Title
Alternatives to the Gravimetric Method for Quantification of Light Duty Vehicles Particulate Emissions

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Alternatives to the Gravimetric Method for Quantification of Light Duty Vehicles Particulate Emissions

A Thesis submitted in partial satisfaction of the requirements for the degree of

Master of Science

in

Mechanical Engineering

by

Yang Li

December 2015

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My parents are always supportive to me. They gave me endless power to face new challenges every day. The author would also like to acknowledge the funding agencies, CARB, for their generous support and guidance.
ABSTRACT OF THE THESIS

Alternatives to the Gravimetric Method for Quantification of Light Duty Vehicles Particulate Emissions

by

Yang Li

Master of Science, Graduate Program in Mechanical Engineering
University of California, Riverside, December 2015
Dr. Heejung Jung, Chairperson

Measurement of particulate matter (PM) emission of light-duty vehicles (LDVs) is a complex issue with many stakeholders, including engine manufacturers, health effect scientists, climatologists and regulatory agencies. With particulate emission regulatory limits in California and United States decreased by more than two orders of magnitude since the 80s, efforts continue to investigate alternatives to the gravimetric method for quantification of LDVs PM emission.

Several alternative metrics including total particle number (TPN), solid particle number (SPN), black carbon (BC), and particle surface (PS) area were measured along with gravimetric PM mass to study the correlation between different methods, using a variety of LDVs chosen to represent different emission levels and a range of current technologies in the modern fleet. It was found that gravimetric PM mass is strongly dependent on chemical nature of the PM. Thus correlations of gravimetrically determined PM mass with alternative metrics were different between two different testing cycles (e.g. FTP vs SFPT-US06). Alternative metrics are free from such cycle dependency which is due to adsorption artifact and therefore considered as a good future metric or supplemental metric such as SPN for EU regulation. Particle surface (PS) area turned out to be very sensitive with wide range and current instrumentation has a room to improve in terms of measuring tunnel blank and reducing electrometer drift.
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# Acronyms and Abbreviations

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<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ARB</td>
<td>Air Resources Board</td>
</tr>
<tr>
<td>AVL</td>
<td>Anstalt fü r Verbrennungskraftmaschinen List (an Austrian based automotive engineering firm)</td>
</tr>
<tr>
<td>BC</td>
<td>Black carbon</td>
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<td>CARB</td>
<td>California Air Resources Board</td>
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<td>CE-CERT</td>
<td>College of Engineering-Center for Environmental Research and Technology (University of California, Riverside)</td>
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<tr>
<td>CPC</td>
<td>Condensation Particle Counter</td>
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<tr>
<td>CS</td>
<td>Catalytic stripper</td>
</tr>
<tr>
<td>CVS</td>
<td>Constant volume system</td>
</tr>
<tr>
<td>D₅₀</td>
<td>50% efficiency cut point of CPC</td>
</tr>
<tr>
<td>Dₚ</td>
<td>Particle diameter</td>
</tr>
<tr>
<td>DC</td>
<td>Diffusion charger</td>
</tr>
<tr>
<td>DMM</td>
<td>Dekati mass monitor</td>
</tr>
<tr>
<td>DOC</td>
<td>Diesel oxidation catalyst</td>
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<tr>
<td>DPF</td>
<td>Diesel particulate filter</td>
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<tr>
<td>EAD</td>
<td>Electrical Aerosol Detector</td>
</tr>
<tr>
<td>EEPS</td>
<td>Engine Exhaust Particle Sizer</td>
</tr>
<tr>
<td>FTP</td>
<td>Federal test procedure</td>
</tr>
<tr>
<td>GDI</td>
<td>Gasoline direct injection</td>
</tr>
<tr>
<td>IPSD</td>
<td>Integrated Particle Size Distribution</td>
</tr>
<tr>
<td>LDVs</td>
<td>Light-duty vehicles</td>
</tr>
<tr>
<td>LNT</td>
<td>Lean NOx trap</td>
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<tr>
<td>LOD</td>
<td>Limit of detection</td>
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<tr>
<td>MPH</td>
<td>Miles per hour</td>
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<tr>
<td>MSS</td>
<td>Micro Soot Sensor</td>
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<tr>
<td>MY</td>
<td>Model year</td>
</tr>
<tr>
<td>PAD</td>
<td>Particle average diameter</td>
</tr>
<tr>
<td>PFI</td>
<td>Port fuel injection</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate matter</td>
</tr>
<tr>
<td>PMP</td>
<td>Particulate Measurement Program</td>
</tr>
<tr>
<td>PS</td>
<td>Particle surface</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle size distribution</td>
</tr>
<tr>
<td>PZEV</td>
<td>Partial zero-emissions vehicle</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>SG</td>
<td>Spray guided</td>
</tr>
<tr>
<td>SFTP</td>
<td>Supplemental federal test procedure</td>
</tr>
<tr>
<td>SPN</td>
<td>Solid particle number</td>
</tr>
<tr>
<td>TC</td>
<td>Turbo charged</td>
</tr>
<tr>
<td>TDI</td>
<td>Turbo charged direct injection diesel</td>
</tr>
<tr>
<td>TPN</td>
<td>Total particle number</td>
</tr>
<tr>
<td>TSI</td>
<td>An America based aerosol instrument firm</td>
</tr>
<tr>
<td>TWC</td>
<td>Three way catalytic converter</td>
</tr>
<tr>
<td>UCR</td>
<td>University of California at Riverside</td>
</tr>
<tr>
<td>ULEV</td>
<td>Ultra-low emission vehicle</td>
</tr>
</tbody>
</table>
US06 ........................................SFTP driving cycle
VERL ........................................Vehicle Emissions Research Laboratory (CE-CERT)
WG .................................................Wall guided
Chapter One: Introduction

Particle emissions cause adverse impacts on climate change and public health and therefore present widespread environmental problems (1) (2) (3). In urban areas emissions from mobile sources is one of major contributors to air pollution.

In January 2012, the California Air Resources Board (CARB) adopted the Low Emissions Vehicle (LEV) III regulations (4), which lowered the particulate matter (PM) emissions standards over the Federal Test Procedure (FTP) for light-duty vehicles (LDVs) from 10 mg/mile to 3 mg/mile beginning with model year (MY) 2017, and to 1 mg/mile beginning with MY 2025. The U.S. Environmental Protection Agency (U.S. EPA) also has proposed the Tier 3 Vehicle Emission and Fuel Standards Program, which lowers PM emission standards for LDVs to 3 mg/mile beginning in MY 2017 (5). With the advances in engine technologies resulting in lower PM emissions, there is need to continue to explore improvements and alternatives to measuring PM mass at very low levels.

This thesis investigated several alternative metrics relative to the gravimetric PM mass over transient cycles using a variety of light duty vehicles chosen to represent different emission levels, and a range of current technologies in the modern fleet. Particle number, black carbon, solid particle number, and particle surface area were measured along with gravimetric PM mass to study the correlation between difference metrics for particle emission measurement. The goal of this thesis was to evaluate correlations of alternative metrics with gravimetric PM mass and to evaluate potential of alternative metrics. Part of the particle size distribution data analyzed using the Integrated Particle Size Distribution (IPSD) method was not discussed in this thesis and published separately (6).
Chapter Two: Literature Review

2.1 Gravimetric method for PM measurement

The PM mass calculated by gravimetric method uses the mass collected on the filters captured by volumes of the diluted exhaust gases flowing through particulate filter. However, the gravimetric filter mass result can be particles combined with gas phase semi-volatiles which can condense on the filter. Researchers found the latter can greatly depend on the sampling conditions (7) (8) . For light duty vehicles with diesel engines, Chase et al. (9) indicated volatile artifact was a major part of PM collected on the filter. More evidences indicated volatile and semi-volatile particles are dominant in low particle emission engine exhaust (10). Researchers suggested to distinguish solid PM and volatile or semi-volatile materials that could be captured by filters by the new definition for particles. Swanson et al. (11) proposed that a particle can be defined as a homo- or heterogeneous cluster of molecules with a mobility diameter larger than 3 nm. Researchers also suggested the poor sensitivity of gravimetric method which masses collected on the filter are at the same level as the dilution tunnel background (12). The particulate measurement by gravimetric method reached the detection limit and for this reason it is a very challenging work to measure PM emission of LEV III regulation by CARB which lowered the PM emissions standards for light-duty vehicles (LDVs) to 1 mg/mile beginning with MY 2025. Over the years, researchers focused to other metrics than mass of PM quantification method. A variety of instruments are used for LDV exhaust PM measurement research based on different physical and chemical properties. Measurement technologies are widely using not only PM but particle number, Black carbon emission, particle surface area as testing metrics.
2.2 Particle number measurement

New engine technologies and exhaust aftertreatment systems have been developed to reduce emissions. The diesel particle filter (DPF) is the most important one. DPF collects particles downstream of the engine and PM emissions of vehicles get to such low levels that the regulated PM method has issues to accurately quantify particle emission. For this reason, particle number measurement has been introduced in Euro 5/6 light-duty vehicle emissions legislation based on Particle Measurement Program (PMP) (13) (14) (15). PMP developed a measurement of solid particle larger than 23 nm to avoid poor repeatability issues by volatile particles of nucleation mode. Good repeatability and reproducibility of particle number counting is achieved by fulfilling PMP protocols. However, counting only solid particles may not be the most effective way from a health effects perspective. Solid particles in nucleation mode are found from heavy-duty diesel vehicles operations (16) (17). For modern engine emission, primary particle size ranged from 19 to 33 nm for a light-duty engine (18). Study about early fuel injection strategy also found the primary particle diameter was between 20 and 25 nm with graphitic structure (19). Researchers found solid ‘core mode’ particles existing at 10-20 nm especially at GDI vehicles in which core mode is used for a separate solid size distribution with peak smaller than 23 nm (20). In a joint PMP study of California Air Resource Board (CARB) and University of California Riverside (UCR), researchers found solid sub-23 nm particles downstream of PMP volatile particle remover (21) (22). PMP procedure also might to fail to quantify the number concentration of potentially harmful sub-23 solid particles fractions (20).
2.3 Black carbon measurement

The primary part of particles is solid soot cores (black carbon) as well as a multitude of organic species of varying volatility (23) (24). Black carbon particle emissions have been studies extensively because it’s known contributions climate change and poor air quality (e.g., higher PM2.5 levels). Black carbon (BC) is the light-absorbing carbonaceous fraction of PM. BC is responsible for adverse effects on human health (25) (26) (27) (28) (29) and scientists tried to characterize the environmental impacts of BC. BC aerosol is the second warming factor after CO₂ relating to global climate change (30) (31) (32) (26) (33). Researchers found evidence which suggests BC is partly responsible for arctic climate change as it’s deposition in the Arctic (34) (35). The two dominant components of primary particulate are BC and primary organic aerosol. Black carbon emission is higher for diesel derived PM (50–70%) than from gasoline engines (30–40%) (36). However, for current and next generation of light duty engines, gasoline direct injection (GDI) will be a core technology focusing on CO₂ emission reduction. BC emissions from GDI engines have been observed to be significantly higher than those from conventional engines (13) (37). The majority measurement method can be classified into three method: thermal/optical carbon analysis, photoacousticis and light attenuation. In the pilot study of BC emission from light-duty gasoline vehicles from CARB in 2013, all three BC measurement methods are evaluated (29). The interest of research in BC emission measurement is the potential of BC emission as an alternative metric or one of the supplementary methods for 2025 1.0 mg/mi PM standard in California. The CARB study suggested that real-time instrument (MSS) had a method detection limit (MDL) of 0.15 mg/mi and it had better repeatability than the time-integrated instruments.
2.4 Particle surface area measurement

Among recent studies, there is a gathering consensus that particle surface area may be an appropriate metric from aerosol (38) and nanotoxicology scientist’s perspectives and relying only on mass concentration measurements is not good enough (39) (40) (41) (42) (43) (44) (45). The consensus is confirmed by studies about the correlation between particle surface area and inflammatory response for different materials (46) (47). Studies assumed that nanoparticles have larger surface area than bigger particles for the same mass which lead to more harmful results (48) (49). Researchers found that surface area is a better quantification metric for strong toxicity of low solubility particles (50) (42). A number of health effect studies suggested ultra-fine particles (<100nm) might be more hazardous than fine particles due to higher deposition fraction of ultrafine particles and higher surface area in contact with human cells (51) (52) (47) (53). The standard method for measuring total exposed surface area of particles is called Brunauer-Emmett-Teller (BET) method (54). BET specific surface area is determined from adsorption of a gas (usually N\textsubscript{2}, but CO\textsubscript{2} or Kr have also been used) on the surface area of the solid. BET is commonly used by health effects studies as the accessible surface area of deposited particles (55) (56). BET method, however, is only available as an off-line tool in lab, and requires a large mass of sample and time to analysis. A practical measurement way to measure surface area is diffusion charging favored by engine manufacturer or environmental protection agency. Several instruments are developed, like LQ1-DC, DC2000CE, and Electrical Aerosol Detector (EAD). A diffusion charger (DC) is used to measure total active surface area. Active surface area is defined as the accessible surface area using DC to release ions instead of atoms onto particles (57). As diffusion chargers have quick response (1s) so they are commonly used to the study of ambient aerosols (58) (59). William et al. (60) studied correspondence between EAD signal and calculated deposited surface area in lung and suggested EAD could be used as a useful indicator of particle
surface area as epidemiologic study tool. Brown et al. studied particle deposition in respiratory region indicating the fraction of surface areas deposited in lung per unit volume of air inhaled is more related to $D^1$ than $D^2$ (or $D^0$ than $D^3$) (61). Jung and Kittelson studied EAD signal that it was proportional to $D^{1.13}$ of charge attached monodispersed particles (62). The response function of DC is based on a calibration within a specified range of particle diameter. Ideal aerosols used in the calibration are different than real-world agglomerates particulate. Researchers are combining DC with other metrics to create comprehensive methodologies to quantify PM emission. Asbach et al. studied the ratio of DC to CPC which gives a measure of the average surface area per particle (63). Cauda et al. studied DC application for diesel exhaust exposure in mines and proved that a single metric of surface area, number concentration or particle mass is not sufficient to fully characterize diesel particulate matter (64). Ku and Maynard suggested DC measured active particle surface area is comparable to the geometric surface area (by TEM) but only below 100 nm and DC underestimates the geometric surface area over 100 nm (65). Pham and Jung (66) reported a calculation method of particle average diameter assuming vehicle exhaust PSD is lognormal distribution and combining real time EAD and CPC data. They suggested that previously studies of DC to CPC ratio overlooked characteristics of the DC and could not properly extract information.
2.5 Overall discussion

Gravimetric method is the standard for evaluation of alternative methods which was precisely defined on many aspects of the sampling process (e.g., dilution air and dilute mixture temperatures, dilution air filtering, sample flows, environmental conditions in the filter weighing room and better balance precision etc.). However, the accuracy of gravimetric method is not sufficient to quantify new PM emission standard which will be at 10% of old standard. The adsorption of semi-volatile gas molecules on a sampling filter or on solid PM may contribute to relatively high limit of detection (LOD) and less sensitive to ultrafine particles.

For solid particle number (SPN) concentration measurement, PMP studies have shown measurement results are repeatable to 20-30% (11). However, the well-established technique is under several limits like CPC D$_{50}$ is set to 23 nm assuming particles smaller than 23 nm will be very efficiently filtered by exhaust particle filter required to meet the exhaust particle number standard. PMP approach excludes a significant fraction of sub-23nm particles which are mainly semi-volatile particles.

Total particle number (TPN) concentration has the advantage of easy to measure however CPCs exhibit strong dependence on composition near their D$_{50}$. Also CPC measurements often exhibit variability due to the variability of the source but not the instrument performance. More detailed correlation of TPN with particle mass for LDVs from a wide variety of engine technologies are needed to further elucidation.

Black carbon emission as a metric for quantification of LDVs has the advantage that it is related to both climate and health effects. The exclusion of non-black carbon particles leads environmental regulatory agency would not take BC emission as a primary alternative method to gravimetric method for LDVs.
Particle surface (PS) area is not at all clear how to measure and how to be defined. Multiple approaches have been investigated. The application of DC to quantify PS emission rate is well-suited for dynamic and transient tests of LDVs emission. Swanson et al. compared particle number measured by CPC, active surface area measured by diffusion charger and alternative methods used to improve mass concentration estimates for nonspherical particles (11). He proposed measurement of active aerosol surface area in combination with the CS the most promising alternative metric. The active surface technique combining with CPC gives additional information of average surface area per particles. Pham and Jung’s (66) PAD method was evaluated in the thesis.

Other method, for example Integrated Particle Size Distribution (IPSD), is based on certain assumptions and inferences. Although IPSD method is capable to convert to all physical property metrics, on-line instrument is still under development phase and more studies are needed to focus on effective density to replace a single effective density correction applied to all situations.
Chapter Three: Investigation of alternative metrics and cycle dependent characteristics of gravimetric method to quantify very low PM mass emissions

3.1 Methodology

3.1.1 Experiment Setup

Vehicles were tested at the University of California, Riverside Center for Environmental Research (CE-CERT) Vehicle Emissions Research Laboratory (VERL). The facility is equipped with a Burke E. Porter 48-inch single barrel light duty dynamometer. Vehicle exhaust pipe was fully connected to the Constant Volume System (CVS). Clean ambient air was also connected to the CVS tunnel to provide dilution air. Vehicle was prepared FTP pre-run cycle before the testing date and located on the dynamometer.

On-line instruments and gravimetric filter samples were drawn in parallel downstream of the CVS tunnel, as shown in Figure 3-1. PM was collected on two sets of 47 mm Whatman Teflon®-membrane filter with pore size of 2 µm hosted in a filter holder (GELMAN Sciences 2220). A single composite filter was used at a constant filter-face velocity over all three phases of the FTP or US06 cycle. This approach reduces any uncertainty associated with the per-filter gravimetric analysis. PM mass samples were collected cumulatively over the entire FTP or US06 cycle, with one sample collected for each test. The typical weighting factors for each phase of FTP cycle were not used in this study to allow a straight comparison with alternative metrics. Tunnel blanks were estimated based on 12 samples that were collected in conjunction with this study, as well as other programs that were ongoing in the laboratory. Blank filter subtraction was not conducted for gravimetric PM results presented in this study to show the potential magnitude of measurement artifact. The filter face velocity was maintained at 100 cm/s, consistent with Part 1065, but other provisions of Part 1065, such as control of the temperature at the filter face to 47±5 °C and meeting requirements on residence time were not implemented. The gravimetric method PM results were previously reported in another journal paper (6).
Figure 3-1 Experimental setup
(Note the EAD was place either directly off of the CVS or downstream of the secondary dilution tunnel depending on the test.)

3.1.2 Instrumentation

Engine Exhaust Particle Sizer 3090 (EEPS™, TSI), Micro Soot Sensor (MSS, AVL) and Electric Aerosol Detector 3070A (EAD, TSI) took sample flow in parallel with gravimetric filter directly off of a constant volume sampling system (CVS). A secondary dilution tunnel with dilution ratio of 3.86 was also connected to the CVS. Two Ultrafine Condensation Particle Counter 3776 (CPC3776, TSI) took samples off of the secondary dilution tunnel. One of the two CPCs is equipped with a Catalytic Stripper (CS) upstream to remove semi-volatiles. Ntziachristos et al. suggested that the CS offers similar performance characteristics to the PMP when tested on diesel exhaust (67). In tests with the gasoline vehicle, the CS-CPC measurement has been shown
to report lower particle concentrations than the PMP method, indicating that a large number of solid particles could also be removed as volatiles due to the penetration lost. In some test conditions, EAD sampled downstream of the secondary dilution tunnel.

The discussion within this paper is focusing on the methodology’s correlation between gravimetric method and alternative metrics, such as total and solid particle number (TPN, SPN) counting, Black carbon (BC) emission, particle surface (PS) area emission, and particle average diameter (PAD) method. While the detailed information of all aerosol instruments used in this study can be found in the user manual, the authors would like to highlight a few important features of these instruments serving PM quantification methods.

### 3.1.2.1 EEPS

The EEPS is a particle size distribution measurement instrument. It measures particle size distributions based on electrical mobility classification and electric current measurement from electrometers. EEPS total particle concentration is the integration of total 32 size bin particle number. Li et al. indicated the sensitivity of the EEPS for measuring particle size distributions and particle mass should be adequate for measuring at LEV III emission levels (6). However, EEPS underestimated GDI vehicle aggregate mobility size in Li et al.’s study. Zheng et al. (68) also indicated that EEPS underestimate the size of soot aggregate compared to a fast-SMPS. Wang et al. indicated the EEPS concentration is underreported relative to SMPS for diesel particulate measurements greater than 200 nm (69). In the recent study, new EEPS matrix was developed by TSI and Dr. Xiaoliang Wang of Desert Research Institute, and University of Minnesota Center for Diesel Research (70). The new matrix corrected the discrepancies which have been reported between EEPS and SMPS and special designed ‘Soot’ matrix is special customized for agglomerates aerosol like engine exhaust.
3.1.2.2 CPC

Total particle number was measured by CPC3776 measurement after secondary dilution tunnel. The maximum particle number concentration is $3 \times 10^5$ particles/cm$^3$.

The condensation of liquid on particles is the operational principle of CPC to grow particles to a detectable size for optical particle counter. CPC uses light scatter pulse detection of ‘grown’ particles. For the study, particles pass a condensational tube where butanol-based condensing fluid vapor condenses on particle surface. CPC 3776 has a quick response of 1 Hz updating rate. CPC response is also affected by particle size. The counting efficiency is normally determined by the 50% cut point of a CPC ($D_{50}$) which particles are counted at 50% efficiency at this diameter value. CPC3776 has a $D_{50}$ cut point at 3.5 nm. CPC has a great sensitivity on solid particles but has difficulty in measuring semi-volatile HC and sulfur containing compounds from light duty vehicle exhaust.

3.1.2.3 CS

A Catalytic Stripper (CS) was used as semi-volatile compound remover upstream of a parallel CPC 3776. The functions of catalytic stripper are the evaporation and oxidation for the volatile compound (71). One sulfur-trap (S-trap) and one oxidation catalyst are the main parts for the catalytic stripper. They are working under wall temperature at 300 °C. Ntziachristos et al. suggested that the CS offers similar performance characteristics to the PMP when tested on diesel exhaust (67). In tests with the gasoline vehicle, the CS has been shown of leading to lower particle concentrations than the PMP, indicating that a larger number of particles can be removed as volatiles.

For my thesis study, the CS sampling condition was setup as 1.5 lpm flow rate and 300 °C of temperature. Accordingly, our combined CS penetration rate was calculated by particle
penetration lost and thermophoresis lost. $D_{50}$ is at 30 nm diameter in the CS sampling line. Particles smaller than 30 nm are removed in SPN counting.

### 3.1.2.4 MSS

This study measured BC emission of exhaust PM using Micro Soot Sensor (MSS) which is based on the photoacoustic principle. When light-absorbing particles are heated by periodically modulated laser beam, it creates a periodic pressure pulsation and it is detected by the microphone as acoustic waves. The Micro Soot Sensor used in this study has a time resolution of 1 second and detection limit is more than 20 times better than the detection limit of the standard PM measurement.

### 3.1.2.5 EAD

EAD is a diffusion charger which sets up the charging region as a counter flow configuration for better charging. The operating principle of EAD is based on diffusional charging of the particles and a current measurement caused by the trapped particles to determine particle total length. Jung and Kittelson (62) reported that EAD signal was proportional to $d_p^{1.13}$ from the measurement of charged monodispersed particles. It should be noted EAD reported particle length concentration of mm/cm³ is due to the fact that aerosols of interest say 0.01 to 1 um particles are in transition and continuum regime-slightly more weighted toward continuum regime for diffusion charging.

### 3.1.3 Vehicles and Fuels

Six vehicles were tested in this study, including four GDI vehicles, one PFI vehicle, and one diesel vehicle. These vehicles included a 2012 Mazda 3, a 2009 VW Tiguan, a 2012 Mercedes Benz E350 coupe, a 2012 Nissan Versa, and a 2009 VW Jetta. Vehicle specifications are summarized in Table 3-1 Vehicle information.
Table 3-1 Vehicle information

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Make/Model</th>
<th>Model Year</th>
<th>Engine Technology</th>
<th>Mileage</th>
<th>Emission Category</th>
<th>After-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDI-1</td>
<td>Mazda 3</td>
<td>2012</td>
<td>WG GDI</td>
<td>19k</td>
<td>California PZEV</td>
<td>TWC</td>
</tr>
<tr>
<td></td>
<td>Mercedes Benz</td>
<td>2012</td>
<td>SG GDI</td>
<td>10k</td>
<td>California PZEV</td>
<td>TWC</td>
</tr>
<tr>
<td>GDI-3</td>
<td>VW Tiguan</td>
<td>2009</td>
<td>TC GDI</td>
<td>57k</td>
<td>California ULEV II</td>
<td>TWC</td>
</tr>
<tr>
<td>PFI-1</td>
<td>Nissan Versa</td>
<td>2012</td>
<td>PFI</td>
<td>2k</td>
<td>California ULEV II</td>
<td>TWC</td>
</tr>
<tr>
<td>DIE-1</td>
<td>VW Jetta</td>
<td>2009</td>
<td>TDI</td>
<td>114k</td>
<td>California ULEV II</td>
<td>DPF LNT</td>
</tr>
</tbody>
</table>


3.1.4 Driving Cycles and Measurement Procedure

Vehicles were tested over the Federal Test Procedure (FTP) and US06 driving. The FTP is the primary emission certification test for all LDVs in the U.S. and is designed to represent city driving conditions. The cycle duration is 11.04 miles with an average speed of 21.2 miles per hour (MPH). The FTP is 3 phase cycle. The first phase is the “cold start” phase, which represents operation when the vehicle is first started for the day. Because the engine and TWC are cold, a majority of the particle and gaseous emissions are produced during this phase of the cycle. Phase 2 occurs immediately after phase 1 and is known as the stabilized phase, representing driving after the engine and aftertreatment system are warm. A “hot soak period” is immediately after phase 2, where the engine is turned off for 10 minutes. After the hot soak period, phase 3 is started which is identical to phase 1. The FTP cycle vehicle speed is shown in Figure 3-2.
The US06 cycle is part of the composite Supplemental Federal Test Procedure (SFTP) and simulates aggressive driving. The US06 cycle is the supplemental cycle representing aggressive driving behavior which limits emissions under a wide range of common vehicle driving conditions. It includes high speed, high acceleration, and rapid speed fluctuations. Vehicle speed over the US06 cycle is shown in Figure 3-3.

Figure 3-2 FTP cycle

Figure 3-3 US06 cycle
3.2 Particle emission results by different metrics

Table 3-2 gives the final particle emission result using gravimetric method, total particle number concentration, solid particle number concentration, black carbon concentration, particle surface area and particle average diameter.

The testing car, engine type, cycle name was given in the first three columns. PM in the unit of mg/mile was calculated by gravimetric method weighing the filter mass changed before and after the cycle and divided by the total distance. TPN was calculated by the real time particle number concentration data from CPC3776. CPC saturation time was provided meaning the duration of real time particle number concentration data were exceeding the maximum CPC concentration. SPN was calculated by CPC3776 downstream of the CS which excluded volatile particles smaller than 30 nm. The saturation time for SPN calculation was provided as CS-CPC saturation. BC emission rate was calculated using MSS real time soot concentration. PS emission rate was calculated using EAD real time particle length concentration. Particle average diameter was calculated using Liem’s method which is explained in detail in chapter 3.5. Geometric mean diameter (GMD) of the equivalent lognormal PSD was given in $d_g$ value which used real time EAD and CPC data for calculation.

PM gravimetric method was not available for DIE-1 vehicle US06-4, 5 cycles. EAD was malfunctioning during GDI-1 vehicle US06-4 cycle and PFI-1 vehicle US06-1 cycle due to the flow out of range. The PAD value was not available accordingly for these two cycles. For DIE vehicle, CPC saturated more than 200 seconds over the whole US06 cycle. So PAD was not able to give accurate results for DIE vehicle US06 cycles.

Please note TPN and SPN were measured by CPC3772 for PFI vehicle FTP-1 cycle. CPC3772 has $D_{50}$ of 10 nm and a maximum particle concentration of $10^4$ particles/cm$^3$. 
Table 3-2 Summary of particle emission result by different metrics

<table>
<thead>
<tr>
<th>Car Type</th>
<th>Cycle</th>
<th>PM (mg/mile)</th>
<th>TPN (#/mi)</th>
<th>CPC sat. (s)</th>
<th>SPN (#/mi)</th>
<th>CS-CPC sat. (s)</th>
<th>BC (mg/mi)</th>
<th>PS (mm/mi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDI</td>
<td>FTP-1</td>
<td>4.82</td>
<td>8.51E+12</td>
<td>81</td>
<td>3.45E+12</td>
<td>29</td>
<td>2.96</td>
<td>5.86E+08</td>
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<td></td>
<td>FTP-2</td>
<td>2.11</td>
<td>2.58E+12</td>
<td>20</td>
<td>8.77E+11</td>
<td>0</td>
<td>1.55</td>
<td>1.55E+08</td>
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<td></td>
<td>US06-1</td>
<td>19.61</td>
<td>8.25E+12</td>
<td>63</td>
<td>1.90E+12</td>
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<td>3.35</td>
<td>4.21E+08</td>
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<td></td>
<td>US06-2</td>
<td>8.87</td>
<td>4.52E+12</td>
<td>33</td>
<td>1.08E+12</td>
<td>3</td>
<td>1.21</td>
<td>2.01E+08</td>
</tr>
<tr>
<td></td>
<td>US06-3</td>
<td>4.60</td>
<td>1.33E+12</td>
<td>10</td>
<td>2.96E+11</td>
<td>0</td>
<td>0.64</td>
<td>1.84E+07</td>
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<tr>
<td></td>
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<td>1.07E+11</td>
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<td>0.22</td>
<td>Malfunction</td>
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<td>1.34E+08</td>
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<tr>
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<td>2.59E+11</td>
<td>0</td>
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<td>3.73E+07</td>
</tr>
<tr>
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<td>1.73E+11</td>
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<td>3.83E+10</td>
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<td>0.06</td>
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<td>0.24</td>
<td>2.12E+11</td>
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<td>4.60E+10</td>
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<td>2.24E+06</td>
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<td>2.94</td>
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<td>2.32E+12</td>
<td>1</td>
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<td>3.66E+08</td>
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<tr>
<td>PFI</td>
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<td>0.65</td>
<td>1.88E+11*</td>
<td>68</td>
<td>4.42E+10*</td>
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<td>0.05</td>
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<tr>
<td></td>
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<td>1.96</td>
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<tr>
<td></td>
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<td>1.76E+10</td>
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<tr>
<td></td>
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<td>8.35E+10</td>
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<td></td>
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<td>7.91E+11</td>
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<td>2.61E+11</td>
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<tr>
<td></td>
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<td></td>
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<td>6.16E+10</td>
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<td>0.11</td>
<td>9.27E+06</td>
</tr>
<tr>
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<tr>
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<td>FTP-2</td>
<td>0.26</td>
<td>3.77E+10</td>
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<td>3</td>
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<td></td>
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<td>2.60E+13</td>
<td>237</td>
<td>3.95E+11</td>
<td>0</td>
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<td>5.20E+09</td>
<td></td>
</tr>
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<td>US06-5</td>
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<td>5.02E+11</td>
<td>0</td>
<td>0.73</td>
<td>3.14E+09</td>
</tr>
</tbody>
</table>

(Note: The asterisk TPN and SPN were measured by CPC3772. All other cycles TPN and SPN were measured by CPC3776.)

### 3.3 Correlations of TPN, SPN, BC and PS with gravimetric PM mass

Figure 3-4 Correlation between different metrics with gravimetric method shows correlations between alternative metrics and gravimetric PM mass over the FTP. The solid lines and equations are results of linear regression. All metrics examined in the study have shown good correlations with the gravimetric method. Figure 3-4 showed the linear regression slopes for TPN and SPN versus gravimetric method as $1.9 \times 10^{12}$ and $7.3 \times 10^{11}$ respectively. The slope for the TPN was
62% larger than that for SPN in part due to inclusion of semi-volatile particles and small size particles. Note that $D_{50}$ of the CS used in this study was 30nm and details are described in 3.1.2.3. It should be also noted CPCs were beyond maximum detection limit for certain periods of time during testing. The duration of the CPC saturation was specified in the figure. For example the slope for TPN vs PM mass would have been steeper if CPCs were not saturated. The relationship between BC and PM mass in LDV emissions were assessed and the results are plotted in Figure 3-4c. The regression slope is 0.64 which is predominantly determined by the high BC emitted from GDI engine with the $r^2$ of 0.90 in Figure 3-4c. Figure 3-4d shows the correlation between PS and PM with $r^2$ of 0.92. Figure 3-4abcd showed positive x-intercept reflecting influence of organic artifact in the gravimetric method. Mohr et al. (10) demonstrated non-mass-based methods, including CPC, diffusion battery, diffusion charger, ELPI and light scattering instruments, showing rather poor correlation with gravimetric method. However, CPC and DC measurement exceeded others in relatively simple metrics, good repeatability and excellent sensitivity. Mohr et al. reported the correlation factors $r^2$ of CPC measured TPN with gravimetric method is 0.17 and diffusion chargers, LQ1-DC (Matter Engineering and EAD (TSI), are 0.47, 0.50 separately. The volatile or semi-volatile fraction of condensed material on PM which cannot be detected by CPC and DCs were the key issue of poor correlation between alternative metrics with gravimetric method. Mohr et al. also suggested that the nucleation of volatile material in the sampling line has to be avoided to ensure good performance in repeatability of CPC and DC measurement results. It should be noted Mohr et al.’s data was tested on a heavy-duty diesel engine with Euro 3 certification level.
Figure 3-4 Correlation between different metrics with gravimetric method for FTP cycle
   a) TPN vs gravimetric method for FTP cycle
   b) SPN vs gravimetric method for FTP cycle
   c) BC vs gravimetric method for FTP cycle
   d) PS vs gravimetric method for FTP cycle

Figure 3-5 shows correlations between alternative metrics and gravimetric PM mass over the US06 tests. The US06 cycle has more frequent hard acceleration compared to FTP. In Figure 3-5a, the linear regression between TPN and gravimetric method was made excluding two diesel data
points because DPF regeneration happened during US06 cycles. CPC was unable to capture total particle number accurately since saturation lasted for about 250 seconds in each US06 cycles. In Figure 3-5d, the linear regression coefficients between PS and gravimetric method were determined by five GDI and three PFI data points. EAD malfunctioned during one GDI and one PFI testing and two diesel data points were excluded due to the DPF regeneration. To authors’ surprise, correlations of the alternative metrics with the gravimetric PM metric were changed dramatically when the test cycle was changed from FTP to US06. The slopes of TPN, SPN, BC and PS were reduced by 78, 86, 73 and 82% comparing to the slopes of FTP test results. PM from the US06 contained about 17% BC based on the slope between BC and gravimetric PM. Figure 3-5ab showed the linear regression slopes for TPN and SPN versus gravimetric method as $4.2 \times 10^{11}$ and $9.9 \times 10^{10}$ respectively. The slope for the TPN was 76% larger than the slope for SPN partly due to inclusion of semi-volatile particles and small size particles. Again the saturated data points prevented more definite quantification of the correlation but the trend seems valid when other unsaturated metrics such as BC and PS were compared to gravimetric PM mass.
Figure 3-5 Correlation between different metrics with gravimetric method for US06 cycle
a) TPN vs gravimetric method for US06 cycle.
b) SPN vs. gravimetric method for US06 cycle.
c) BC vs. gravimetric method for US06 cycles.
d) PS vs gravimetric method for US06 cycle.

The above results showed that the correlation between gravimetric PM mass and alternative metrics is dependent on the chemical nature of the PM. On the other hand correlations among alternative metrics discussed in detail in the next section showed no dependency on the testing cycle or chemical nature of the PM. This reveals that the gravimetric PM, which is a physical
quantity for regulation, strongly depends on the chemical nature of the PM. This resulted in systematic bias in correlation with alternative metrics between FTP and US06 cycle. The difference is significant by quantity and it is unwanted considering the choice of current Teflon filter is to minimize the effect of organic artifact compared to more adsorbing filter medium such as TX40 filter.

3.4 Evaluation of active aerosol surface area method

Among the alternative metrics this study measured, author considered particle surface area is the most promising. Swanson et al. (11) compared particle number measured by CPC, active surface area measured by diffusion charger, alternative methods used to improve mass concentration estimates for nonspherical particles, and proposed measurement of active aerosol surface area in combination with the CS the most promising alternative metric.

Figure 3-6 shows real time active aerosol surface area measured using the EAD over FTP tests. Concurrent EEPS signal was converted to corresponding EAD signal, which was using EEPS measured PSDs assuming the PS response of the EAD is proportional to \( d_p^{1.13} \) (62). The PM emissions rate of plotted cycle in Figure 3-6 ranged from 0.4 mg/miles to 4.8mg/mile. The WG GDI vehicle has PM emission rate of 4.82 mg/mile with a PS emission rate of \( 5.86 \times 10^8 \) mm/mile. The EAD measured and calculated matched well during phase 1, 2, and 3 except the calculated EAD response had higher LOD due to higher noise level of the EEPS. The EAD electrometer is designed to have a wide dynamic range, while the EEPS electrometer is designed for fast response, high sensitivity and low cost. Both types of electrometers are susceptible to noise, so need zeroing the electrometers from time to time. The EEPS electrometer uses charge accumulation mode for sensitivity, but when the concentrations is high the counter gets saturated quickly (72).
The SG GDI vehicle has PM emission rate of 0.8 mg/mile with a PS emission rate of $1.34 \times 10^8$ mm/mile. The PFI vehicle has PM emission rate of 0.65 mg/mile with a PS emission rate of $7.64 \times 10^8$ mm/mile. The DIE vehicle has PM emission rate of 0.42 mg/mile with a PS emission rate of $2.88 \times 10^7$ mm/mile.

Figure 3-6bcd show EAD response for SG GDI, PFI and DIE vehicles with emissions 0.80, 0.65, and 0.42 mg/mile respectively. SG GDI engine shows similar level of cold start PM emissions but after 400s the particle emissions becomes much lower compared to WG-GDI engine. There was very little particle emissions during phase 2 but measurable emissions were observed during phase 3. Data were also collected during vehicle soaking time which is from 1432 to 2031s. Signals during this period show CVS tunnel background. The tunnel background ranged from 0.01 to 0.1 mm/cm$^3$ and 0.03 to 2.6 mm/cm$^3$ for EAD and EEPS calculated signal. This can be either due to change in tunnel background particle concentration or drift of the electrometers. More investigation is needed for further understanding. Figure 3-6c shows emissions from PFI. It shows lowest cold start emissions during phase 1, no emissions during phase 2 and little emissions during phase 3. Figure 3-6d shows emissions from light duty diesel engine. It is interesting to observe higher emission during phase 2 compared to that of SG GDI. It should be noted none of other alternative metrics could show such a detailed temporal evolution of particle emissions with such a good sensitivity. Dekati DMM could show qualitative trend of particle mass in real time over FTP test but its accuracy has issues and does not have as good sensitivity as active surface area measurement. Mamakos et al. (73) showed the DMM overestimates PM mass from 3 to 40% over transient cycles. Xue et al. (74) suggested they have been unsuccessful in unequivocally pinpointing the source of error or discrepancy due to the “black-box” operation of the DMM, which uses a proprietary method for calculating particle effective density and size distribution. AVL MSS measures BC and it measures wide range of
emissions in real time. It also has a good detection limit of 1.0 ug/m$^3$ (75). But the MSS does not respond to non-light absorbing part of PM, and its sensitivity is not as good as active aerosol surface area measurement. For example none of the above two methods or instruments can quantify PM emissions from PFI vehicle well.
Figure 3-6 Comparison of EEPS converted PS signal with real time EAD signal
a) WG GDI vehicle for FTP cycle.
b) SG GDI vehicle for FTP cycle.
c) PFI vehicle for FTP cycles.
d) DIE vehicle for FTP cycle.
3.5 Correlations of alternative metrics to active surface area method

Figure 3-7, Figure 3-8 and Figure 3-9 compares correlations among alteration metrics. Particle surface area was chosen as a reference metrics for convenience but very similar results can be found when other reference alternative metric was chosen as shown in Figure 3-10. It was found that the correlations among alternative metrics chosen for this study remain the same regardless of the test cycle (either FTP or US06) which is on the contrary to what was discussed in the previous section regarding gravimetric method. Again some CPC data had saturated period during the test and those tests should be repeated in the future after adopting higher secondary dilution ratio. Regardless, Figure 3-7 to Figure 3-10 show consistent picture that alternative metrics using online instruments measured suspended PM emissions without being influenced by any artifact. The correlation of SPN with PS is shown to be very good in Figure 3-8, which means easy translation of PMP SPN standard to surface area metrics. For Euro 5/6 SPN LDV regulation, $6.0 \times 10^{11}$ particles/km can be converted to $1.6 \times 10^{8}$ mm/mile from the correlation of Figure 3-8.

![Figure 3-7 Correlations of TPN emission vs PS emission](image)

(The linear regression coefficient was calculated using GDI-1 FTP and US06 data set, GDI-2 FTP and US06 data set, GDI-3 FTP data, PFI-1 FTP and US06 data set and DIE-1 FTP data. The malfunctioning EAD cycles are excluded and Jetta US06 cycle data are excluded.)
Figure 3-8 Correlations of TPN emission vs PS emission
(The linear regression coefficient was calculated using same data set as Figure 3-7.)

Figure 3-9 Correlations of BC emission vs PS emission
(The linear regression coefficient was calculated using same data set as Figure 3-7.)

Figure 3-7, 3-8 and 3-9 show minimal presence of y or x axis intercept, which reflects absence of systematic measurement artifact. It should be noted that the alternative metrics chosen for this study measure physical properties of suspended particles free from filter artifact of the
gravimetric method. It is known that the influence of organic artifact on the gravimetric method is more pronounced for very low PM mass determination. Figure 3-10 shows correlations for SPN vs BC, TPN vs BC, and TPN vs SPN. It should be noted that diesel US06 test data were excluded to calculate linear regressions for Figure 3-10bc. The test diesel vehicle had strong DPF regen event during the test therefore there was a high concentration nucleation mode particles. These regen events make correlation with TPN different from rest of the tests without regen thus excluded for regression calculation but included in the figure.
Figure 3-10 Correlations for SPN vs BC, TPN vs BC, and TPN vs SPN
(a) Correlation of SPN and BC. The linear regression coefficient was calculated by all cycle data.
(b) Correlation of TPN and BC. The linear regression coefficient was calculated all data set excluding DIE US06 cycles.
(c) Correlation of SPN and TPN. The linear regression coefficient was calculated all data set excluding DIE US06 cycles.
Figure 3-11 shows regeneration event occurring around 280 second when the catalyst temperature remained above 500 °C as shown in upper plot. The last plot shows a snapshot of EEPS measured PSD heavily weighted in nucleation mode. It is very interesting to observe that EAD signal (the active aerosol surface area) seems not saturated even under this high concentration regen event thanks to the wide range electrometer of the EAD.
Chapter Four: Conclusion

This study investigated alternative metrics to quantify very low vehicle exhaust PM emissions with focus on aerosol active surface area. It was found that gravimetric PM mass is strongly dependent on chemical nature of the PM. Thus correlations of gravimetrically determined PM mass with alternative metrics were different between two different types of testing cycle (e.g. FTP vs SFPT-US06). This is certainly unwanted characteristics of the gravimetric method and more pronounced when quantifying very low PM mass. Considering more stringent PM mass regulations of 3 and 1 mg/mile for light duty vehicles in the US, this characteristics of gravimetric method should be taken into account when imposing emission standard using other than FTP cycle. Alternative metrics are free from such cycle dependency which is due to adsorption artifact therefore considered as a good future metric or supplemental metric such as SPN for EU regulation. Active aerosol surface area turned out to be very sensitive with wide range and current instrumentation has a room to improve in terms of measuring tunnel blank and reducing electrometer drift. Further study is needed to determine accuracy, repeatability and reproducibility of active aerosol surface area measurement to quantify very low PM mass emissions from vehicle exhaust.
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