

Motor Vehicle PM Emissions Measurement at LEV III Levels

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ABSTRACT

This paper examines the issues concerning particulate matter (PM) emissions measurement at the 3 mg/mi level proposed as the future LEV III standard. These issues are general in nature, but are exacerbated at the low levels contemplated for upcoming emissions standards. They are discussed in the context of gasoline direct injection (GDI) engines, where they can have an important impact on the continued development of this technology for improved fuel economy. GDI particulate emissions, just as engine out diesel PM, contain a high fraction of soot. But the total PM mass is significantly lower than from diesel engines, and there can be significant variations in emissions rate and apparent PM composition between cold-start and running emissions. PM emissions levels depend on sampling method and location. As a result, there can be substantial differences in PM sampled and diluted directly at the exhaust pipe, as opposed to measurements from a dilution tunnel. Some of these differences can be understood in terms of sampling conditions; others are the result of storage / release artifacts. Use of real time PM instruments and thermodenuders facilitates reconciliation of these effects and is important for guiding engine and aftertreatment development. The potential for particle number counting to alleviate the interference and variability issues associated with gravimetric measurements at very low PM levels is examined. Comparison of simultaneous PM mass and number data reveal a strong correlation, with the same 2×10^{12} particles/mg of particulate matter as reported recently for diesel PM emissions. This correlation holds in the absence of a nucleation mode and is explained in terms of the characteristic size distribution associated with accumulation (soot) mode PM from internal combustion engines. We examine the common perception that the EU PMP solid particle counting standard regulates only solid particles larger than 23nm in diameter and argue

that it also effectively limits emissions of particles in the tail of the accumulation mode below 23 nm, as well as condensed semivolatile PM.

INTRODUCTION

Two factors are drawing increased attention to particulate matter (PM) emissions from gasoline fueled vehicles. The first is the introduction of gasoline direct injection (GDI) engine technology as a means to quickly deliver improved fuel economy and CO₂ emissions benefits, and the second is the current discussion of next generation emissions regulations by the California Air Resources Board (ARB) [1]. Although GDI engines were already introduced more than a decade ago [2,3], the current technology differs considerably from these earlier engines and is undergoing rapid change [4]. The prospect of more stringent PM emissions standards will further stimulate development in both engine and aftertreatment strategies.

The current situation differs from that of nearly a decade ago when the Environmental Protection Agency (EPA) introduced its 2007 standards (10 mg/mi for light duty vehicles and 10 mg/hphr for heavy duty engines) [5]. Diesel engine-out emissions were sufficiently high to require use of diesel particulate filters (DPF) to meet these standards. Artifacts and interferences were found to be present at the levels of post-DPF PM measurements [6]. But this did not pose a serious problem for development and certification, because the very high efficiency of DPFs overachieves the standards by a sufficiently large margin to make allowance for measurement uncertainties and biases.

PM is a physically and chemically heterogeneous substance. In the past it has been measured gravimetrically in motor vehicle exhaust with relative success based on collection onto filter media through a constant volume sampling (CVS) -

dilution tunnel system [7]. But such a one dimensional measure of a complex substance is inherently problematic. And this is exacerbated at low PM levels. Investigations of the EPA 2007 method uncovered variability issues dependent on dilution ratio, residence time, and filter face velocity, which arise from differences in gas - particle partitioning during sampling [8]. In addition, biases arise from filter composition dependent gaseous adsorption artifacts, which at low emissions levels can be comparable to the PM collected [6,8].

The past 15 years has seen considerable progress in particulate matter sampling and measurement methodology. Aerosol instrumentation, such as the electrical low pressure impactor [9], electrical mobility spectrometers [10,11], and the photoacoustic soot sensor [12] provide the ability to make time resolved PM measurements. Equally important, sampling approaches, such as ejector pumps and the rotating disk diluter, permit sampling exhaust directly at the tailpipe, avoiding the need to transfer it to a dilution tunnel. Use of a porous tube diluter, or an in-situ diluter, give the ability to sample at ambient temperature and, thus, to an extent mimic new particle nucleation that can occur in the ambient when engine exhaust exits the tailpipe [13,14]. Both approaches utilize immediate dilution without the need to transfer the exhaust gases and have been shown to compare well with real-world atmospheric dilution occurring in the vehicle exhaust wake. The volatility of these particles can be examined via a thermodenuder [15].

The aim of the present paper is to utilize these techniques to elucidate concerns about the continued ability of the conventional dilution tunnel - gravimetric filter method to serve the needs of engine and aftertreatment development and vehicle certification. The emphasis is not to identify some alternative method, but rather to understand the interferences and confounding factors that arise when attempting very low PM emissions measurements. We explore which aspects of PM are affected most by these effects and compare their impacts on total PM mass versus solid particle number metrics.

EXPERIMENTAL METHODS

VEHICLES, FUELS, AND DRIVE CYCLES

PM measurements are reported from a variety of gasoline direct injection development vehicles. The majority employs a 3.5 L V6 engine; some test vehicles have 2.0 or 1.6 L engines. The emissions from these vehicles are generally within the range of production GDI vehicles, for example, as reported by Zhang et al [16]. But they were tested at various levels of development to provide a range of PM emissions, and so the results reported here should not be considered as representative of emissions from the final production

vehicles. The vehicles were primarily run with certification test gasoline; however, some tests employed an E10 ethanol blend. This distinction is not important for the purposes of this paper, because the aim here is to ascertain by comparative PM measurements the issues associated with very low level PM measurements, and not to compare engine or fuel effects on PM emissions.

The vehicles were run on a 48-in. single roll, ac electric dynamometer. The emissions tests utilized a variety of vehicle operating conditions. These included the Federal Test Procedure (FTP) and US06 drive cycles as well as various steady state and custom cycles.

EXHAUST PM SAMPLING

CVS Tunnel

Three exhaust sampling methods were employed: a) CVS dilution tunnel, b) ejector diluter, and c) porous tube diluter (Fine Particle Sampler (FPS), Dekati). The dilution tunnel is made from 30.4 cm diameter stainless steel tubing. Dilution air is heated to 38 °C to reduce humidity to a -9 °C dewpoint and filtered to remove 90+% of the particles. The total flow in the tunnel was set to between 8 and 30 m³/min depending on test vehicle, with most tests done at 20 m³/min. Subsonic venturis at the entrance and exit of the dilution tunnel measure the dilution air and total flow rates. Vehicle exhaust is carried to the dilution tunnel through a 5.8 m long, 9.1 cm diameter, heated / insulated (T>113 °C) corrugated stainless steel transfer hose. Vehicle exhaust flow depends on engine operating condition, but typically ranges from 0.1 m³/min at idle to ~3 m³/min during high load operation. This translates to transfer hose residence times in the range of 1 to > 10 s. The exhaust enters axially into the dilution tunnel flow just upstream of an orifice plate that helps promote mixing. Samples for gravimetric filter analysis and aerosol instrument measurements are drawn at least 10 tunnel diameters downstream to ensure complete mixing.

Direct from Tailpipe

The ejector diluter is an in-house designed system capable of sampling PM from high temperature / pressure sources (200 °C and 4 bar) [17]. It is based on two in-series Dekati ejector pumps, the dilution of which is calibrated as a function of temperature and pressure. Nitrogen is used as the diluent / pumping fluid. The sample enters via a simple impactor constructed from a 1/4" swagelock "tee" to remove large particles that might clog the ejector entrance orifice. The first stage diluter and diluent were generally heated to 190 °C to prevent condensation and to reduce thermophoretic deposition at the orifice, but some tests were conducted at room temperature. Secondary dilution occurs at room temperature. The overall dilution is nominally a factor of 64, but varies depending on exhaust temperature and pressure.

The latter quantities are recorded second-by-second and used to calculate the real-time dilution ratio. Note that this design is similar to the dilution system established by the European Union for solid particle counting, except for the lack of a heated evaporation tube [18]. Thus, while the ejector diluter used here might not achieve complete removal of volatile particles, it would suppress their nucleation relative to dilution tunnel sampling, as well as real-world dilution.

The porous tube fine particle sampler was designed for use in the Particulates Program to investigate nucleation mode formation during laboratory testing of motor vehicles [19]. The FPS provides two stages of dilution. The first stage introduces diluent (nitrogen in this work) radially through the walls of the sample inlet. The radial flow opposes diffusion and thermophoretic deposition and, thereby reduces probe clogging. An ejector pump provides second stage dilution. In this way the FPS allows use of room temperature, or cooler, dilution while sampling directly from vehicle exhaust. Although total dilution factors as high as 200 can be selected, the system operates most stably in the range of 20 - 50. The present work generally used a dilution factor of 30. The diluent temperature was kept at room temperature to allow for nucleation and condensation of semivolatile material approximately as it might occur under ambient conditions.

PM MEASUREMENT

Filter Collection

Particulate matter from the dilution tunnel was collected onto 47 mm quartz and 2 μm Teflo filters. The sample flow is 56.6 L/min, which implies a 94 cm/s filter face velocity. Samples are drawn both directly from the tunnel and via a Horiba HF-47, which holds the filter temperature at $47 \pm 5^\circ\text{C}$. Teflo filters are equilibrated for at least 2 hours prior to initial and post test weighing in a temperature ($23 \pm 0.5^\circ\text{C}$) and humidity ($50 \pm 1\%$) controlled environment, with a low velocity HEPA filtered 4.5 air exchanges per minute. The filters are electrostatically discharged using ^{210}Po strips in a holder designed to allow uniform radiation from the radioactive source [20], weighed with a 0.1 μg resolution Mettler UMT2 microbalance, and corrected for buoyancy.

Quartz filters are pre-cleaned by baking in a furnace at 1000°C . After PM collection they are analyzed for organic carbon (OC) and elemental carbon (EC) content using a Horiba MEXA 1370PM thermal analyzer. This instrument heats a quartz filter to 980°C in two stages over a period of about 4 minutes: first in a nitrogen stream, and then in oxygen. As illustrated by Figure 1, semivolatile organic and sulfur containing gases that evolve under nitrogen flow are subsequently oxidized to CO_2 and SO_2 , respectively, detected by non-dispersive infrared detectors, and attributed to semivolatile organic and sulfate particulate matter. Subsequently, the filters are heated in an oxygen atmosphere,

and the evolved CO_2 is equated to elemental carbon. The semivolatile organic fraction (SOF) mass is corrected for hydrogen content assuming a molar H/C ratio of 1.85, which is in the range of 1.772 to 1.919 reported for a variety of diesel fuels by Fanick and Williamson [21].

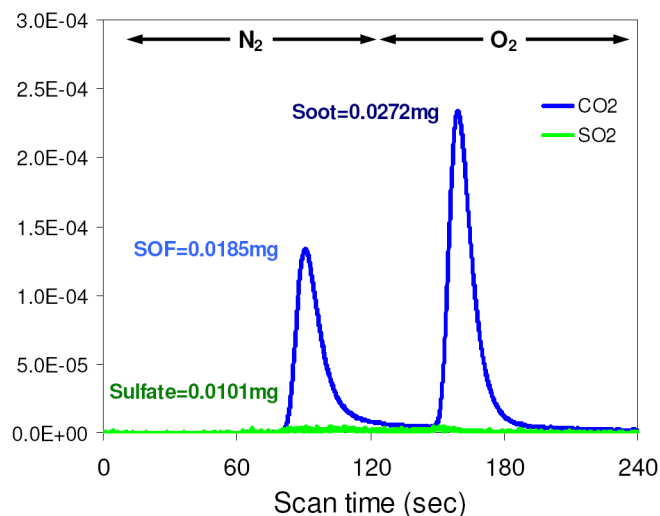


Figure 1. Typical OC/EC scan by MEXA 1370PM thermal analyzer.

Aerosol Instruments

Transient PM mass is measured with a Dekati Mass Monitor (DMM). It consists of a corona discharge, a mobility stage, and a 6 stage cascade impactor. The corona discharge charges the particles in the diluted exhaust. The mobility stage has a 50% cutpoint at $\sim 50\text{ nm}$; thus, it records the fraction of particles with mobility diameters below 50 nm. Based on the assumption of a lognormal distribution, this provides the mean mobility diameter of the sample aerosol. The cascade impactor, with stages ranging from 30 - 1000 nm, then records the aerodynamic diameter of the particles. The combination of mobility and aerodynamic diameters allows estimation of particle density, and knowledge of the corona discharge charging efficiency yields particle number concentration from the measured electrical currents. Particle concentration, size, and density are then combined to determine PM mass in the diluted sample. Comparisons of the DMM against gravimetric PM measurements at exhaust levels above $\sim 10\text{ mg/mi}$ reveal that the mass is generally within $\sim 15\%$. Calibration of the DMM using laboratory generated $\sim 100\text{ nm}$ oil droplets also gave agreement with gravimetric filter and scanning mobility particle sizer data of $\sim 10\%$. These results are consistent with, but somewhat better, than previously reported for diesel emissions measurements [22].

Total particle counts are recorded using a TSI 3010 condensation particle counter (CPC). It is operated at the standard 17°C temperature difference between saturator and

condenser. Thus, the lower size 50% detection efficiency is ~ 11 nm [23]. The CPC counting efficiency was calibrated against an aerosol electrometer using 70 and 100 nm poly α -olefin oil droplets.

Particle size distributions were measured during steady state vehicle operation with a TSI scanning mobility particle sizer (SMPS), and over transient drive cycles with a DMS500 aerosol spectrometer. In the former case, the diluted sample is first brought to a Boltzmann charge equilibrium using a ^{210}Po neutralizer. It then passes through a cylindrical electrical field where the positively charged particles are selected as a function of mobility diameter, by scanning the applied voltage, and then counted by a TSI 3025 CPC. The flows are set using a bubble flow meter. And particle concentrations are corrected for small fractions of multiply charge particles produce by the neutralizer. The DMS500 employs a segmented cylindrical differential mobility analyzer. In this case, the aerosol sample is first charged using a corona discharge, and the resulting transient currents are simultaneously recorded as a function of electrical mobility. Owing to extensive multiple charging these currents must be deconvoluted to yield the underlying time varying size distribution. The DMS500 uses its own dilution system, which is set to 150 °C to avoid water condensation.

PM mass is calculated by the DMM (also for SMPS and DMS500) assuming a fractal-like effective density for the soot particles (as described in more detail below). The DMM estimates particle density based on simultaneous measurement of aerosol mobility and aerodynamic size data and the assumption that density scales with a fractal dimension 2.5 size dependence. An approximate transient PM mass is also measured with a TSI DustTrak (model 8520). Particles are detected by 90° light scattering. This method of detection is not optimal for sub-micron particles, but our experience is that the DustTrak tracks DMM and filter based PM measurements with semi-quantitative accuracy.

A thermodenuder (Dekati) is used in some experiments to assess the volatility of the PM. Particles are heated to 300 °C in the first stage of the thermodenuder to evaporate semi volatile PM components. The heated aerosol then passes through a charcoal denuder that removes organic gases to suppress re-nucleation and condensation. The data are corrected for a $\sim 30\%$ thermophoretic loss of particles passing through the thermodenuder.

RESULTS

FILTER ARTIFACTS

Results from two filter based PM emissions measurement approaches are discussed in this section: gravimetric determinations with Teflo filters and thermal analysis of PM collected onto quartz filters. The former is the certification

method; but, its high variability at very low emissions measurements precludes a careful understanding of artifact effects. The EC/OC data from the latter is more informative, but, as discussed below, quartz exhibits a higher propensity for gaseous adsorption artifacts than Teflon. This phenomenon has been well studied in the case of ambient particulate matter sampling [24,25]. A variety of approaches, such as secondary filters and denuders, have been investigated to correct for this problem [26,27]. In the area of motor vehicle emissions measurements, however, adsorption artifacts are less well understood.

Figure 2 compares the “PM” measured in various blank tests. As panel b) demonstrates, nominally clean filters baked in a furnace to 1000 °C are not devoid of “PM”. Panel a) verifies that this is not measurement variability. Here, the filters are cleaned by running them through the thermal analysis cycle, leaving them in the nitrogen purge of the instrument, and then the analysis cycle is reinitiated. The small amount of sulfate that appears in all panels is statistically zero; the noise in SO_2 measurement is larger than for the CO_2 detector. Thus, exposure of the quartz filters to the atmosphere is sufficient to accumulate ~ 0.4 mg/mi equivalent of PM, which is mostly present as organic material.

Panel c) illustrates the PM registered in tunnel blank tests, where vehicle exhaust is not present. The PM is again dominated by organic material, but the level now approaches 1.5 mg/mi, nearly half of the proposed LEV III standard. To put this in perspective, though, the amount of material collected on the filter is roughly equivalent to a thumbprint, as shown by panel d). At first glance, Figure 2 suggests that soot is also present in the tunnel blank and thumbprint. This most likely arises during the first stage of analysis where heating to desorb the organic material also causes a small amount of hydrocarbon pyrolysis. The phenomenon has received much attention in ambient EC/OC measurements, where correction protocols have been evaluated [28].

