

A New Approach for Very Low Particulate Mass Emissions Measurement

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ABSTRACT

Pending reductions in light duty vehicle PM emissions standards from 10 to 3 mg/mi and below will push the limits of the gravimetric measurement method. At these levels the PM mass collected approaches the mass of non-particle gaseous species that adsorb onto the filter from exhaust and ambient air. This introduces an intrinsic lower limit to filter based measurement that is independent of improvements achieved in weighing metrology. The statistical variability of back-up filter measurements at these levels makes them an ineffective means for correcting the adsorption artifact. The proposed subtraction of a facility based estimate of the artifact will partially alleviate the mass bias from adsorption, but its impact on weighing variability remains a problem that can reach a significant fraction of the upcoming 3 and future 1 mg/mi standards. This paper proposes an improved PM mass method that combines the gravimetric filter approach with real time aerosol measurement. In this work we employ a photoacoustic soot sensor (PASS), which achieves a substantially better detection limit than filter weighing. PM emissions are recorded simultaneously by a Teflon filter and the PASS over the three phase FTP drive cycle. The weighted composite emission rate is determined as follows: Comparison of the net filter weight gain to the time integrated PASS signal serves to calibrate the latter to a gravimetric equivalent PM mass. The adjusted PASS data are then integrated for each test phase and combined with the proper weighting for the FTP average. By utilizing a single filter, this procedure achieves an approximately 3-fold decrease in artifact bias and 2-fold reduction in variability. It provides two additional advantages: a reduction in the time consuming step of filter weighing and time resolved data that can help improve low emissions development.

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INTRODUCTION

In early 2012 the California Air Resources Board adopted LEV III amendments to its Low Emissions Vehicle regulations. These call for a phased-in reduction of the PM emissions standard from 10 to 3 mg/mi over the 2017-2021 model years and then to 1 mg/mi between 2025 and 2028 [1]. PM measurements are to be made using the gravimetric filter method according to the procedures described in the Code of Federal Regulations Part 1065 - Engine testing procedures [2]. The United States Environmental Protection Agency (EPA) is also in the process of revising its emissions standards to Tier III, which will likewise lower the light duty vehicle PM standard to 3 mg/mi. Concurrently it is working

on Part 1066 regulations to update light duty vehicle emissions test procedures.

Under typical exhaust dilution and filter flow rate conditions about 20 µg of PM are collected onto the filter when the emissions rate is 1 mg/mi. This is within the capability of modern weighing metrology, where metal weights can be weighed on a 0.1 µg resolution balance with a repeatability of about 0.5 µg, given sufficient attention to temperature, humidity, airflow, buoyancy, and electrostatic control [2,3]. Static charge can be a problem when weighing the Teflon filters recommended for low PM emissions applications, but proper neutralization can reduce reference filter weighing repeatability to nearly 1 µg [4]. The problem



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is that filters adsorb gases, predominantly organics, present in ambient air. The mass of this adsorption is on the order of 5 μ g, but highly variable.

This gaseous artifact was identified in engine testing when weigh room improvements were underway to address EPA's 2007 lowering of the heavy duty PM standard to 10 mg/hphr [5,6]. Subsequent experience suggests the artifact is ubiquitous; similar 5 $\pm$ 10 μ g weight gains are observed for gasoline tunnel blanks, filtered gasoline and diesel exhaust, and test cell air, but there have been very few detailed studies of this. It is possible that the artifact depends on engine technology and fuel, but this has eluded discernment due to its very low level and high variability.

Recent work by Höglström et al. [7] examined hydrocarbon adsorption using adjustable pentadecane / soot mixtures, but with respect to Teflon coated glass fiber filters (TX40), which exhibit a large artifact [5] and are not recommended for low PM applications. An analogous artifact on quartz filters is known to the ambient aerosol community in the context of elemental / organic carbon measurements (EC/OC) analysis [8,9]. EC/OC analysis of engine exhaust shows that gaseous adsorption onto quartz filters comes from organic species in the exhaust [10]. The adsorption is described in terms of the partitioning of semivolatile species between gas and liquid phases, a process that depends on the species' volatilities, the local temperature, and the local species concentrations [11]. With the feasibility of long sampling times, a correction for adsorption can be made in ambient sampling by placing a backup filter behind the first one. This doesn't work very well when placing quartz filter behind quartz filter, since adsorption by the first filter perturbs the species concentrations too much for an effective correction. This problem is reduced by instead placing a quartz filter behind a Teflon filter, which exhibits less adsorption and hence causes a smaller perturbation. A similar correction is not feasible when it is the Teflon filters that need correcting.

The past decade has seen the development of a number of real time aerosol instruments for recording engine exhaust PM, including the photoacoustic soot sensor (PASS) [12], electrical low pressure impactor (ELPI) [13], electrical aerosol spectrometer [14], and solid particle number counting [15]. These instruments measure particle size, number concentration, and mass concentration with significantly greater sensitivity and lower susceptibility to artifacts than filters provide. To employ the high sensitivity of particle counting, the European Union took the approach of defining a new solid particle method, where semivolatile particles are first evaporated to avoid their propensity for high variability [16]. As it is number based and lacks sensitivity to liquid aerosol components, this technique is unacceptable for monitoring total PM mass.

Ideally one wants an artifact free aerosol instrument that conforms to the regulatory definition of PM mass. A multi-instrument comparison with diesel exhaust by Kinsey et al. [17] found the tapered element oscillating microbalance

(TEOM) to correlate well with gravimetric mass. But being filter based, at low PM levels it suffers adsorption artifacts similar to the gravimetric method. The ELPI and electrical aerosol spectrometer can determine mass via measurement of particle concentration and size, which agrees well with gravimetric values, but requires additional information about particle morphology and composition (density) [18,19]. Based on light absorption, the photoacoustic method provides a relatively direct measure of mass. It compared well to the filter method in recent evaluations of instruments for US and EU in-use heavy duty diesel PM monitoring [20,21]. But it only registers soot and not total PM, so the correlation deteriorated for DPF equipped diesels. This deficiency has recently been overcome in the area of "not to exceed" (NTE) testing of PM emissions by utilizing the PASS and a gravimetric filter in parallel [22]. NTE regulations require in-use testing where there is no drive cycle to clearly demark the start and end of filter collection. Therefore, the filter is used to collect PM over the entire test, and the PASS is used to determine what fraction of these occurred during NTE "events". The present paper proposes an analogous approach to measuring PM emissions over the 3-phase Federal Test Procedure (FTP) drive cycle. The idea is to reduce the impact of gaseous artifact by limiting it to a single filter, and to employ a concurrent second by second PASS measurement to apportion the emissions to the three test phases for calculating the composite emissions rate.

EXPERIMENTAL METHODS

This section describes in detail the methods used in Ford's Vehicle Emissions Research Laboratory to evaluate the single filter plus real time instrument approach to PM mass emissions measurement. The paper also makes use of data obtained from Ford's certification and vehicle emissions laboratory to examine measurement variability. Filter handling in that facility follows CFR Part 1065 requirements. Vehicle testing and PM sampling follow Part 86 protocols. The test methods are essentially the same as described below.

Vehicles and Fuels

The comparison between conventional 3 filter versus single filter plus real time PM measurement is examined for 3 current technology 3.5L gasoline direct injection (GDI) engine equipped light duty vehicles. These are vehicles involved in various research projects. They were selected for emissions rates between 1 and 3 mg/mi, representative for the upcoming and future LEV III standards. All are equipped with 3-way catalyst systems. Vehicles 2 and 3 are actually the same base vehicle, but as vehicle 2 it was equipped with a prototype catalyzed gasoline particulate filter (partially damaged at time of testing), whereas later it was tested with the standard 3-way catalyst. The vehicles were run with E10 certification test fuel (10% ethanol).

Chassis Dynamometer

Test vehicles were run on a 48" single roll AC electric dynamometer over the Federal Test Procedure (FTP) drive cycle. The exhaust is captured into a full flow constant volume sampling (CVS) dilution tunnel. This system maintains a constant flow of exhaust plus diluent, which means that the dilution factor varies as a function of engine speed and load. In our laboratory dilution occurs in a "remote mix tee" connected to the vehicle tailpipe via a 1 meter corrugated stainless steel transfer hose. This is done to reduce storage release artifacts associated with long hoses commonly used to transport hot exhaust from the tailpipe to dilution tunnel [23]. The dilution air is taken from the test cell, filtered (>90% particle removal), temperature controlled (38 °C), and brought to low humidity (−9 °C dewpoint). A 25 cm diameter Teflon tube, with conductive coating to avoid electrostatic losses, transfers the diluted exhaust to a 30 cm diameter electropolished stainless steel dilution tunnel. All particle measurements are from the dilution tunnel. The added length from remote mix tee to dilution tunnel assures thorough mixing of exhaust and dilution air prior to sampling by filters and instruments. The CVS total flow rate was set at 350 CFM (9.9 m³/min) for vehicle 1 and 700 CFM (19.8 m³/min) for vehicles 2 and 3. The increased flow rate was needed to accommodate US06 cycle tests for the latter two vehicles.

Gravimetric PM & EC/OC Analysis

Diluted exhaust is sampled by 47 mm diameter 2 µm expanded PTFE Teflon filters (Pall) for weighing and 47 mm quartz filters for elemental carbon / organic carbon (EC/OC) analysis. Sample flow in both cases is 2 CFM (57 L/min), which equates to 100 cm/s filter face velocity. The Teflon filters were sampled without active temperature control. The average filter temperatures were 35 °C for vehicle 1, 39 °C for vehicle 2 and 38 °C for vehicle 3. Quartz filters are pre-cleaned by heating to 1000 °C in air and loaded into a Horiba HF-47 sampler for PM collection. This sampler includes a 2.5 µm cyclone and maintains Part 1065 required 47 ± 5 °C filter temperature. It was not used for the gravimetric PM measurements because it cannot accommodate the simultaneous sampling required in the present experiments to collect PM both phase by phase and integrated onto a single totalizing filter. As discussed below, comparison between the quartz and Teflon filter measurements shows no discernible effects arising from the lack of temperature control. In principle, temperature affects gas - aerosol partitioning, both "true" semivolatile PM and artifact, but in this limited temperature range it is not discerned from test variability.

Quartz filters are thermally analyzed using a Horiba MEXA 1370PM [24]. The filter is heated to 1000 °C, first in nitrogen to evaporate organic species, and then in air to oxidize soot. The volatilized organics are subsequently oxidized, detected as CO₂, and mass corrected assuming an average H/C ratio of 1.85 for the OC. Teflon filters are weighed on a 0.1 µg ultra-microbalance (Mettler Model

UMT2) in a temperature (23 ± 0.5 °C), humidity (50 ± 1%), and air flow controlled room (4½ HEPA filtered air changes per minute). Filters are neutralized in a specially designed enclosure that evenly exposes their surfaces to Po-210 strips [4]. Pre and post filter weights are each determined from the average of 3 weighings.

Real Time PM

Three real time instruments simultaneously recorded the PM concentrations in the dilution tunnel: a) a photoacoustic soot sensor (PASS) (AVL Micro Soot Sensor), b) a Diffusion Size Classifier (DiSC) (Matter Engineering), and c) a TSI Dust Trak II aerosol monitor. The photoacoustic method records PM by exposing the aerosol sample to a chopped visible light source [12]. This periodically heats optically absorbing particles, which causes pressure waves as the particles cool that are detected by a microphone. In the context of engine exhaust, PASS measures soot plus ash, but is not sensitive to semivolatile hydrocarbons or sulfate. The instrument is factory calibrated to gravimetric PM using a soot generator source. To the extent that diesel and gasoline vehicle soot exhibit different indices of refraction, PASS measures an "equivalent" soot mass. However, comparisons to EC/OC analysis reveal good agreement between EC and PASS for diesel [20] and GDI soot (see Figure 7).

The DiSC operates by charging the aerosol sample with a corona discharge and passing the charged particles sequentially through diffusion screens and a filter; thus, it is sensitive to both solid and semivolatile PM [25]. The total current measures particle concentration in terms of its "active surface". The diffusion screens preferentially trap small particles; thus, the relative currents registered by diffusion screens versus filter provide information about mean particle diameter. The DiSC was laboratory calibrated against size selected soot particles. This revealed that the total charge scales as $d_m^{1.34}$, where d_m is the mobility equivalent particle diameter. It also showed that the DiSC underestimated soot particle size by 37%, possibly because the larger aspect ratio of soot agglomerates allows more efficient trapping by the diffusion screens than for spherical particles. After making this size correction, PM mass is calculated assuming a lognormal size distribution and a fractal-like density for the soot agglomerates plus condensed semivolatiles. Owing to the diffusion screens, the DiSC is very sensitive to nanometer size nucleation mode particles. Such particles were not detected over the FTP drive cycle, but were observed in some instances during US06 cycle testing. To avoid overranging, the DiSC sampled from the CVS tunnel through an ejector pump that provided a factor of 8.5 secondary dilution.

The Dust Trak measures PM, semivolatile and solid, by light scattering. The aerosol sample passes through a laser light sheet and a gold spherical mirror captures the scattered light and focuses it onto a photodetector. The response is calibrated against Arizona Test Dust (ISO 12103-1). Although not specifically designed for engine exhaust

applications, it has shown success in engine PM measurement [26].

RESULTS

Artifact Impact on PM Variability

Gaseous adsorption onto filter surfaces and/or possibly the collected particulate matter is known to interfere with filter based PM measurements in both ambient and source testing [5,8,9]. The extent of this gaseous artifact varies with filter material, with the currently recommended Teflon filters exhibiting the lowest adsorption. Nevertheless, this artifact presents a limitation to very low PM mass measurements as will be required under LEV III and Tier 3 standards. Figure 1 illustrates the weighing variability experienced under four scenarios relevant to test cell PM measurements, but devoid of exhaust particles. These include: 1) weighing metrology, 2) “trip blanks”, which represent the handling associated with pre-weighing the filter, taking it to the test cell, mounting it in the filter sampler, removing it from the sampler, and post-weighing the filter, 3) filter handling plus sampling dilution air from the CVS tunnel, and 4) a real vehicle test, except that the test filter is mounted behind a primary filter to remove any PM in the diluted exhaust.

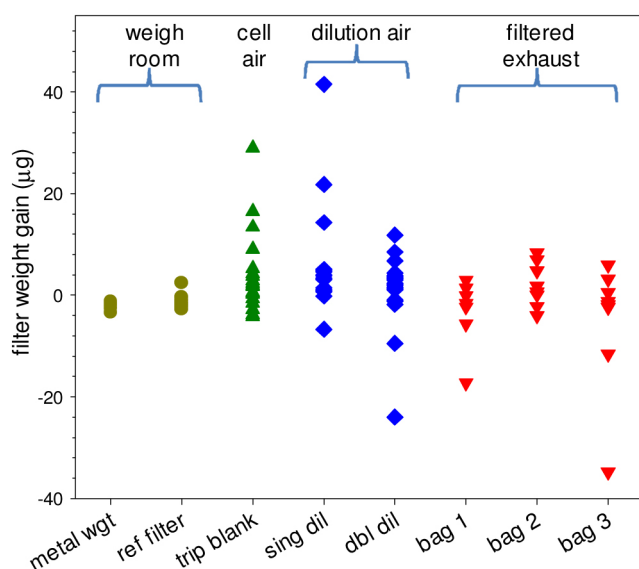


Figure 1. Filter weight gain variability incurred during:
1) weighing, 2) transport and exposure to cell air, 3)
exposure to dilution air, and 4) exposure to filtered
exhaust.

When weighed over long time periods without rezeroing, metal weights exhibit a $-1.8 \mu\text{g}$ bias and $0.5 \mu\text{g}$ standard deviation. The bias arises from a slow negative drift due to balance heating, something that can be compensated for during filter weighing. The variability more than doubles to $s = 1.3 \mu\text{g}$ for reference filter weighing, likely due to residual electrostatic effects after charge neutralization. But once the filters are handled, whether trip blanks, exposure to dilution

air, or exposure to filtered exhaust, there is a marked increase in variability to $\sigma = 7.2, 8.8,$ and $8.9 \mu\text{g}$, respectively. It is apparent from Figure 1 that, aside from the increased spread in the data, there are occasional outliers more than 3σ from the mean. These outliers may arise from dust falling onto / off of the filter or other reasons. If we ignore the outliers, filter weight gains deviating more than $20 \mu\text{g}$ from the mean, the variability reduces to $4.9, 5.0,$ and $4.4 \mu\text{g}$, respectively for trip blanks, tunnel blanks and filtered exhaust. Without the outliers, the corresponding mean biases are $2.7, 3.1,$ and $0.2 \mu\text{g}$. The first two are consistent with findings from other laboratories; the filtered exhaust result might be lower because of adsorption by the primary filter, but more likely this represents statistical variability of the mean.

The variability in filter weight gain is an order of magnitude higher than the $0.5 \mu\text{g}$ observed for metal weights. Its origin is not entirely clear. Circumstantial evidence points to the artifact being organic material. This comes from observations of a similar positive artifact when sampling cell air, dilution air and filtered vehicle exhaust using quartz filters. In this case, EC/OC analysis identifies the artifact as organic [10]. Apparently there is a sufficient quantity of low volatility organic compounds even in the ambient air to saturate the filter surface.

Owing to the inability to account for gaseous adsorption on a test to test basis, the proposed Part 1066 procedure is to subtract a facility average artifact of up to $5 \mu\text{g}$ per filter. Current evidence suggests that the adsorption effect saturates, i.e., it doesn't scale with PM concentration; therefore, the artifact adjustment is performed on the raw filter weight gain. To understand how the artifact impacts calculation of FTP weighted emissions rates, let us write the raw mass gain of each filter as

$$\text{Filter mass gain} = PM_i + a_i \quad (1)$$

where a_i are random variables with mean μ_{art} and standard deviation σ_{art} that describes the artifact weight gain on filter i . The FTP weighted average PM emission rate is then

$$\text{FTP wtd PM} = \frac{Q}{\text{dist}} \sum_i (PM_i + a_i - \mu_{art}) \text{wgt}_i \quad (2)$$

where $Q = \text{CVS flow} / \text{filter flow} * \text{secondary dilution factor}$, $\text{dist} = 7.45$ miles, and wgt_i is $0.43, 1,$ and 0.57 , respectively, for bags 1, 2, and 3 of the FTP drive cycle. Eq. (2) includes the subtraction of a facility average artifact (μ_{art}) from the filter for each phase, subject to the requirement that negative results are assigned zero. There are two implicit assumptions in equating the facility average artifact to μ_{art} . One is that the exhaust gas doesn't add additional adsorption bias to what is measured in the dilution air. The second is that we ignore the experimental error associated with the facility average. This will generally be a running average of n tunnel blank filters; thus, the error is approximately $\sigma_{art}/\sqrt{n}$, which should be small compared to the individual filter variabilities entering