

Uncertainties in Filter Mass Measurements Made to Determine Compliance with the 2007 Diesel PM Standard

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ABSTRACT

The 2007 Diesel particulate matter (DPM) standard of 0.01 g/bhp-hr represents a 90% reduction of the previous standard and corresponds to roughly 100 micrograms (μg) gained on the filter sample used to determine compliance. The factors that influence the accuracy and precision by which this filter can be weighed are analyzed and quantified. The total uncertainty, representing best and typical cases, is between 1 and 5 μg . These uncertainties are used to compute the total uncertainty of the brake specific emission calculation. This uncertainty also depends on flowrate uncertainty, face velocity, and secondary dilution ratio. For a typical case, the total fractional uncertainty is in the range of ~5 – 70% at 10% of the standard and ~1 – 10% at 90% of the standard.

INTRODUCTION

The determination of aerosol mass concentration by gravimetric analysis is a common measurement made by aerosol scientists. This procedure has been used to determine compliance with heavy-duty Diesel Particulate Matter (DPM) standards since their inception in 1988. Generally, the mass collected on a filter¹ has decreased as the standards have gotten progressively tighter from 1988 to 2007. The decrease is primarily due to lower

absolute levels. Previous Diesel and ambient air quality standards have recommended a minimum amount of collected mass to achieve acceptable sampling and mass measurement errors. For example, the current federal reference method for measuring ambient $\text{PM}_{2.5}$ states that 2 $\mu\text{g}/\text{m}^3$ is the lower limit of detection. Samples are taken in 24 hour increments so 48 μg is the lowest recommended mass. There is no specific recommendation for sampling 2007 DPM. The European Automobile Manufacturer's Association (ACEA) [1] estimated the repeatability and reproducibility of Diesel mass measurements at 2007 levels would be worse than $\pm 20\%$ and $\pm 50\%$, respectively. Other authors suggest that gravimetric analysis is not a sensitive measure of 2007 emissions [2-4] and have investigated sources of variability in the measurement [5, 6]. However, the reasons for the lack of sensitivity are not fully articulated.

The EU Particulate Measurement Programme, working under the auspices of the United Nations Economic Commission for Europe (UNECE), was initiated in 2001. One objective was to recommend changes to improve the EU's mass measurement procedure and by design, their gravimetric methods align with those of EPA. Currently, there are few differences but notable differences include use of a 1 μg resolution microbalance (rather than 0.1 μg), less stringent control of environmental room conditions, and no requirements for static charge measurement. More details are found in the final regulation that is posted elsewhere (http://www.unece.org/trans/main/wp29/wp29wgs/wp29gen/wp29ap_jun08.html).

¹ Filters are abbreviated in the text as "ringless glass fiber" (common trade name: Pall TX40®), "PMP (polymethylpentene) ringed" (Pall Teflo®), and "PFA (perfluoroalkoxy) ringed" (Measurement Technology Laboratories)

The uncertainty, measured as the coefficient of variance (COV: standard deviation/mean), in the filter mass measurement procedure depends most directly on the amount of mass collected on the filter. For steady-state conditions, the mass collected is given by

$$M_f = \left(\frac{BSPM}{BSFC} \right) \cdot \left(\frac{F}{1+F} \right) \cdot \left(\frac{V_f \cdot A_f \cdot t}{DR} \right) \cdot \rho_e$$

where M is the mass collected on the filter, BSPM, BSFC are the brake-specific emissions and fuel consumption, respectively, F is the fuel/air ratio; V_f is the face velocity; A_f is the filter area; t is the time and ρ_e is the mixture density [7].

The current on-road heavy-duty Diesel (HDD) standard of 0.01 g/bhp-hr results in roughly 100 μg of DPM collected on the filter. Emissions are certified during a driving-cycle and filter mass values obtained during such certifications are confidential but representative data are available. On the US side, mass loadings range from 0 to 130 μg when HDD and Diesel passenger car engines with emissions control devices are tested using steady state and transient conditions [8-11]. Under EU emission standards and protocols, the collected mass is higher for HDD engines, 100 to 300 μg , and less for passenger car engines, 0 to 50 μg [12, 13]. Diesel engines with emission control devices, such as the combination of an oxidation catalyst and particulate filter, can significantly outperform 2007 DPM standards. For example, Khalek [6] observed DPM emissions at 5% of the standard.

OBJECTIVES & ORGANIZATION

The objective of this work is to evaluate how the following ten factors affect the uncertainty of the mass measurement. In order of appearance, these factors are:

1. Weigh room environmental conditions
2. Buoyancy
3. Balance performance
 - Resolution
 - Precision
 - Linearity
 - Drift
4. Off-center loading
5. Drafts
6. Electrostatic charge
7. Filter handling

For each case, we identify the issue with literature review and show the results from our experiments. We consider both filter types allowed for US DPM measurements: ringless glass fiber filters and PMP or PFA ringed filters.

The error analysis described in [7] was revised and updated. We discuss the uncertainty contribution of sampling [11] and filter mass measurement with respect to determining compliance with the 2007 DPM standard

and with respect to the determination of the suspended particle mass (SPM) emissions.

REVIEW, EXPERIMENTS, AND ANALYSIS

WEIGH ROOM ENVIRONMENTAL CONDITIONS – After a filter has collected DPM, it is transported to a weigh room where temperature, humidity, and particle concentration are controlled. The primary effects of these parameters on filter mass and weighing uncertainty are generally understood but the magnitudes of the effects are not.

An increase in dewpoint causes an increase in the amount of vapor that adsorbs to the filter. Adsorbed water can also alter the vapor pressure of other collected materials, particularly sulfuric acid, making it more or less likely that the substance is retained on the filter. Temperature will have the inverse effect; the higher the temperature, the less water vapor molecules will adsorb. Suspended particles may settle on or diffuse to the surface of a filter. Weighing filters in the recommended class 1000 clean room seems to be a “good engineering practice,” but filters are unlikely to collect suspended particles if stored in covered Petri dishes, as required. Taylor [14] gave a detailed description of clean rooms with respect to DPM measurements but did not quantify their importance. In practice, temperature is easier to control than dewpoint, thus further focus will be on the effects of humidity.

The change in filter water-weight depends upon the filter material, chemical composition of the collected material, and the relative humidity (RH). The influence of humidity change on filter mass was recognized as far back as 1948 [15] and standard practice requires the control of relative humidity. Current practice suggests that the use of a reference filter(s) as a laboratory blank can approximate the weight change of the sample filter due to changes in relative humidity. Lawless and Rodes [16] found that water adsorption contributes 1 $\mu\text{g}/\%RH$ for 25 mm quartz filters between 20 and 50%RH and less than 0.17 $\mu\text{g}/\%RH$ for 25 mm blank PMP ringed filters between 20 and 80%RH. Andersson et al. [12] found an average weight gain of 0.44 $\mu\text{g}/\%RH$ and 0.25 $\mu\text{g}/\%RH$ for two reference ringless glass fiber filters.

It is conceivable that the water-weight change of a filter can be corrected using published weight gain sensitivities but the weight gain of a blank filter may be different from a PM loaded filter. If so, loosely regulating humidity would allow the chemical composition of the collected material to influence the measurement. Consider the case of 20 μg of a hygroscopic sulfuric acid aerosol, as shown in Figure 1. The graph shows the relationship between the aerosol mass and relative humidity [17]. A relative humidity increase from 37 to 53 %RH at 25°C increases the apparent mass by 8 μg due to uptake of water by the acid. On the other hand, Vartiainen et al. [18] measured water adsorption on large quantities of Diesel soot (3 mg). A linear

interpolation of their results suggests that the weight change of 100 μg of soot would be only 0.4 μg . Thus, the influence of soot on water vapor adsorption is expected to be negligible.

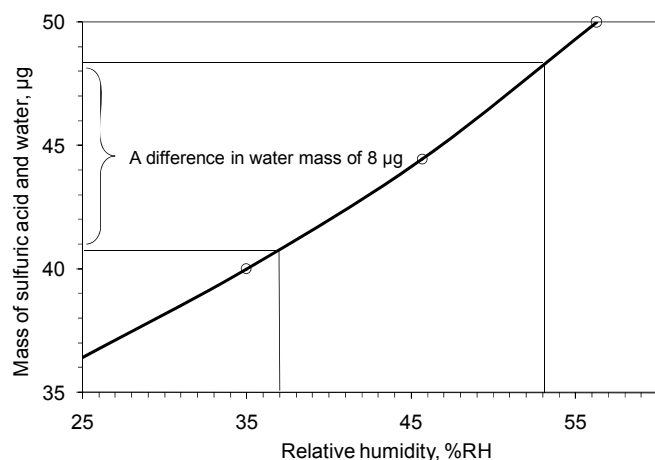


Figure 1. Predicted change in particle mass due to equilibrium water uptake by 20 μg of sulfuric acid.

Experiments were performed to evaluate the magnitude of water vapor adsorption on PMP ringed and ringless glass fiber filters. In each experiment, 6 (of each) doped and blank filters were tested. The doped filters were doped with 20 μg of sulfuric acid, simulating the presence of a hygroscopic aerosol that had been collected from a 2007 emission compliant engine. We showed in [11] that the sulfuric acid doping process does not add volatile organic carbon contamination to the filter. The blank filters were taken directly out of the manufacturer's shipping box and equilibrated in the weigh room. In each experiment, the set of doped and blank filters of like media was weighed repeatedly with a Cahn 31 microbalance as the dewpoint was incrementally increased from 4°C to 12°C and the temperature was held constant at 22°C. The entire experiment, including doping, equilibration, and weighing took <60 hrs. Each filter was allowed to equilibrate for >30 minutes and <12 hrs after each change in dewpoint.

The results of these experiments are summarized in Figure 2. To obtain each slope, a linear least squares regression was performed on each filter's dataset ($r^2 \sim 0.85$ to 1.0) and the average of all slopes and two-standard deviation error bars were calculated. The slope for the blank and doped ringless glass fiber filters was very similar, 1.87 $\mu\text{g}/^\circ\text{C}$ and 1.99 $\mu\text{g}/^\circ\text{C}$, respectively. These values are not significantly different ($p < 0.05$), which is inconsistent with the equilibrium data shown in Figure 1 that predicts a change of 1.38 $\mu\text{g}/^\circ\text{C}$ for a 20 μg sulfuric acid aerosol in equilibrium. The difference in the average slopes of 0.45 $\mu\text{g}/^\circ\text{C}$ and 1.5 $\mu\text{g}/^\circ\text{C}$ for blank and doped PMP ringed filters, respectfully, is more consistent with the equilibrium data, although a discrepancy still exists.

Two conclusions can be drawn from these data. First, blank ringless glass fiber filters gain more weight per

change in dewpoint than blank PMP ringed filters by a factor of 4. Current regulations allow the dewpoint to vary by 2°C. Thus, the worst-case weight change at constant temperature is 4 μg and 1 μg for the ringless glass fiber and PMP ringed filters, respectively. The EU regulation variation in dewpoint is 5°C, suggesting that an almost 10 μg weight change is possible by changing environmental conditions. If temperature and dewpoint changes occur, the weight change may be greater. Secondly, the difference between the doped and blank filter weight gain for either filter media is not understood. The results imply that the adsorbed H_2SO_4 and water solution behaves differently on the filter surface than the solution in bulk or in droplets.

BOUYANCY – The buoyancy correction is used to add the mass of air displaced by the filter to the measured filter mass. Although the volume occupied by the filter does not change significantly between weighings, changes in the environment cause the air density to fluctuate causing the buoyancy correction to potentially vary between the pre- and post- weighing. Koistinen et al. [19] discussed the theory and methods for performing this correction and it is reproduced here using the

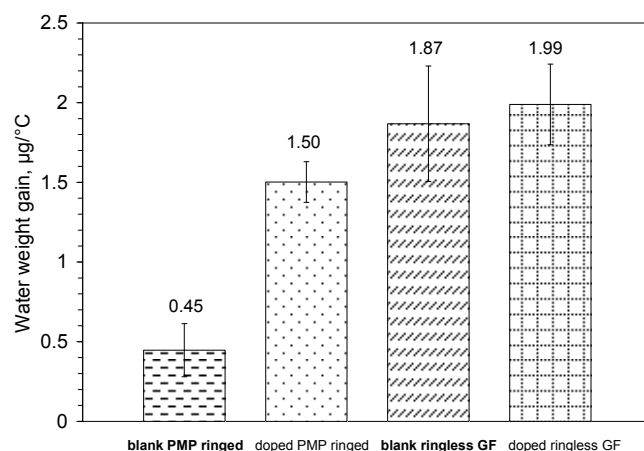


Figure 2. Water vapor adsorption for blank and sulfuric acid doped PMP ringed and ringless glass fiber (GF) filters. Error bars indicate 95% confidence intervals.

maximum permissible changes specified by the 2007 regulation for temperature (23→21°C) and dewpoint (10.5→8.5°C). Since the buoyancy correction is also affected by ambient pressure, a conservative 3 kPa change is assumed that is reflective of an annual maximum range at a given location. EPA provides the equation to use for 2007 buoyancy corrections:

$$M_{\text{corrected}} = M_{\text{measured}} \cdot \left(1 - \frac{\rho_{\text{air}}}{\rho_{\text{cal weight}}} \right) / \left(1 - \frac{\rho_{\text{air}}}{\rho_{\text{filter}}} \right)$$

where M refers to the filter mass and p subscript refers to the density of the indicated substance. The mass of displaced air depends on the filter volume (or mass/density). For a given air density, the magnitude of PFA ringed, PMP ringed, and ringless glass fiber filter corrections will be different.