CRC Report No. E-99

Very Low PM Mass Measurements
Executive Summary

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COORDINATING RESEARCH COUNCIL, INC.
5755 NORTH POINT PARKWAY • SUITE 265 • ALPHARETTA, GA 30022

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CRC Project No. E-99:
Very Low PM Mass Measurements

Prepared for:
Dr. Christopher J. Tennant
Coordinating Research Council Inc.
5755 North Point Parkway, Suite 265
Alpharetta, GA 30022
(678) 795-0506

And

Hector Maldonado
California Air Resources Board
1001 "I" Street
Sacramento, CA 95812

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Dr. Heejung Jung[1] PI
Dr. Kent C. Johnson[1] Co-PI
Dr. Robert L. Russell[1]
Dr. Thomas D. Durbin[1]
Dr. Wayne Miller[1]
Dr. Eric J. Xue[1]

Dr. Jacob Swanson[2]
Dr. David Kittelson[3]

[1]University of California
CE-CERT
Riverside, CA 92521
951-781-5799
951-781-5790 (fax)

[2]Minnesota State University – Mankato
[3]University of Minnesota

Executive Summary

Present motor vehicle particulate matter (PM) emissions measurement regulations (Code of Federal Regulations [CFR] 40 Parts 1065 and 1066) require gravimetric determination of PM collected onto filter media. There have been discussions about whether current sampling and measurement practices are sufficiently accurate in quantifying PM at the upcoming 3 mg/mi standards, and even more so at the 1 mg/mi PM emissions standards for low-emission vehicle (LEV) III light-duty vehicles. Although the PM mass measurement methodologies were improved considerably with the application of 40 CFR Part 1065 to the 2007 PM standards for heavy-duty engines, there is a need to improve understanding of and confidence in mass measurements for light-duty vehicles given the potential of significant impacts on the automotive industry.

CRC's E-99 project was launched to investigate long-standing questions about the measurement of the particulate matter ($PM_{2.5}$) emissions from motor vehicle exhaust at very low levels. The complexity of the effects of multiple parameters on PM mass measurements were such that even basic questions about the accuracy near the lower detection limit, the robustness or stability of the current federal test procedures and the sensitivity of the various measurement parameters have remained unanswered. E-99 was designed as a systematic investigation of key procedures in the current federal method. This included questions about a number of key measurement parameters, such as the following:

1. Does increasing filter face velocity (FFV) decrease variability and improve signal-to-noise while not appreciably altering the measured PM emissions?
2. Does decreasing dilution factor (DF) decrease variability and improve signal-to-noise while not appreciably altering the measured PM emissions?
3. Does collecting cumulative filters over the entire Federal Test Procedure (FTP) or performing an extended 4-bag (as opposed to 3-bag) FTP decrease variability and improve signal-to-noise while not appreciably altering the measured PM emissions?
4. How do practices and measurement accuracies vary over a wide range of laboratories weighing PM filters for low level PM mass measurements of vehicle exhaust?
5. Would a partial flow sampling system (PFSS) provide advantages in measuring low level PM mass in light duty emissions applications?

Throughout the E-99 project, the focus was to better understand the sensitivity of the measured $PM_{2.5}$ mass to various procedural changes rather than to suggest modification of current federal methods. Although PM emission rates are presented, they are based on testing results for two vehicles and are not designed to represent the in-use fleet. Any reference to the emission factors should be considered in light of the few vehicles studied.

Program Scope and Experimental Procedures

For this program, a Lower PM Source vehicle (a port fuel injected (PFI) vehicle) with an emissions rate of <1 mg/mi and a Higher PM Source (a gasoline direct injected (GDI) vehicle) with an emission rate just below 2 mg/mi were evaluated over a series of tests utilizing the 3-bag FTP test, 4-bag FTP test, and the US06 test cycle. These vehicles were targeted to be representative of the PM emissions levels that could be found for vehicles meeting the upcoming 3 mg/mi and 1 mg/mi standards. The vehicles are not meant to represent the vehicle technology that would be prevalent when these standards are implemented in the future. Testing was conducted in two phases: a screening test phase and a confirmation testing phase.

The screening tests were designed around varying several parameters, such as FFV and DF, over different extremes, and using cumulative filters, with the goal of recommending a combination of these factors that provides the most PM mass gain, while providing stable, repeatable emissions. A total of 11 FTP tests were conducted on the Lower PM Source and 9 FTP tests were conducted on the Higher PM Source during the screening testing. Six US06 tests were also conducted on each vehicle. The changes in key parameters evaluated during the screening tests included the following:

- FFV was varied from 100 to 175 cm/sec at increments of 25 cm/sec. This was done using three different sampling probes in the constant volume sampler (CVS) dilution tunnel, such that sampling could be conducted simultaneously at three flow rates for each test. The FFVs for the PFSS were also varied from 100 to 150 cm/sec.
- Comparisons were made between probes in the CVS where PM was collected cumulatively over the full FTP vs. a probe where PM was collected individually for each FTP bag.
- Comparisons were made between 3-bag and 4-bag FTP tests. For each vehicle, 3 tests were conducted in the 4-bag configuration and the remaining tests were conducted as 3-bag tests.
- Three DFs were evaluated: 3, 5, and 7. The changes in DFs were evaluated using a PFSS while the DF in the main CVS tunnel was maintained at 7.

The confirmation testing used the conditions deemed optimal based on the screening tests. The confirmation testing included 6 FTP tests on both the Higher and Lower PM Source, and 6 and 2 US06 cycles on the Lower and High PM Source, respectively. Recommendations that were implemented for the confirmation testing:

- A 3-bag FTP test can provide sufficient filter masses for vehicles with PM emissions level near those of the Higher PM Source (~2 mg/mi).
- A 4-bag FTP test can increase the amount of mass on the vehicle filters closer to those for the Lower PM Source (~0.25 mg/mi).
- The screening tests suggested the FFV be limited to 150 cm/sec. Separate probes in the CVS were sampled at FFVs of 100, 125, and 150 cm/sec, while the PFSS was set at an FFV of 150 cm/sec.
- The screening tests suggested that the minimum DF should be 5. The DF for the PFSS was set at 5, while the DF for the CVS tunnel was set at 7.
- The screening tests suggested that a robust and consistent preconditioning procedure be used for the US06 tests. The US06 pre-conditioning sequence is an FTP, followed by a US06 (prep) followed by a US06 (test) where the time between the US06 (prep) and US06 (test) is between 1 to 2 minutes.

Results and Conclusions – Emissions Testing

A summary of the results and conclusions of this study are provided as follows. Note that the discussion primarily focuses on the results of the confirmation testing, where the most extensive testing was conducted under conditions considered to be most advantageous for PM mass measurement. In some cases the screening data were also used to help explain observations. This will be noted when used.

General Confirmation Testing Observations

This section discusses the general observations relating to PM emission rates and filter masses. The following observations were made regarding PM mass emissions (mg/mi):

- The confirmation PM emissions agreed closely for the Higher PM Source FTP tests, with the average for different CVS PM probes for six tests ranging between 1.9 mg/mi to 2.0 mg/mi (with individual tests ranging from 1.7 to 2.1 mg/mi for different CVS PM probes).

The US06 tests were more varied, with the average for different CVS PM samplers ranging from 2.0 mg/mi to 2.4 mg/mi (with individual tests ranging from 1.9 g/mi to 2.6 g/mi for the different probes).

- The confirmation PM emissions for the Lower PM Source had much lower overall PM emission levels as well as higher relative errors between the different probes compared to those for the Higher PM source. The Lower PM Source's emission rate for different CVS PM samplers averaged from 0.09 to 0.11 mg/mi (with individual tests for different CVS PM samplers ranging from 0.04 to 0.24 mg/mi) for the FTP test and 0.19 to 0.24 mg/mi (with individual tests for different CVS PM samplers ranging from 0.10 to 0.30 mg/mi) for the US06 test. The averaged difference between each CVS probe was 0.02 mg/mi for the FTP tests, but the variability between tests was much larger and ranged from 0.04 to 0.24 mg/mi. The low average PM mass emission rate differences suggest the Lower PM Source FTP results were consistent, but the individual tests demonstrated much higher variability.
- Statistically significant differences at the 95% confidence level were found between the average PM mass emissions rates measured by the PFSS during FTP testing compared to the CVS probes for the Higher PM Source. This included statistically significant between the PFSS and all the CVS tunnel probes, with the exception of the probe that sampled PM emission separately for each FTP bag. It is suggested that these differences in PM mass emission rates may be due to differences in measurement approach and not differences in lower DF and higher FFV.

The following observations were made regarding filter weights (μg/filter) collected during the confirmation testing:

- The filter weights increased in proportion with increased FFVs and lower DFs for all test cycles and both vehicles. Thus, the signal-to-noise ratio improved at higher FFVs and lower DFs. This would lower measurement uncertainty that results from the PM measurement method's lower detection limits.
- The Higher PM Source filter weights varied from 205 μg for the PFSS and to 417 μg for the cumulative filter samples.
- The Lower PM Source filter weights varied from 26 μg for the PFSS to 39 μg for the cumulative filter samples.
- Tunnel blanks (TBs) were measured by sampling dilution air through the sampling for the same duration as the FTP test. The TBs averaged 5±4 μg for the CVS and 1±1 μg for the PFSS during the confirmation testing. These TBs were well below the Higher PM Source filter weights, but were closer to Lower PM Source filter weights.
- The US06 test cycle showed lower filter weights than the FTP test cycle partly due to the absence of the cold start, shorter length cycle, and fewer transients than the FTP test.

The following overall observations were made regarding the PM composition and particle size distributions (PSDs) for the different test cycles and test vehicles:

- During confirmation testing, the PM composition for both test vehicles were mostly soot for the FTP test cycle and about 50% soot for the US06 test cycles.
- The PSDs were generally bimodal, with peaks in both the nucleation and accumulation mode size ranges.
- The cycle averaged PSD for the US06 test cycles showed a peak for nucleation particles at a diameter of 10 nm that was two orders of higher in particle number concentration compared to the same peak for the FTP cycle. The particle number concentrations for the accumulation modes particles, from approximately 80 to 100 nm, were similar in magnitude for the FTP and US06 for each of the vehicles. The Higher PM Source showed higher particle number concentrations in the accumulation mode than the Lower PM

Source, consistent with the differences seen in the PM mass emission rates between the two vehicles.

- Evaluating the PSDs on a mass basis, the Higher PM Source showed a shift in the peak mass averaged concentration from a diameter of 105 nm (FTP cycle) to 80 nm (US06 cycle), while the Lower PM Source showed a shift in the peak mass averaged concentration from 105 nm (FTP) to 10 nm (US06). The change in peak diameters for the mass average PSD for different cycles and vehicles would change the theoretical filtration efficiency as FFV varies.
- The PM composition and PSD varied over the course of confirmation testing. This shows that the findings of the study with respect to low level PM mass measurements were consistent even as the physical properties of the PM varied.

It should be noted that the study was designed to represent optimal conditions for PM mass measurement, including the use of dedicated vehicles, the same fuel (E10), a single test site at one facility, the use of one driver, ideal low dilution factors of 7:1, dedicated PM probe hardware, the same environmental conditions, no intermittent contamination from high emitter vehicle testing (contamination), the same PM filter weigh room / filter handling procedures, etc. The variability of PM measurements in the real world would inevitably be higher than the variabilities found in this study, where multiple facilities, different vehicle architectures, different drivers, different PM probe suppliers, sites exposed to different fuels (gas, diesel, CNG, E85, etc.), carry over from higher emitting vehicles, higher DF's up to 20 or more (hybrids), different environments, varying blank test (or background PM) corrections, etc. would be encountered.

The Impact of Filter Face Velocity, Dilution Factor, the Partial Flow Sampling System, and Combining or Collecting Cumulative Filters, and 3-bag vs. 4-bag FTPs

The findings from varying the filter face velocity during the screening tests include:

- For most cases, increasing the FFV from 100 to 175 cm/s does not have a statistically significant impact on the mean mass emission rates for either the Higher or the Lower PM Sources.
- The PM net filter weights increased for higher FFVs compared to lower FFVs, which increases the signal (i.e., filter mass). Although the overall signal-to-noise ratio was improved for the higher FFVs, although an f-test, which is a statistical test comparing the amount of variability between different sampling conditions, did not show a statistical improvement in the variance for the higher FFVs.
- At a FFV of 175 cm/s, some tests of the higher PM source showed evidence that FFV filter overloading could occur.

Differences in the dilution factor, where a PFSS was used with a DF=5 and CVS measurements were taken with a DF=7 showed that:

- For the Lower PM Source tests, in general, there were no differences in PM mass emission rates that were statistically significant at a greater than 95% confidence level for the 4-bag FTP or US06 tests.
- The Higher PM Source showed more mixed results, with the FTP tests showing a statistically significant difference in means for PM mass emission rates at a 95% confidence level for the different DFs, while the US06 tests showed no statistical differences for the different DFs. The US06 testing had larger variability and fewer samples (n=2) due to testing complications.
- The Higher PM Source mean emissions showed a low relative error rate of between -2.7% and -5.9% between the PFSS (DF=5 FFV=150) and the CVS system (DF=7). A relative error of 5% is a reasonable and relatively small error considering the 20% variation in PM

measurements between different laboratories reported by others during PM mass and number cross lab correlations.

- It should be noted that although statistically significant differences in means between the CVS and PFSS were found, the differences were relatively small and could be attributed to errors in the exhaust flow, proportionality, and other PFSS details. These possible sources of bias between the CVS and PFSS sampler, and the low absolute differences in the means suggest that the lower DF may not be having an impact on the PM mass emission rates.
- The f-test values for most of the comparison cases were greater than p=0.05, suggesting that the PFSS does not have a statistically lower variability compared to the flow-weighted CVS probes with a FFV from 150 to 100, or compared to the individually collected filters.
- The TB results for the PFSS were lower than the CVS TBs (1 µg vs 5 µg), while the f-test suggests there is no difference in the variability between the CVS and the PFSS for any of the FFVs and DFs evaluated. This suggests the impact of the PFSS's lower TB was not a significant influence on the PFSS performance compared to the CVS method.
- Tests were also conducted at a DF=3 during the screening portion of the study, but results indicated that at this DF, filter overloading could occur under different sampling conditions with the vehicles selected.

Findings regarding combining filters were based on comparisons between CVS probes where PM was collected cumulatively over the full FTP compared to a probe where PM was collected individually for each FTP bag. They include:

- Combined filters have the advantage of collecting more PM mass on a single filter, but have the disadvantage of reduced flow rate for some bags in order to flow-weight the accumulated PM mass as needed for the proper emission calculations.
- The FTP Lower and Higher PM Source tests did not show a statistical difference in means for cumulative filters compared to the filters collected individually by bag.
- The signal-to-noise ratio (as represented by the filter mass) did not necessarily improve for the combined filters. Typically, the filter mass collected for the cumulative filters was reduced by the flow-weighting conditions for the single phase filter when compared to the filter masses for all of the individual FTP bags added together.
- Although the signal did not increase, the variability in the single filter method is statistically lower than for the multiple filter measurement for the Lower PM Source on the 4-bag FTP. This was confirmed for both the screening and confirmation testing portions of the project. This does suggest the signal-to-noise ratio could be improved by reducing the noise part of the ratio, particularly at lower PM mass emission rates.

Calculations were also done to evaluate the theoretical potential for reducing variability for different sampling conditions. These calculations showed the following:

- When the combined conditions of composite filters, 150 FFV, and lower DF=5 are utilized with a 4-bag FTP, the uncertainty in filter weighing / sampling can potentially be reduced by a factor of 4.5 compared to traditional sampling conditions with an individual filter 3-bag FTP (1 filter per phase), FFV=100, and a minimum DF=7. The extent to which this is realized in the actual PM uncertainty depends on whether the PM is dominated by filter weighing / sampling or by other factors, such as driver, vehicle, or environmental variability.

PM Filter Survey

A filter survey was performed to: (a) evaluate the ability of different laboratories to weigh 47 mm Teflon™ filters that are standard for sampling PM from vehicles, (b) estimate the uncertainty in the weighing process, and (c) consider practices that may lower this uncertainty. Thirteen laboratories across North America, representing industry, agencies, research institutes, and academic institutes, responded to the survey, and eleven laboratories provided filter data. Their responses included raw data on quality control (QC) checks performed by each laboratory, and information relating to elements that might influence the weighing process such as environment (moisture, temperature control, etc.), equipment (micro balance, etc.), methods and procedures (human vs. robot, direct read vs. double substitution, etc.), and quality control and assurance (reference checks, etc.). Analyses were conducted for types of QC filters, including *reference* filters, which are filter that remain in the filter weighing chamber and are never removed, and TBs. The primary analyses were conducted for *reference* filters, as this was the filter type with the largest amount of data. Selected results from the filter survey regarding the Teflon™ filter include:

- The *reference* filter variability (one standard deviation), within a given day over periods as short as one hour, ranged from 0.61 µg to 5.0 µg for the 5th and 95th percentiles and 2.0 µg for the 50th percentile (n>40,000 weights and 317 reference objects).
- *Reference* filters were found to gain weight on the order of 0.17 to 0.56 µg per day (50th percentile) and 0.8 to 1.8 µg per day (95th percentile). Some additional analysis done on metal reference objects that were utilized in conjunction with Teflon™ reference filters showing that the metal reference objects didn't gain weight over longer periods of time. This suggests some type of gaseous phase adsorption artifact occurring within the micro balance area.
- Robotically weighed *reference* filters showed lower variability (0.8±0.3 µg) compared to filters manually weighed.
- Robotically weighed *reference* filters also showed a much lower mass gain per touch at 0.01 µg/event.
- *Tunnel blank* mean biases (n=615) were much higher than the reference filter mean bias, ranging from 1.1, 2.8, and 13.0 µg, for the 5th, 50th, and 95th percentile, and on average was 3.6 µg at one standard deviation for all the laboratories pooled together.
- Robotically weighed *tunnel blanks* also had higher mean biases compared to reference filters. The biases for robotically and manually weighed filters were similar for TBs. Thus, the advantages of robotically weighing reference filters did not carry over to the weighing of TBs, with the exception of one laboratory that used robotic weighing and was able to maintain a TB mean bias and single standard deviation of 1.0±0.2 µg (n=80).
- The higher values for the TBs compared to the reference blanks suggests that the sample collection system is a relatively significant contamination source for Teflon™ gravimetric filters.
- Robotic filter weighing appears to be one element that can reduce filter weighing variability, as shown by the reference filter, this may needs to be combined with other 'best filter measurement practices', such as proper filter handling before, during, and after emissions testing, storage filter media, etc. in order to achieve consistently low TB contamination also.
- As an additional note, previous research at University of California Riverside (UCR) has shown hot TBs (200°C) in a diesel tunnel have higher and more variable PM artifact contribution compared to TB collected at room temperature. Thus, the room temperature TB values presented may be conservatively low in comparison to the hot conditions of the sample systems during actual vehicle emissions testing.

General Screening and Confirmation Testing Observations

The screening results were used primarily to select and recommend the FFV and DF conditions used during the confirmation testing. However, the two sets of tests showed some differences in terms of variability and drift. These are highlighted below: The variability in PM emissions from the Lower PM Source was noticeably larger during the screening testing compared to the confirmation testing (from 0.1 to 0.5 mg/mi over the FTP cycle). This may be due to environmental conditions, but the gaseous emissions did not show the same level of variability.

- The lower PM Source showed a relatively constant soot or elemental carbon (EC) emissions rate of about 0.1 mg/mi for both the screening and confirmation testing, while the volatile organics varied from test to test. The EC fraction of the PM varied from 0.22 to 0.97, with an average of 0.67 for the FTP test cycle. The test with the lowest fraction of EC at 0.22 was also the test with the highest emission rate of 0.5 mg/mi. This suggests the contribution of test-to-test variability may be a result of volatile organic PM for the Lower PM Source.
- The Higher PM Source also showed a relatively large variability (~2 times from 1.2 to 2.1 mg/mi over the FTP cycle) during the screening testing. Most of this variability appeared to be vehicle related but it could be due to environmental conditions as well.
- The PM emissions appeared to drift during the screening testing for both vehicles; however, t-tests do not indicate this drift to be outside the scope of natural variability. During the confirmation testing, upon which the major study conclusions are based, the vehicles demonstrated more stabilized PM emissions.

Future work

The E-99 project revealed several confounding influences for the quantification of vehicle PM emissions that suggest areas for further investigation. These include:

- Understanding test-to-test variability, which could exceed 100% between tests conducted over a 12 month time period.
- PFSS to CVS comparisons, where a 5-10% absolute bias was reported.
- Characterizing PFSS dilution factors to identify possible sources of bias between CVS and PFSS.
- Understanding sample contamination between tests where excessive exhaust temperatures may contribute to PM emissions variability.

To address these issues future tests should evaluate differences between different PFSSs, noise sources, PFSS and CVS tunnel conditioning, sensitivity to exhaust flow measurement, sample proportionality issues, sample proportionality modeling, PFSS advantages and disadvantages, and overall improvements recommended for both CVS and PFSS.