

Measurement of In-use PM using Soot Augmented with a Gravimetric Reference

William M. Silvis
 AVL North America Inc.

ABSTRACT

Diesel PM is understood to comprise elemental carbonaceous particles, an organic fraction of soluble or volatile hydrocarbons and sometimes a sulfate fraction. The need to measure such diesel PM at very low levels and to measure it outside of the usual engine test laboratory makes it helpful to sharpen our understanding of this detail composition and how it comes about. Real time instruments for measuring soot and particle number concentrations make it possible to discern emissions levels much lower than filter based laboratory measurements, but an understanding of the relationships between these measurements and the historical reference methods makes them more useful for development and certification of engines. Efforts to use soot measurements in-use in order to meet NTE requirements have shown good correlation to the laboratory reference and have also provided some new information on the shortcomings of the reference methods. This paper will report on measurements made with a photo-acoustic soot instrument augmented by a filter gravimetric method, including results from tests with the laboratory reference method and those made in-use on vehicles. It references related work done decades ago, updating and refining what was learned then with observations made with today's more modern instrumentation, data collection and data processing.

CITATION: Silvis, W., "Measurement of In-use PM using Soot Augmented with a Gravimetric Reference," *SAE Int. J. Engines* 5(3):2012, doi:10.4271/2012-01-1254.

INTRODUCTION

Emissions regulations define the reference measurement of particulate matter (PM) as the increase of a collection filter's mass when it samples diluted exhaust over a test cycle. There is a need to make a similar measurement outside of the laboratory setting, in-use, while the vehicle is being driven normally. However, the diesel particulate aerosol is not just one thing, but a composite. Its major components are soot, or elemental carbonaceous material, SOF, the soluble or organic fraction, and the sulfate fraction. In addition to these, there may be small traces of metal and ash that come from engine wear and oil additives.

$$PM = \text{soot} + \text{SOF} + (\text{sulfate \& water}) \quad (1)$$

Each of these components has different physical properties, so that devising modern instrumentation that responds exactly as does the CVS gravimetric reference method is problematic. One indicator of this is the widely differing mass densities of each, listed below [1].

- Carbonaceous Fraction (soot) - 2-2.5 g/cm³
- Organic Fraction (SOF) - 0.85-0.88 g/cm³

- Sulfate Fraction (SUL) - (hydrated at 7) 1.5 g/cm³

The carbonaceous fraction is the most dense, the soluble fraction is relatively light, and the mass incorporated in the sulfate fraction is highly variable, since the sulfate attracts water in an amount that is equilibrium with the local relative humidity and may comprise, in addition to sulfuric acid, varying amount of sulfate salts.

These collective properties confound attempts to infer lab reference PM mass by using instruments that count particles, respond to one of their geometric properties, or measure size distributions. The measurement technique described here begins with a selective measurement of just one of the components, usually the dominant one, which is then augmented by a filter reference and a time weighting function to apportion out when the non-soot components were emitted. The result is an estimate of total PM mass over relatively short NTE zone measurement intervals as well as estimates of the speciation of this mass among the three components.

Below we give information on the soot measurement technique itself and on its application to in-use measurements. To provide context for comparisons to the reference method, there is a discussion of the nature and the formation physics of the SOF portion and how a filter

reference can be used to characterize it. We also discuss some measurement issues that arise in practice because DPF equipped engines are so clean that a day of sampling still may collect very little mass on a measurement filter. Finally, we suggest a method to characterize the sulfate dominated emissions during DPF regenerations.

DISCUSSION

The aerosol that is captured by measurement filters after a dilution and cooling process is unlike the blend of precursor particles and gases that are emitted directly from an engine. As depicted in Figure 1 below, during the sampling process, relatively small primary combustion soot particles agglomerate into larger, filament-like structures, organic gasses adsorb to the soot nuclei or if present in high concentration may nucleate into droplets, and any sulfate gas present may undergo a binary homogenous nucleation with water vapor to form sulfate nanoparticles. Therefore a good understanding of what one has measured in any given situation requires a consideration of the different behaviors of these different components.

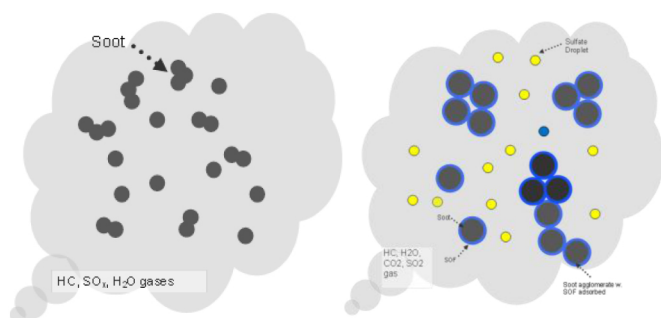


Figure 1. Schematic diagram of particulate elements before and after sampling

THE SOOT PART

The soot component of PM is the one component that is actually created in the engine during the combustion process. It's composed for the most part of elemental "black" carbon from pyrolyzed fuel in the fuel rich portions of the combustion flame. Its blackness means that it absorbs all wavelengths of light, so one can be chosen to avoid interferences with other absorbers and a laser can be used to deliver a powerful enough excitation. The amount of light absorbed is in proportion to the mass present, so it can measure the mass of soot in a manner analogous to how an NDIR analyzer responds to the mass of CO₂.

The light absorption sensing principle of the Micro Soot Sensor MSS 483 used here is based on photo-acoustics, first demonstrated by A.G. Bell in 1889. It is extensively described in its manual and in an SAE publication [2]. An outline of its principle of operation is listed here.

- A chopped laser beam (4000 Hz, 50/50 duty cycle) irradiates the particles in the measuring volume.

- When the soot particles absorb the radiation, the freely movable π electrons are excited - which is equivalent to an increase of the internal particle temperature.
- When the laser beam is "off", the elevated internal temperature is equilibrated by heat transfer to the surrounding gas (and from there to the walls of the measuring cell).
- Periodic heating and cooling of a gas causes a periodic pressure wave - in other words, a sound wave.
- The amplitude of the sound wave is enhanced by using a resonant acoustic cell, whereby a standing acoustic wave is produced.
- The acoustic wave is detected with sensitive microphones, placed in the anti-node of the standing wave.
- The signal is processed with digital electronic "lock-in" technology to discriminate the soot generated sound from ambient acoustic noise.

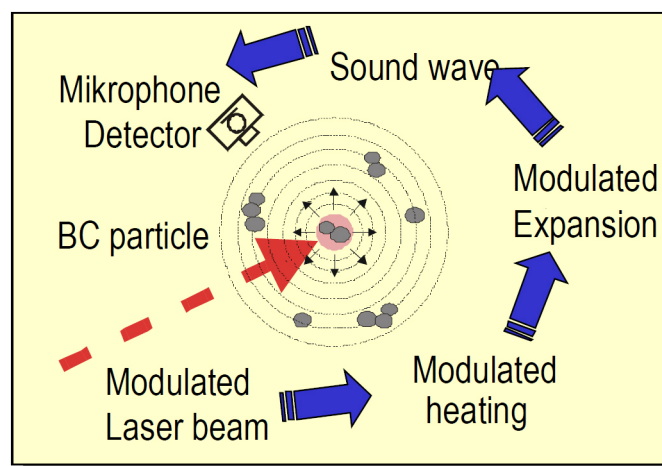


Figure 2. Schematic diagram of photo-acoustic measurement principal

This MSS photo-acoustic soot sensor was first formally used to measure in-use soot in the CARB Pre-pilot program [3]. This program used a vehicle without engine after treatment. The correlations to CVS were slope 0.68 and R² 0.95 reflecting a capture of the PM soot portion with very good repeatability. The MSS was also evaluated in the European PM PEMS program giving differences in the order of 15-20%, which after chemical analysis of the PM filters were found to be SOF and sulfates [4]. A more extensive program was conducted by the EMA and EPA CARB as part of a comprehensive effort to establish a measurement uncertainty allowance for in-use measurements, and data from the validation portion of this program [5] is presented below and referred to as the HDIUT MA study. These measurements were made using a model year 2007 truck equipped with a DPF that was partially bypassed so that enough PM would be emitted to properly assess the

repeatability of measurements near the certification limits of 0.030 mg/hphr. Reference measurements were made by the CeCert MEL, Mobile Emissions Laboratory which was equipped with a full-flow CVS and gravimetric particle measurement system. In-use NTE events were simulated manually and triggered when vehicle operation was in NTE-like conditions for long enough to collect sufficient mass on the CVS filters. The agreement between the soot measurements made with the MSS 483 and the CVS is shown on the chart below.

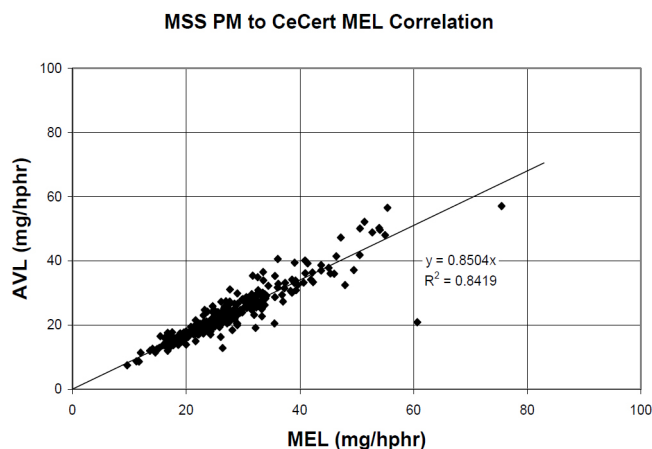


Figure 3. Correlation of soot measurements with MEL CVS PM measurements during HDIUT MA study

The soot measurement shows a very nice correlation and a slope of 0.85, indicating that in addition to soot the CVS PM was composed of about 15% of semi-volatile mass. To address this semi-volatile component, the MSS 483 was equipped with its own on-board measurement filter, however unlike the CVS, configured to collect PM over the whole measurement day. The PM to soot relationship from this filter is then used to adjust the soot measurements and account for the semi-volatile component.

THE SOF PART

The SOF or soluble organic fraction portion of what is measured using the filter-based gravimetric reference method in the laboratory is perhaps the most complicated component of PM that we might wish to characterize. It is not formed in the engine, but rather formed in the process of sampling, so what is measured is affected by sampling system design and parameter settings.

When sampled, the hot vapors of unburned hydrocarbons from the fuel and lubricating oil in the exhaust adsorb onto the surfaces that they come into contact with as they are cooled and diluted. When these gasses adsorb to the walls of the sampling system, they form the HC hang-up that sometimes confounds FID measurements. They may collect to the surfaces of the measurement filter media, adding mass to the filters without entering a particle phase [6]. They adsorb as well to the surfaces of soot particles, where they become a part of PM. And if present at quite high

concentrations, they may nucleate into droplets of liquid hydrocarbon and become volatile particles.

The approach to stabilizing and improving the variability of this component as measured in the laboratory has been to recognize that it is a substance with an operational rather than scientific definition, and to standardize the design and parameter settings for the sampling systems used to measure it [7]. These sampling systems create and collect the aerosol over long time intervals and obscure the dynamic formation processes that may have taken place at different times in a test interval. They are not well-suited to assess what the diesel aerosol is like over short intervals like NTE events. In order to give background into how an in-use measurement might take some fair account of this component and how it may change as the organic precursor gasses in the engine aerosol vary, we briefly discuss its dominant formation process.

Adsorption

A number of researchers (Clerc [8], Plee [9], Reichel [10], etc.) had recognized some time ago that the primary mechanism for the formation of the SOF portion of gravimetrically measured PM mass was the adsorption of the vapors to soot particles rather than the formation of liquid droplets. Liquid droplet nucleation implied lower temperatures and higher concentrations than those expected from the hydrocarbon species and dilution ratios normally observed in diesel exhaust. We give an overview of the physics of the adsorption process as it applies to SOF formation below.

If a solid surface is exposed to a gas at low pressure, the pressure is decreased noticeably. The gas adsorbs onto the surface. We can think of the adsorption as a chemical reaction. A molecule in the gas “reacts” (not necessarily chemically) with the surface to become a molecule on the surface. Furthermore, a molecule may adsorb to the surface or to another gas molecule already on the surface, as illustrated in Figure 4 below.

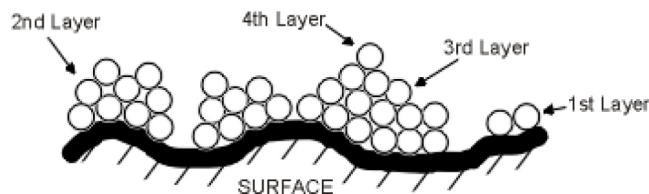


Figure 4. Schematic diagram of multi-layer surface adsorption

At any moment in time, particles are losing some energy by collisions and adsorbing to the surface at the same time that other particles on the surface gain some energy and leave it. An equilibrium that depends on temperature establishes itself between arriving and leaving molecules.

In surface physics, an adsorption isotherm is used to describe how much of a gas is adsorbed to a surface at a given temperature as a function of its partial pressure. The

well-known BET isotherm, (from Brunauer, Emmet, Teller [11]), describes very well the adsorption of a variety of adsorbents and adsorbates and is given by the equation below, as a function of the saturation ratio of the gas.

It has two parameters, the temperature dependent shape parameter C , which is the ratio of the heat of adsorption of the gas onto the solid to its heat of vaporization, and the absorption capacity parameter V_m , which is the adsorbent mass-specific volume of an adsorbed monolayer.

$$\frac{V(x, T)}{V_m} = \frac{C(T) \cdot x}{(1 - x) \cdot [1 + (C(T) - 1) \cdot x]} \quad (2)$$

In simplest terms, the shape parameter, C , is determined by the nature of the adsorbing gas, and the adsorption capacity parameter, V_m , is determined by the nature of the surface. When we apply this to PM sampling, we identify x with the ratio of the HC partial pressure, as reduced by the dilution ratio, to the saturation pressure and $V \cdot lb_{\rho_{SOF}}$ with the SOF to Soot mass ratio.

$$\frac{SOF}{SOL} = V_m \cdot \rho \cdot \frac{V(x, T)}{V_m} \quad (3)$$

As an example, we use the parameters identified by Clerc [8] as a best fit to his data. This model predicts the relationship shown in Figure 5 for the ratio of SOF/SOL and the ppm_{C1} concentration of the chosen prototype adsorbing hydrocarbon, heptadecane.

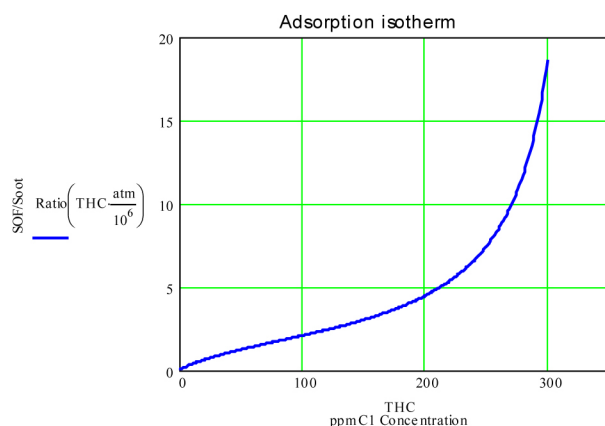


Figure 5. SOF to soot ratio vs. FID ppm for $C_{17}H_{34}$

Thus the SOF to soot ratio increases with HC concentration. The adsorption at lower concentrations is somewhat linear with concentration while surface coverage is sparse and it rapidly increases as the concentration approaches the saturation concentration and multilayer adsorption begins. The steep rise as the saturation concentration is approached corresponds to droplet formation.

Scavenging

The HC concentrations above represent the equilibrium condition between the adsorbed and gaseous phases of the volatile HC's. A heated FID measures these HC's before the adsorption takes place and thus measures both the adsorbed and gaseous phases. The amount by which the gas phase concentration, and thus the equilibrium position on the adsorption isotherm, is reduced depends on the mass concentration of the adsorbing soot. That is, higher soot concentrations will scavenge more of the gas phase HC's and shift the equilibrium to a lower level. Since the heated total HC (THC) is what we are able to observe with emissions measurement, it's useful to gauge the magnitude of this effect. A calculation of this for the isotherm above is shown in Figure 6 below, where the x-axis is now the heated THC reading rather than the equilibrium THC reading.

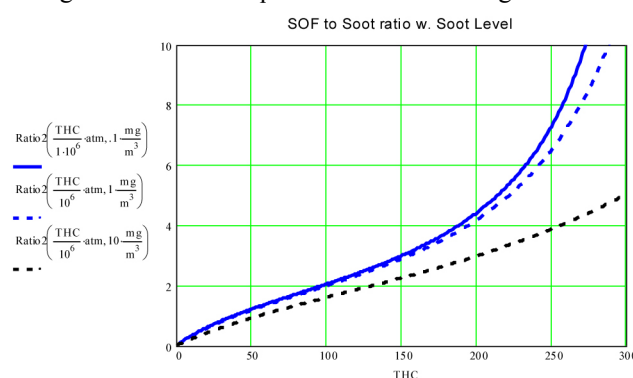


Figure 6. Effective SOF to soot ratios vs. heated FID ppm for different soot concentrations

One notes that a post-DPF soot concentration of 0.1 mg/m³ changes the isotherm very little, while a higher level of 10 mg/m³ more typical of pre-controlled engines shows a stronger effect, and a more linear relationship of adsorbed SOF to total HC concentration. At this soot level, the HC concentration is reduced by about 50 ppm or 25% as that amount of HC's are adsorbed.

Each of the various HC's in the "primordial soup" of SOF pre-cursor HC's are likely to follow a similar adsorption isotherm, with the x-axis appropriately scaled to its saturation concentration. The less volatile ones may be present at lower concentrations, but proportionately closer to their saturation concentrations. Therefore they would be more to the right on their absorption diagrams. The lighter fractions may be toward the left since their concentrations, even at higher absolute levels, are farther below their saturation levels. From the considerations above, the formation of the SOF component we observe with filter measurements is a composite of the behavior of a multitude HC's in proportion to their amounts present in the exhaust. Furthermore, when the emissions are captured in transient conditions, the vapors may not yet be in equilibrium with adsorption sites, and vapors collected later in a transient measurement interval may interact with soot already collected on a filter as well as with

the suspended aerosol. Thus the measurement of a volatile contribution to PM on a second by second basis, or over a brief measurement interval such as an NTE event, in such a way as to correspond scientifically with what might be characterized by the reference CVS method cannot be done with precision.

Nevertheless, a practical technique to estimate this contribution well enough to avoid underestimating a high SOF mode and to assure compliance to NTE emissions regulations can be devised. By collecting a filter sample over a long enough measurement interval, observing the integrated SOF and soot relationship of this measurement, and determining a factor that can be used to scale-up the integrated soot measurements observed during NTE events to account for volatiles, good correlations to the reference methods are achieved. This can also be done in a way that is sensitive to episodes when HC concentrations are higher and correspondingly higher SOF contributions might be expected.

THE GRAVIMETRIC FILTER REFERENCE

The concept of the parallel collection of a gravimetric sample is depicted in Figure 7. Two measurement filters are collected during the sample day in parallel with continuous measurements recorded from the Soot concentration analyzer. The use of the backup filter will be described in more detail below. The filter sample is collected using a metered flow rate sufficient to collect a measureable mass over an 8 hour interval for a hypothetical vehicle emitting at a level that just complies with the standard. The photo-acoustic soot sensor measures the same aerosol in real-time and when multiplied by the filter flow rate is used to determine the amount of soot collected by the on-board filter, and when multiplied by the exhaust flow rate and the dilution ratio, is used to determine the amount emitted from the engine.

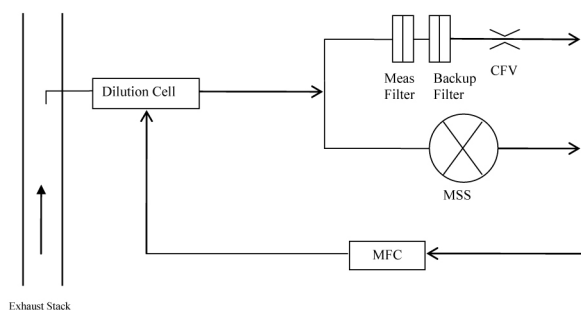


Figure 7. Schematic diagram of instrument with on-board filter reference

The mass of the volatile fraction that is adsorbed to soot particles can be estimated by determining the factor by which the volatile fraction and solid fraction on the on-board filter are related. The scaling factor may be different for different fuels and different aftertreatment systems.

From the ratio of the PM observed on the on-board filter to the amount of soot that passed to the filter as measured by the MSS 483, we calculate the PM to soot ratio:

$$fac = \frac{PM_{GFB}}{\int_0^T Soot(t) \cdot q_{GFB}(t) \cdot dt} \quad (4)$$

This ratio is then used for each NTE event to scale up the soot emitted by the engine and account for the SOF portion when calculating the engine PM emissions for the event.

$$PM_{NTE} = fac \cdot \int_0^{t_{NTE}} Soot(t) \cdot q_{ex}(t) \cdot dt \quad (5)$$

As a refinement, if we also have the THC measurements available, we can use this information to apportion a SOF estimate according to the amount of HC present. This results in the following formulation for an adjustment of the soot measurements. The α parameter is determined from the on-board filter in a manner analogous to equation (4) above. The extra details of this approach are described in the appendix.

$$PM_{NTE} = \int_0^{t_{NTE}} Soot(t) \cdot (1 + \alpha \cdot THC_{filter}(t)) \cdot q_{ex}(t) \cdot dt \quad (6)$$

IN-USE MEASUREMENT RESULTS

When the approach using THC measurements was used during the validation phase of the HDIUT measurement allowance program [5] described above, we obtained the result presented in Figure 8.

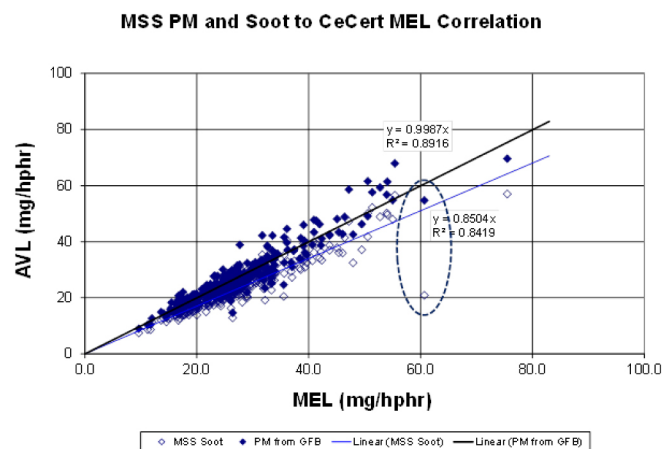


Figure 8. Correlation of Soot and PM adjusted Soot to MEL CVS

The open symbols on this figure represent the soot measurements and the solid ones the PM adjustments. There