nm to 3micron
  - Composition - IR evaporation followed by UV ionization
  - Density – size and composition resolved
  - Fractal Dimension
- SPLAT makes it possible to monitor engine performance in real-time by watching the computer screen
- SpectraMiner is a powerful tool for detailed data analysis
- All particles are internally mixed but there are clear classes
- Particle size, composition and density are a strong function of engine operation
- Density of soot is inversely dependant on particle size
- Non-soot particles have higher aerodynamic diameter
- PAHs are found in particles with unburned fuel, and with soot