Internal Report: Investigations into Diesel Particulate Morphology, Part I

Brian P. Frank
Research Scientist II
Particulate Group
In-Use Programs Section
Bureau of Mobile Sources and Technology Development
Division of Air Resources
New York State Department of Environmental Conservation

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I. Background and Relevance

The objective of the experiments described here was to investigate a method to obtain information on the morphology (shape) of ultrafine diesel particles. These experiments were performed in collaboration with Synergetic Technologies, Inc. (One University Place, Suite D210, Rensselaer, NY 12144, www.synergetic-tech.com), which is developing a unique light scattering technology for measuring the morphological properties of particles (described below). These properties include the shape of aggregate particles as well as their “fractal dimension”, i.e., how loosely or how tightly individual primary particles are packed together to form the aggregate.

Current methods for particle size measurement do not take into account the impact of particle morphology, nor do they take into account the potential difference in morphology of particles from different sources. The two primary technologies for ultrafine particle measurement – Scanning Mobility Particle Sizer (SMPS) and Electrical Low Pressure Impactor (ELPI) – both assume that all particles are spherical in nature. If this assumption is flawed, then there could be fundamental errors in our interpretation of particle sizing data, especially in the use of other metrics derived from particle sizing data such as surface area.

Currently, the only means of obtaining information about the morphology of particles is by means of electron or scanning force microscopy. Initial investigations using such instruments strongly suggests that diesel particulates are composed of spherical monomers that agglomerate and the morphology of these agglomerates are irregularly shaped. However, these methods are slow, expensive and labor intensive. Further, they can only examine particles that have been deposited on a substrate rather than in their native aerosol state, and are also sensitive to the method of sample collection.

The potential advantage of the developing Synergetics’ technology is to provide relatively fast (compared to current methods) information on particle morphology in the native aerosol state, concurrently with particle sizing measurements. Such information could have a significant impact on our fundamental understanding of particle sizing results, especially for metrics such as particle surface area, which is central to evaluating the potential health effects of diesel particulates.
II. Experimental

Prior experimentation in collaboration with Synergetic Technologies was conducted in November-December of 2002, and in February and April of 2004 using earlier versions of the sample cell and experimental apparatus. Experience gained during this earlier testing led to the apparatus used for the experiments discussed here.

The source of diesel exhaust was a diesel generator located at DEC’s Automotive Emissions Lab facility (Sentry-Pro 7.5 kW generator powered by a Kubota model Z482-E, 479 cc, 12.5 horsepower diesel engine), with resistive heating coils used to apply varying loads. Samples were taken from the diesel exhaust using a 1 lpm sample pump and fed into a minidiluter as shown in Figure 1. The sample was then diluted by the addition of filtered and conditioned air metered by a mass flow controller. Individual samples were drawn from the minidiluter for the particle sizing and light scattering instruments.

![Figure 1 – Sampling from the diesel generator exhaust. The sample is drawn from the sampling ports in the generator exhaust line by means of a small pump and fed into the minidiluter. Multiple samples are then drawn from the minidiluter for measurement by individual instruments. The main diesel exhaust line curves underneath the minidiluter to the CVS so that it can be exhausted safely from the building.](image)

Samples from the minidiluter were then introduced to the light scattering instrument (Figure 2). The light scattering instrument under development by Synergetic Technologies employs the measurement of multiple light scattered signals using elliptically polarized light. A He-Ne laser operating at 632 nm is used as the light source, which can be singly or multiply polarized. The sample beam passes through the measurement volume (~1 cc) and the scattered light is directed towards a photomultiplier tube which is movable so that data can be collected at multiple angles. By analysis of the scattering matrix, both the shape and fractal dimension ($D_f$) of agglomerate particles, i.e., how tightly primary particles are packed together in the agglomerate, can be determined (Figure 3). Agglomerate size distribution is also possible, in terms of either the number of
monomers contained in the agglomerates (it is also possible to compute the effective spherical diameter from the agglomerate volume) or assuming the particles/agglomerates are spherical.

Figure 2 - The light scattering instrument elevated to allow the sample cell to be inserted. Details of the cell are discussed below and in Figure 4.

Figure 3 – Various structures of fractal agglomerate and their corresponding fractal dimension ($D_f$) determined from the light scattering matrix

A key issue in this work has been determining how to introduce an aerosol sample into the light scattering instrument, which was originally designed for measuring the properties of colloids in liquid solution. This work has centered on the development of an appropriate sample cell for particles in a gas stream. One of the previous versions of the sample cell is shown in Figure 4.
Figure 4 – A prior version of the light scattering sample cell. The sample gas stream containing the diesel particles flows upward into the measurement region through the center tube. This sample flow is surrounded by an annular sheath flow that passes through the outer tube. This sheath flow contains the sample flow within the measurement region. The path of the laser beam through the measurement region is shown by the red arrow. The duct above the sample cell draws the particulates out of the instrument and safely exhausts them. In the current version of the sample cell, the inner sample flow diameter has been decreased to ~1/4”, with a corresponding increase in the thickness of the outer sheath flow. A mounting adapter was also designed and fabricated by AEL staff to keep the sample cell anchored securely in the correct position within the light scattering instrument.

For comparison to the light scattering results, several particle sizing instruments also drew samples directly from the minidiluter:

**Scanning Mobility Particle Sizer (SMPS):** primary instrument for determining the particle size distribution in this size range. Since the diesel generator is operating at (nominally) steady state, the SMPS can be used in scan mode to measure the particle size distribution from 24 to 980 nm over a period of 5 minutes.

**Electrical Aerosol Detector (EAD):** measures total aerosol length (mm/cc), which can be thought of as the product of the mean of the particle size distribution times the mean concentration.

**Condensation Particle Counter (CPC) 3007:** The CPC 3007 is a portable version of a CPC which uses isopropanol rather than butanol as a working fluid.

**Engine Exhaust Particle Spectrometer (EEPS):** measures particle size from 5.6 to 560 nm on a second-by-second basis. The EEPS is a newly commercialized instrument which is a hybrid of the SMPS and the ELPI.

There were four subsidiary goals of this research. The first was to gain experimental experience running the EEPS, which is a new instrument to our group. The second was the evaluation of the CPC3007 as a fixed, rather than a portable instrument. There were
no obvious problems with the CPC3007 in this application, and it performed well under
direct software control (rather than by datalogging in portable mode). The third was the
evaluation of the “Mobile Lab” desktop computer modified by Aaron Pulaski, which
allows us to run multiple particle sizing instruments with a single desktop computer
rather than requiring multiple independent laptops. The Mobile Lab computer also
performed well, and we did not encounter any problems with program conflicts,
processor speed, etc. The fourth was the intercomparison of results from the various
instruments, i.e., particle size means computed from EEPS vs. SMPS vs. combined EAD
and CPC3007 data. Unfortunately, the particle concentrations were so high from this
source that they were outside the common valid range for the different instruments. We
expect a better basis for intercomparison at the low concentrations measured during our
recent diesel-electric hybrid transit bus testing.

Three variables were manipulated in this series of experiments:
  1) polarization of the light scattering measurements (six (full), two or single
     polarization measurements)
  2) applied load to the diesel generator (0, 25, 50, 75 or 100% of applied load)
  3) dilution factor in the minidiluter (10, 20, 30, 50, 60, 80, 100 to 1)
In general, these variables were manipulated in order to attempt to optimize conditions
for measurement by the light scattering instrument and gas sample cell. The intent was to
determine conditions under which the light scattering instrument could obtain a strong
signal, as well as detect fractal agglomerates.
III. Results and Discussion

(1) Full Polarization Measurements (April 22-23, May 6-7, June 25)

Light Scattering (Figure 5): A series of experiments were performed at full polarization, requiring a measurement time of 30 minutes/measurement. Although the signal appeared strong, the amount of stray light from the beam appeared to skew computation of the scattering matrix. Results for all three sets of measurements showed no fractal-like agglomerates. The size distributions shown were computed assuming spherical particles, and yielded a primary particle size of ~75 nm.

![Figure 5](image1.png)

**Figure 5** – Sample light scattering results from May testing at 100% applied load. No fractal agglomerates were observed; primary particle size is ~75 nm.

![Figure 6](image2.png)

**Figure 6** – Particle size distribution from May testing at 100% applied load. Mean particle size for all dilutions is ~64 nm. Note inconsistent behavior at 10:1 dilution.
Particle Sizing (Figure 6): SMPS results yielded a primary particle size of 64 nm, comparable to that observed by light scattering. Particle concentrations were comparable at all dilutions with the exception of 10:1 dilution. Throughout these investigations, behavior at 10:1 dilution was found to be inconsistent with that at other dilutions, suggesting that 10:1 dilution in the mindiluter may be insufficient to “freeze” then particle distribution by inhibiting the formation of secondary particle formation at these high concentrations.

For some conditions there was a change in the diesel generator exhaust characteristics over time. This was mostly clearly seen in the EAD data shown below, and is supported by data from successive samples taken with the SMPS. It appears to be correlated primarily to the load, rather than to procedural factors such as warmup time. These changes may have had an effect on the light scattering data since they are shorter than the time scale for gathering a data point with the light scattering instrument. However, based on the SMPS results they did not affect our measurement of the mean at all, and affected average concentration values only slightly. Steps were taken during later experimentation to compensate for these effects.

Data at loads of 25, 50 and 75% of full applied load were generally stable with respect to time. At 0% load there was an increase in concentration with time as shown below in Fig 7. Comparison with SMPS data (not shown) reveals that the trend in total aerosol length is due to changes in concentration rather than mean particle size. This effect was independent of the date or step in experimental sequence (i.e., it’s not related to warmup time of the generator).

Figure 7: Total aerosol length vs elapsed time for 0% applied load, 80:1, 4-23-04 only.
At 100% load there was a decrease in concentration with time as shown below in Figure 8. Again, comparison with SMPS data (not shown) reveals that the trend in total aerosol length is due to changes in concentration rather than mean particle size, and this effect was independent of date or when it occurred in the experimental sequence.

![Figure 8: Total aerosol length vs elapsed time for applied 100% load, 10:1, 4-16-04 only. The decrease at the end is due to data points taken past the end of the run.](image)

(2) Two Polarization Measurements (May 14)

Using only two polarizations cuts the measurement time by two-thirds. Unfortunately, the resulting signal value is very low, making the light scattering results indeterminate.

(3) Single Polarization Measurements (April 29, June 24).

Light scattering (Figure 9): Single polarization measurements are very attractive since they require a minimal amount of optics and are very fast (~4 minutes). These measurements appear to have very strong signals in the forward scattering angles, but much weaker signals in the side and back scattering angles. Work was done to attempt to optimize the signal and reduce the number of scattering angles used. As expected, the strongest signals also resulted from 100% applied load. Results from the June testing show fractal behavior. The size distribution was computed assuming fractal structures and is expressed in terms of equivalent spherical diameter.
Figure 9 – Sample light scattering results from June testing at 100% applied load, showing fractal-like agglomerates.

Particle Sizing: SMPS data for the June results yielded a mean particle size of 66 nm as shown in Figure 10. As in the case of full polarization measurements, particle concentrations were comparable at all dilutions with the exception of 10:1. TEM analysis of samples taken during these tests (Figure 11) shows a fractal agglomerate structure with primary particles of ~ 50 nm, consistent with the combined results of the light scattering instrument and the SMPS.

Figure 10 – Particle size distribution from June testing at 100% applied load. Mean particle size for all dilutions is ~ 66 nm. Note inconsistent behavior at 10:1 dilution.
Figure 11 – TEM of sample from June testing, showing fractal agglomerates and primary particle size of ~50 nm.
IV. Conclusions/Future Work

Based on the above results, it appears that single polarization light scattering measurements may be sufficient to obtain morphological data on diesel particulates, and indicates the presence of fractal agglomerates. The fractal nature of the agglomerates was confirmed by TEM, which also yielded a primary particle size similar to that determined by SMPS and light scattering.

However, the gas sampling apparatus is still not sufficiently optimized to produce a reliably strong light scattering signal. This appears to be due to stray light within the instrument produced as a result of particles escaping from the confinement of the sheath flow. In addition, the diesel generator is producing a high concentration exhaust with properties that may not be consistent.

Future work will address both these issues. First, the gas sampling cell is being redesigned with the aim of preventing particles from escaping from the measurement volume. Second, we are investigating use of the CAST combustion aerosol generator for the next set of experiments, which should give us a more controlled and consistent source of diesel particles.

V. Acknowledgments

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