

February 15, 2001

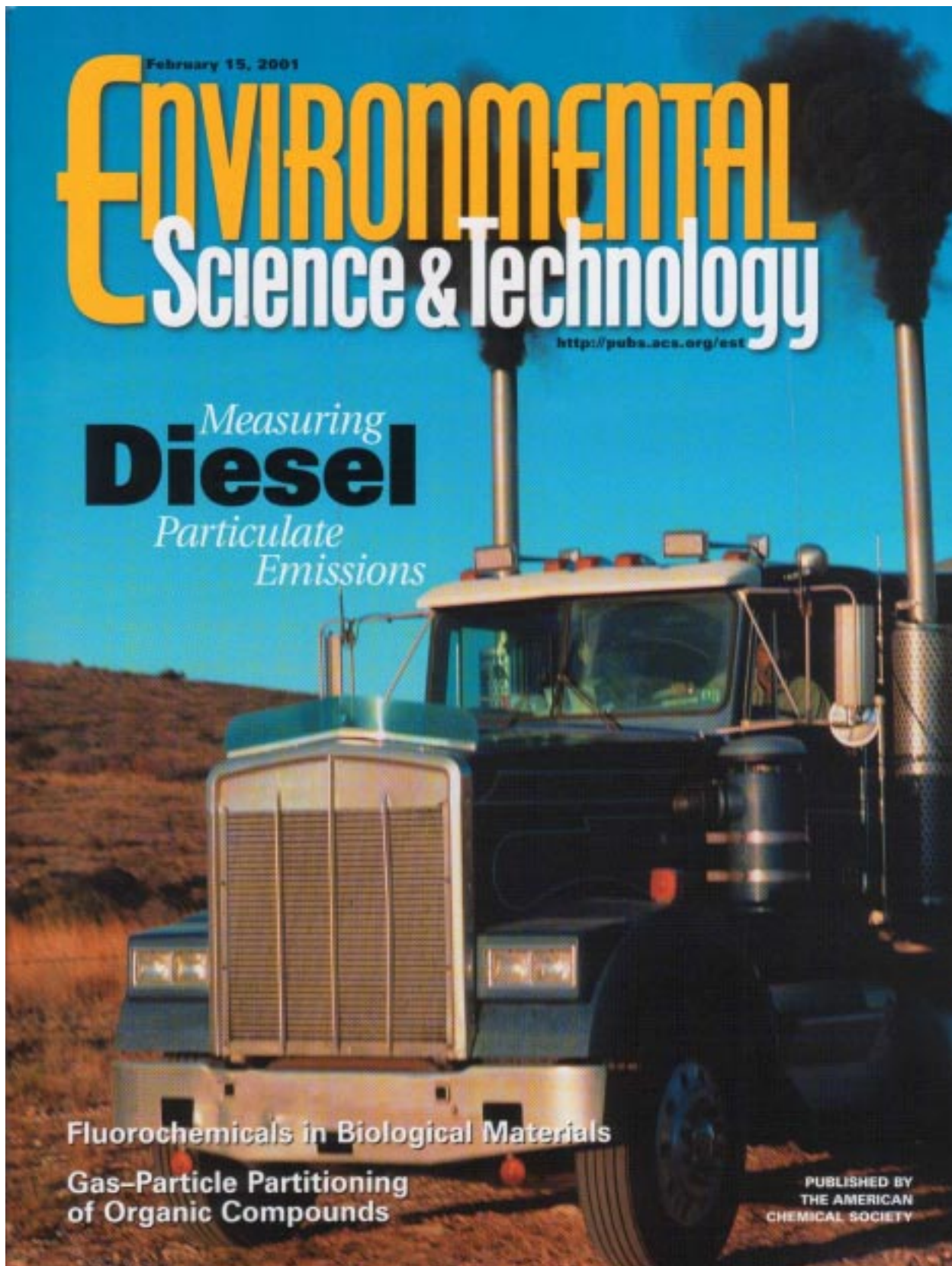
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Measuring
Diesel
*Particulate
Emissions*

Fluorochemicals in Biological Materials
Gas-Particle Partitioning
of Organic Compounds

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To assess diesel vehicle particulate mass emissions in a timely manner as function of engine operating conditions and driving mode, instruments having a time resolution of about 1 second are needed. This is important because much greater particulate mass emissions occur during transient operation, such as hard acceleration, than during steady driving conditions. Despite this requirement, commonly used tests depend on instruments yielding results taking anywhere from minutes to hours to obtain and that often provide poor temporal resolution during transient engine operating conditions. As discussed in "[Time Resolved Characterization of Diesel Particulate Emissions](#)", H. Moosmüller and colleagues at the Desert Research Institute, in Reno, Nevada and J. Collins and colleagues at the University of California, Riverside address this problem by investigating and reporting their evaluation of five promising fast response instruments.

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Time Resolved Characterization of Diesel Particulate Emissions. 1. Instruments for Particle Mass Measurements

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The measurement of diesel vehicle exhaust particulate mass is currently accomplished using filter collection methods according to the Code of Federal Regulations (CFR). Such filter methods limit time resolution to a minimum of several minutes, making it impossible to study emissions during transient operating conditions. Extensive testing of five different measurement methods has demonstrated that fast response measurements of diesel exhaust particulate mass concentrations, consistent with CFR filter measurements, are feasible using existing technology. The measurement principles of choice are the real time weighing of exhaust samples as implemented in the tapered element oscillating microbalance (TEOM) and the measurement of light scattering from exhaust particles as implemented in the DustTrak nephelometer. Each of these two instruments has distinctive strengths. The TEOM excels in the area of constant calibration, independent of vehicle. For the DustTrak, this calibration varies by vehicle. On the other hand, the DustTrak has an excellent signal-to-noise ratio, freedom from interference due to other exhaust sample properties, good time resolution, and simplicity. The strengths of the two measurement methods are complimentary, so an obvious suggestion is to integrate them. The nephelometer would obtain a fast response signal, with near real time calibration provided by the microbalance.

Introduction

The measurement of diesel vehicle particulate mass emissions is commonly accomplished using Code of Federal Regulations (CFR) defined filter collection methods on exhaust sampled from a dilution tube (1, 2). To ensure reproducible measurement of volatile and semi-volatile components absorbed on the filter and on collected particles, the methods require that the filters equilibrate (usually 6–24 h) in a standard atmosphere at defined temperature and humidity levels before each mass determination (3). The time required for the CFR filter sample collection can vary from several minutes

to a few hours per filter, resulting in poor temporal resolution during transient engine operating conditions. Therefore, CFR filter methods are unable to determine particulate emission factors as function of speed, acceleration, and operating mode as needed for modal emission models. All together, the minimum time needed to obtain a mass emission value for a specific experiment is about 1 day.

To study diesel vehicle particulate mass emissions as function of engine operating condition and driving mode, instruments with a time resolution on the order of 1 s are needed. This kind of time resolution is particularly important as significantly greater particulate mass emissions occur during transient operating conditions such as hard acceleration. In addition, real time or near real time data availability is desirable for the timely evaluation of test results. Driving distance-based mass emission rates can be calculated from these concentrations if vehicle speed and tunnel flow rates are known.

Evaluation of such fast response instruments is nontrivial as neither reference measurement methods nor reference sources exist. Criteria that can be used for evaluation include (i) degree of correlation of time-integrated results with CFR filter measurements, (ii) reproducibility, (iii) noise and interference from nonparticulate mass sample properties, (iv) time resolution, and (v) simplicity and cost.

Five promising candidate methods (four optical, one inertial mass) were identified, and instruments based on these methods were developed or acquired. To test these fast response instruments, three diesel vehicles were operated on a chassis dynamometer using the Federal Testing Procedure (FTP) driving cycle. Particulate data were collected during these driving cycles with CFR filter methods and by the fast response instruments.

Experimental Section

Real Time Instrumentation. Five different methods with potential for yielding a simple, accurate, and user-friendly instrument for the fast response measurement of particle mass in diesel exhaust have been identified. These methods include an inertial mass measurement method (tapered element oscillating microbalance, TEOM) and four optical methods: a light scattering method (nephelometer, DT); two light absorption methods, one that measures light absorption of aerosol deposited on a filter (aethalometer, AE) and one that measures light absorption in situ (photoacoustic instrument, PA); and a light extinction method (smoke meter, SM). Some of these methods have previously been used to measure diesel particulate mass emissions. The five instruments are described in the following sections.

Tapered Element Oscillating Microbalance (TEOM Series 1105). A continuous measurement of the inertial mass of aerosol deposited on a filter substrate has been implemented using tapered element oscillating microbalance technology (4, 5). This technology utilizes a hollow tube with the wide end of the tapered tube fixed. The narrow end of the tube holds a filter cartridge, and a sample is passed through the filter and tube to a flow controller. The tube-filter unit acts as a simple harmonic oscillator with its oscillating frequency being a function of filter mass loading. The system can be calibrated by placing a calibration mass on the filter and recording the frequency change due to this mass (6). As the oscillating frequency is a function of temperature, the tapered tube, filter, and sampled air are temperature stabilized, typically at 50 °C. The heating prevents condensation and provides a standard sample conditioning in respect to the removal of semi-volatile components. However, this aerosol

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conditioning is different from CFR filter sampling techniques and may remove more volatile compounds due to heating (7–14).

A commercially available TEOM designed for the real time measurement of diesel particulate mass (Rupprecht & Patashnick Co., Inc. TEOM Series 1105) has been used in this study (7, 14–16). While this TEOM is capable of operating with a time resolution of 0.5 s, for our work it has been operated with a time resolution of 3 s for an improved signal-to-noise ratio.

Nephelometer (TSI DustTrak 8520). Nephelometers measure light scattered by aerosol introduced into their sample chamber. Nephelometers can be fairly simple and compact instruments with excellent sensitivity and time resolution. However, scattering per unit mass is a strong function of particle size and refractive index. If particle size distributions and refractive indices in diesel exhaust strongly depend on the particular engine and operating condition, this may not be an effective way to measure exhaust particle mass. However, it has been shown that mass scattering efficiencies for both on-road diesel exhaust and ambient fine particles have values around $3 \text{ m}^2/\text{g}$ (17–19). Mass scattering efficiencies for diesel exhaust sampled from a dilution tunnel may be significantly lower (18).

For this project, a TSI DustTrak 8520 nephelometer (DT) measuring 90° light scattering at 780 nm (near-infrared) was used. This instrument displays its measurement as mass density (i.e., units of mg/m^3) through a calibration with ISO 12103-1, A1 test dust. The DustTrak is a very practical, compact, and low-priced instrument.

Aethalometer (Anderson RTAA-800). The aethalometer measures optical aerosol absorption in real time by monitoring optical extinction through a filter tape while aerosol particles accumulate on the filter tape (20). Once the spot monitored on the filter tape exceeds a certain optical density, the instrument automatically advances the tape to a new spot. In this manner, the aethalometer can perform months of ambient monitoring without operator involvement. The measured extinction is reported as black carbon (BC) concentration after conversion with an empirically determined factor. Aethalometers are mostly utilized for ambient monitoring (21–23). They have also been operated with time resolution on the order of seconds for monitoring on-road EC emissions (24). Aethalometer measurements have been shown to correlate well with thermal EC measurements and photoacoustic measurements (25–28). However, there has been some discussion about the proper calibration factor (27). For this project, a single wavelength ambient aethalometer operating at 880 nm (Anderson RTAA-800) was used for the measurement of BC.

Photoacoustic Instrument (DRI PA). The photoacoustic instrument (PA) detects the absorption of a laser beam by aerosol placed in its acoustic resonator. The laser beam power is modulated at the acoustic resonant frequency. Light absorbing aerosol components, i.e., elemental carbon (EC), convert laser beam power to an acoustic pressure wave through heating, accompanied by gas expansion. An acoustic resonator amplifies this pressure wave by its quality (Q) factor. A microphone detects the acoustic signal that provides a measure of light absorption (29). Photoacoustic instruments have been used for the measurement of automotive particle emissions for more than 2 decades (18, 30–38). The particle mass absorption efficiency is independent of particle size for size parameters smaller than the wavelength of light (32). Therefore, a measurement of aerosol absorption results directly in a measurement of EC particle mass independent of particle size. As EC constitutes a sizable part of diesel particulate mass emissions, this makes the photoacoustic absorption measurement a potential surrogate for a direct mass measurement.

TABLE 1. Diesel Vehicles Used

	1999 Ford F250 S.D.	1996 Dodge RAM 2500	1988 Ford F250
engine	7.3 l Navistar	5.9 l Cummins	7.3 l Navistar
injection type	direct	direct	indirect
turbo loaded	yes	yes	no
transmission	4-speed auto	4-speed auto	3-speed auto
catalytic converter	oxidation	oxidation	none
weight (lb)	7500	7000	6500
mileage	20133	18336	79947

The photoacoustic instrument used for this work operates at a laser wavelength of 532 nm (i.e., green) and with a laser power of 75 mW. It is an improved version of a prototype instrument previously used for ambient measurements (28, 29).

Smoke Meter (DRI SM). Smoke meters are based on the extinction of light by particles. To get a measurable change in extinction, the sensing volume must contain a large particle concentration. This makes these instruments less suitable for ambient measurements in clean environments, while they are commonly used for emission measurements. Total extinction is the sum of absorption and scattering extinction and can be a function of both particle composition and size. Smoke meters have been previously used with good success for the measurement of diesel particulate mass emissions (18, 34).

A custom smoke meter tailored for diesel emission measurements has been built for this project. This instrument utilizes a 670-nm, 3-mW diode laser as light source and a large-area photodiode as detector. The time response is set to 1 s through the photodiode amplifier. The detector signal is digitized, recorded, and analyzed by a personal computer.

Dynamometer Facility and Particle Sampling. Instrument testing was done at the Vehicle Emissions Research Laboratory (VERL) of Bourns College of Engineering—Center for Environmental Research and Technology (CE-CERT) at the University of California, Riverside. A Pierburg positive displacement pump—constant volume sampler (PDP—CVS) exhaust gas dilution system was used to sample exhaust. A 12-in. dilution tunnel dedicated to diesel sampling was utilized for particulate emission measurements. This dilution tunnel was fitted with three isokinetic particulate sampling probes to accommodate simultaneous collection of multiple samples. Two isokinetic probes were used for drawing filter samples from the dilution tunnel. The five continuous aerosol monitors sampled from the third isokinetic probe via a sample distribution manifold. Filter and instrument flows were audited using standard DRI field performance audit procedures. All measurements were corrected to standard atmospheric density (i.e., 1013 mB, 293 K).

Results and Discussion

Measurement Overview. Two modern vehicles (1996 Dodge and 1999 Ford; Table 1) and an older vehicle (1988 Ford; Table 1) were operated according to the FTP driving cycle for instrument testing (2). The older vehicle was used during only one driving cycle to determine if the instruments are applicable to diesel engines based on older technology. The FTP consists of three phases. Phase 1 begins with a cold start and is directly followed by phase 2, which is followed by a hot soak and phase 3, which is a repeat of phase 1, but with a hot start. Normally, one filter is used per phase to determine time-integrated particulate mass emissions. To obtain more filter data for comparison with real time measurements, each phase was subdivided into three segments and one filter per segment was used, yielding nine filter measurements of

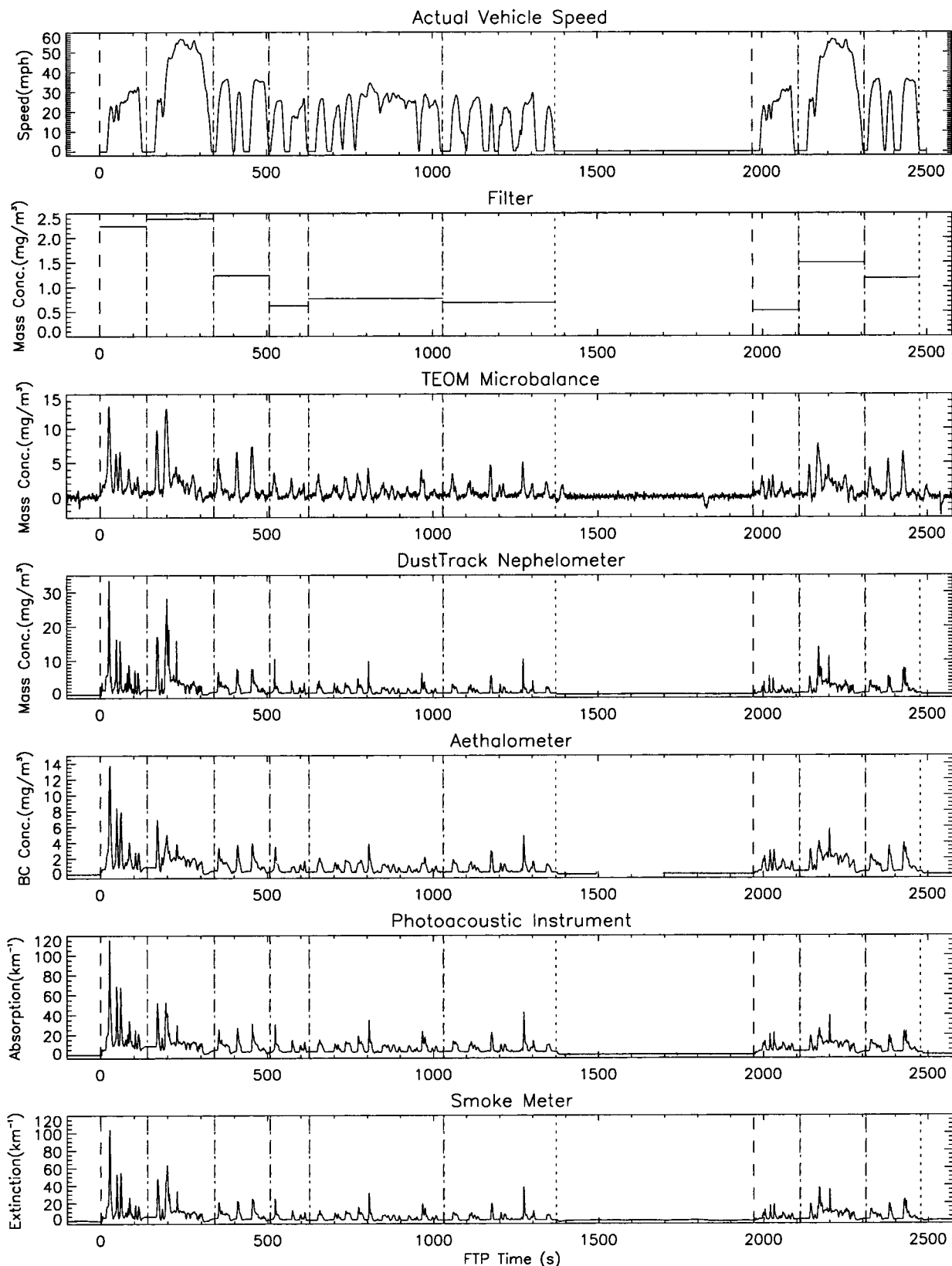


FIGURE 1. Example of speed, CFR filter, and fast response particulate measurements for the 1996 Dodge.

particulate mass emissions per FTP. Sampling was switched between filters at zero vehicle velocity, i.e., while the vehicle was standing still. The timing of the individual segments is shown in Figure 1 (top panel) together with vehicle speed as function of time. As only one FTP driving cycle can be run for each vehicle per day, LA4 driving cycles (FTP phase 1

with hot start followed by FTP phase 2) were used for tests of instrument response to nonparticulate emissions.

All tested vehicles were fueled with "California Equivalent Fuel", i.e., with fuel from an arbitrary California gas station. To test for any unusual fuel properties, a 1-L sample was drawn from each vehicle and submitted for testing and

chemical analysis. The fuel was in general compliance with California standards. Exceptions were some distillation specifications for all three samples and excessive nitrogen content for the sample from the 1988 Ford.

Diesel particulate mass emissions were characterized during 10 FTP cycles with five fast response instruments and CFR filter measurements. With the exception of the aethalometer, the instruments recorded complete data sets during all FTP cycles. The filter of the TEOM was exchanged before each cycle to reduce filter loading and potential interferences from semi-volatile particles collected during a previous cycle. The three in-situ optical instruments (PA, SM, and DustTrak) were operated without maintenance, cleaning, or requiring supplies. No deterioration of their measurement capabilities or visible deposition of particles in the instruments was observed over the course of the testing period. The aethalometer was not able to sample exhaust from the CE-CERT dilution tunnel directly as it is an ambient measurement instrument designed for high sensitivity and low aerosol concentrations. A secondary dilution system was built and optimized. Toward the end of the testing program, it was possible to collect complete aethalometer data sets without gaps resulting from tape advances. The secondary dilution system introduces additional errors into the aethalometer measurements due to uncertainties in the value of its dilution ratio.

An example of fast response and CFR filter measurements of diesel particulate emissions together with actual vehicle speed and filter timing is shown in Figure 1 for the 1996 Dodge. The highest particulate concentrations occur during the accelerations around 25 and 200 s into the FTP, resulting in peak particulate concentrations between 1 and 2 orders of magnitude higher than CFR filter mass concentrations. Only much smaller concentrations are recorded in phase 3 after the hot soak. This behavior, indicative of the warm-up of the catalytic converter, has also been observed in CO and THC traces, but not in the NO_x trace, as its simple oxidation catalyst does not reduce NO_x concentrations. Note that the ratio between different peaks is different for each of the individual real time instruments due to their different measurement methods. Similar traces of particulate measurements for the 1999 Ford do not show warm-up of the catalytic converter, and the highest particle concentrations occur during the hard accelerations around 25 and 2180 s into the FTP. For the older vehicle (1988 Ford), the filter sample-determined particulate mass concentrations are about an order of magnitude larger than for the newer vehicles. However, the real time measurement peaks are not substantially higher than for the newer vehicles. Instead the peaks are wider and more uniformly distributed over the different operating conditions, resulting in higher time-integrated emissions. These qualitative observations imply that time-resolved data are essential for correlating particle emissions with specific engine operating regimes or driving modes.

Reproducibility. One of the criteria for a good instrument is the precision of its measurements, i.e., the requirement that its measurements are reproducible. Lacking a calibrated source of diesel exhaust with well-defined reproducibility, measurements during multiple FTP cycles were performed for the 1999 Ford (4 FTP cycles) and the 1996 Dodge (5 FTP cycles). For the aethalometer, not enough data were available for this statistical analysis. As the vehicles themselves have somewhat different emissions during each FTP cycle, reproducibility was judged in comparison to the CFR filter method. Fast response measurements were integrated over the nine filter collection segments of each FTP, and averages and standard deviations were calculated for each segment, yielding nine averages and nine standard deviations for each vehicle. These values were averaged for each vehicle over

TABLE 2. Reproducibility of Particle Mass Measurements

	CFR filter (mg/m ³)	TEOM (mg/m ³)	DT (mg/m ³)	PA (km ⁻¹)	SM (km ⁻¹)
1999 Ford					
weighted average	2.01	1.89	2.41	15.01	12.88
SD	0.17	0.09	0.13	0.49	1.20
coeff of variation (%)	8.6	4.8	5.5	3.3	9.3
normalized coeff of variation (%)	100	57	64	39	109
1996 Dodge					
weighted average	1.35	1.13	1.77	7.66	6.62
SD	0.25	0.15	0.23	0.39	1.13
coeff of variation (%)	18.6	13.0	12.8	5.1	17.1
normalized coeff of variation (%)	100	70	69	28	92

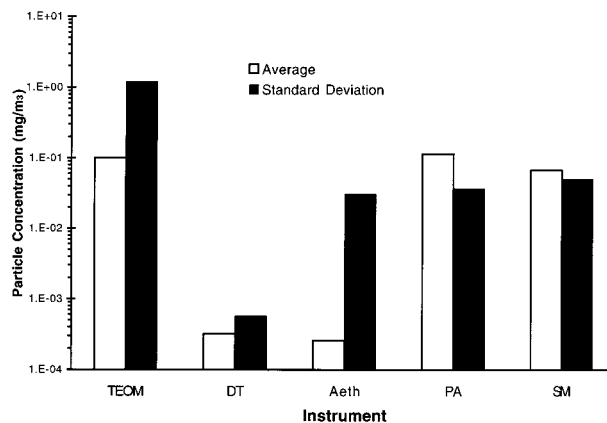


FIGURE 2. Fast response measurements of particle concentrations for particle free exhaust.

the nine segments, weighted by the duration of each segment. Results and the ensuing coefficients of variation are shown in Table 2. Four of the fast response instruments had a comparable (i.e., SM) or significantly smaller (i.e., DT, TEOM, and PA) coefficient of variation as compared to the CFR filter method. This means either that statistical errors are larger for the filter method or that some fast response instruments do not record changes in particle mass concentrations as well as the CFR filter method.

Characterization of Interferences. Instruments for the measurement of particle mass emissions may be sensitive to other properties of the sampled exhaust such as gaseous composition, temperature, and pressure. Such interferences have been characterized during LA4 driving cycles after removing all particles from the exhaust sample with two "HEPA" filters in series. The capture efficiency of these commercial, high-capacity HEPA filters was verified by a condensation particle counter directly downstream from them. With particles removed from the exhaust sample, each fast response instrument still registers some signal. Averages and standard deviations (to characterize fluctuations) of these signals were calculated for each segment of the LA4 driving cycle. Results are summarized as averages over the individual test segments in Figure 2. Values for two optical instruments (PA, SM) were converted from the inverse distance to particle mass concentration with an estimated conversion factor of 10 m²/g and should therefore only be used qualitatively.

The DustTrak has by far the smallest interference from nonparticulate sources. Its average signal and standard deviation are comparable in magnitude. Most of the time, the DustTrak reads 0 mg/m³. Sometimes its zero calibration is not perfectly stable, and it switches to one of its smallest readings of ±0.001 mg/m³. Occasionally a higher reading is observed, which generally consists of a single data point.

TABLE 3. Correlation of Time-Averaged Fast Response Data with CFR Filter Data

	TEOM	DT	AE	PA	SM
Newer Vehicles					
slope	0.88	1.3	0.64	4.7 m ² /g	4.8 m ² /g
offset	0.04 mg/m ³	-0.09 mg/m ³	0.55 mg/m ³	3.2 km ⁻¹	1.3 km ⁻¹
R ²	0.87	0.87	0.48	0.59	0.74
1988 Ford					
slope	0.80	0.55	0.18	0.65 m ² /g	0.81 m ² /g
offset	-0.23 mg/m ³	1.7 mg/m ³	1.98 mg/m ³	23.3 km ⁻¹	15.0 km ⁻¹
R ²	0.98	0.98	0.80	0.37	0.57
All Vehicles					
slope	0.77	0.65	0.27	2.1 m ² /g	1.7 m ² /g
offset	0.21 mg/m ³	1.0 mg/m ³	1.2 mg/m ³	7.7 km ⁻¹	6.7 km ⁻¹
R ²	0.98	0.89	0.65	0.65	0.65

Overall, its performance is excellent in respect to gaseous interferences.

Readings from the other four instruments are often correlated with each other especially for larger values. This indicates that these instruments are not just noisy but that other physical exhaust properties interfere. The aethalometer has a very low average reading, while its 2 orders in magnitude larger standard deviation indicates fluctuations around zero with a positive peak generally being followed by a negative one. The TEOM data also exhibit negative peaks after positive ones. However, the magnitude of this effect is more than an order in magnitude larger for the TEOM than for the aethalometer. No such oscillatory behavior is observed for the other instruments. The aethalometer and TEOM are the only instruments depositing particles on a filter and calculating time-resolved properties by differentiation with respect to time. A positive peak followed by a negative one could be interpreted as material being deposited or condensed on the filter and subsequently being removed.

The photoacoustic instrument and the smoke meter both have relative high average values combined with smaller standard deviations. In the case of the photoacoustic instrument, the relatively large average is most likely due to the optical absorption by nitrogen dioxide (NO₂) at its green operating wavelength (i.e., 532 nm). Operation at a different laser wavelength in the near-infrared (i.e., 1047 nm) with negligible gaseous absorption has been shown effective in removing this interference. For the smoke meter, operating in the red at 670 nm, NO₂ interference is about 1 order of magnitude smaller than at 532 nm and does not explain most of this interference.

The TEOM average is about as high as those of the photoacoustic instrument and smoke meter, and its standard deviation is by far the highest of all instruments. Its signal is relatively noisy and seems susceptible to interference from temperature and pressure fluctuations, semi-volatile material depositing on its filter, and vibration. Some of these effects can be observed in the FTP data shown in Figure 1. During the hot soak, the TEOM has by far the noisiest signal. During this period, a negative TEOM signal coincides with the turn-on of the dilution tunnel pump. Similarly, the pump turn-on before and turn-off after the FTP cycle coincide with sizable TEOM signals. Negative TEOM signals are common and may represent the evaporation of semi-volatile material from the TEOM filter and temperature and pressure fluctuations.

It should be kept in mind that these interferences are small as compared to particulate signals observed here. During FTP cycles, peak signals of tens of milligrams per cubic meter and average signals of a few milligrams per cubic meter are common, resulting in good signal-to-noise ratios for most instruments and an adequate signal-to-noise ratio for the TEOM.

Correlation with CFR Filter Methods. The correlation of real time measurements with CFR filter measurements indicates the degree to which the five fast response instruments can serve as fast response replacement for CFR filter measurements. If the correlation is good, the values of the slope and offset can be used as calibration coefficients for the individual instruments. These calibration coefficients may be valid only for an individual vehicle, a class of vehicles, or all vehicles. Coefficients that vary between vehicles result in a poorer correlation if different vehicles are included in a single correlation analysis by linear regression. Correlations of FTP data are presented for the newer vehicles (i.e., 1996 Dodge and 1999 Ford), for the 1988 Ford, and for all vehicles.

Three of the instruments (i.e., DustTrak, TEOM, and AE) yield measurements with the same dimension as the CFR filter measurements (i.e., particle mass/gas volume) and units of milligrams per cubic meter are used. This results in slopes of unit one (1) and offsets of unit milligrams per cubic meter. The other two instruments (i.e., SM and PA) yield measurements with dimensions of inverse distance and units of 1/km are used. This results in slopes of m²/g and offsets of 1/km. The slope value can be interpreted as the extinction and absorption efficiency of the emitted particles for the smoke meter and photoacoustic instrument, respectively.

Newer Vehicles. For the newer vehicles (i.e., the 1999 Ford and 1996 Dodge), the best correlation with the CFR filter mass is achieved by the DustTrak nephelometer and the TEOM microbalance (R² = 0.87; see Table 3). Both regressions have very small zero offsets and slopes of 1.3 for the DustTrak and 0.88 for the TEOM. These slopes reflect DustTrak calibration with a different aerosol and potential losses of semi-volatile particles for the TEOM. The light absorption instruments (i.e., PA and AE) have relatively poor correlation coefficients (0.59 for PA and 0.48 for AE) and moderate zero offsets. The slope of the photoacoustic instrument (i.e., absorption efficiency) is a reasonable 4.7 m²/g and the aethalometer slope is 0.64, in general agreement with the EC mass content of diesel particulate emissions. The correlation coefficient of the smoke meter ranks again between those of the nephelometer and photoacoustic instrument, reflecting its sensitivity to both particle scattering and absorption. The corresponding zero offset is small (1.3 km⁻¹) and the extinction efficiency (slope = 4.8 m²/g) is reasonable.

1988 Ford. For the 1988 Ford, the DustTrak and the TEOM have the best correlation with CFR filter measurements, both with excellent correlation coefficients (R² = 0.98; see Table 3). Zero offsets are small for the TEOM (i.e., -0.23 mg/m³) and moderate for the DustTrak (i.e., 1.7 mg/m³). The slope for the TEOM (0.80) is comparable to that for the newer vehicles (0.87), while the slope for the DustTrak (0.55) is more than two times smaller than for the newer vehicles (1.3). This

indicates that the fraction of semi-volatile mass is comparable for all three vehicles, while the mass scattering efficiency (in m^2/g) as measured by the DustTrak is substantially smaller for the 1988 Ford than for the newer vehicles. The aethalometer results also correlate well with the CFR filter mass ($R^2 = 0.80$); however, only 4 (out of 9) data points were available, making this less meaningful. The slope is about 2.5 times smaller than for the newer vehicles, and the aethalometer zero offset is quite large as compared to the small slope. For the smoke meter (SM) and photoacoustic instrument (PA), the correlations with the CFR filter mass are relatively poor (0.57 and 0.37, respectively) and the zero offsets are quite large. The slopes (absorption efficiencies) are in these cases about five times smaller than for the newer vehicles. These results indicate that the particles emitted by the 1988 Ford have a lower scattering efficiency and much lower absorption and extinction efficiencies than for the newer vehicles.

All Vehicles. Grouping all three vehicles together and judging the correlation between averaged fast response and CFR filter measurements indicates how applicable these methods are, with a single calibration, for this class of vehicles. Particulate mass emission rates are nearly an order of magnitude larger for the 1988 Ford than for the newer vehicles. Performing linear regression analysis on the data set including measurements for all three vehicles results in a slope, which is largely determined by the 1988 Ford values, a zero offset largely determined by the small values from the newer vehicles, and a correlation coefficient that indicates the overall ability to calibrate the respective measurement method for these diverse data. Note that the single FTP results for the 1988 Ford have a disproportionate influence on all linear regression results. The regression line connects the "near-zero" cluster of measurements for the newer vehicles with the few high value measurements for the 1988 Ford. For all instruments, with the exception of the TEOM, one clearly sees a slope within this near-zero cluster, different from the overall regression slope. The TEOM measurements have excellent correlation with the CFR filter mass measurements, showing by far the highest correlation coefficient ($R^2 = 0.98$; see Table 3) of all real time instruments. The TEOM zero offset is very small ($0.21 \text{ mg}/\text{m}^3$) and the slope is 0.77 indicative of the loss of some semi-volatile material. The excellent correlation coefficient reflects the near constant regression results of the TEOM data for all three vehicles. While the DustTrak had similar correlation coefficients as the TEOM in all other regressions, its substantially lower scattering efficiency (slope) for the 1988 Ford reduces the correlation coefficient when all measurements are analyzed together. While its correlation coefficient of 0.89 is still very good, it reflects the need for individual, vehicle-dependent calibration for this instrument. The DustTrak slope of 0.65 is largely determined by the 1988 Ford slope of 0.55, and its zero offset is small ($1.0 \text{ mg}/\text{m}^3$). The smoke meter, photoacoustic instrument, and aethalometer have identical correlation coefficients of $R^2 = 0.65$, moderate offsets, and small slopes, indicating that these instruments respond to only a fraction of the exhaust mass, likely the elemental carbon component.

Overall Instrument Evaluation. From the measurements and analysis presented above, it can be concluded that real time measurements of diesel exhaust particulate mass concentrations, consistent with CFR filter measurements, are feasible using existing technology. The measurement principles of choice are the real time weighing of exhaust samples as implemented in the TEOM and the measurement of light scattering from exhaust particles as implemented in the DustTrak nephelometer. Each of these two instruments has distinctive strengths. The TEOM excels in the area of constant calibration, independent of vehicle, relative to CFR

filter mass measurements. For the DustTrak, this calibration varies by vehicle (type). However, it compensates for this weakness with an excellent signal-to-noise ratio, freedom from interference due to other exhaust sample properties, good time resolution, simplicity, and low price. The strengths of these two instruments are quite complimentary, so an obvious suggestion is to operate them together to utilize the strengths of each instrument. The DustTrak would obtain the high time resolution signal, with high signal-to-noise ratio, while the TEOM would be used to calibrate this signal in near real time, say every 30 s. Adding a light scattering detector to the TEOM would fulfill the same purpose and yield a more integrated instrument.

Acknowledgments

This research was supported in part by the U.S. Department of Energy under Cooperative Agreement DE-FC02-98EE50563, by the National Science Foundation under Grant ATM-9871192, and by the Applied Research Initiative of the State of Nevada.

Literature Cited

- (1) Protection of the Environment. *Code of Federal Regulations*, Title 40, CFR 86.110-82, 1995; pp 542–548.
- (2) Protection of the Environment. *Code of Federal Regulations*, Title 40, CFR 86.130–86.142, 1995, pp 613–656.
- (3) Protection of the Environment. *Code of Federal Regulations*, Title 40 CFR 86.112-91, 1995, pp 570–571.
- (4) Patashnick, H.; Hemenway, C. L. *Rev. Sci. Instrum.* **1969**, *40*, 1008–1011.
- (5) Patashnick, H.; Rupperecht, E. G. *J. Air Waste Manage. Assoc.* **1991**, *41*, 1079–1083.
- (6) Horodecki, J.; Fissan, H. *Staub-Reinhalt. Luft* **1996**, *56*, 5–10.
- (7) Shore, P. R.; Cuthbertson, R. D. *SAE Tech. Pap. Ser.* **1985**, No. 850405.
- (8) Allen, G.; Sioutas, C.; Koutrakis, P.; Reiss, R.; Lurmann, F. W.; Roberts, P. T. *J. Air Waste Manage. Assoc.* **1997**, *47*, 682–689.
- (9) Patashnick, H. *J. Air Waste Manage. Assoc.* **1998**, *48*, 195–197.
- (10) Allen, G. *J. Air Waste Manage. Assoc.* **1998**, *48*, 197–199.
- (11) Patashnick, H. *J. Air Waste Manage. Assoc.* **1998**, *48*, 199–200.
- (12) Rogers, C. F.; Watson, J. G.; Day, D.; Oraltay, R. G. *Aerosol Sci. Technol.* **1998**, *29*, 557–562.
- (13) Allen, G. A. *Aerosol Sci. Technol.* **1998**, *29*, 563–565.
- (14) Okrent, D. A. *SAE Tech. Pap. Ser.* **1998**, No. 980409.
- (15) Whitby, R.; Johnson, R.; Gibbs, R. *SAE Tech. Pap. Ser.* **1985**, No. 850403.
- (16) Patashnick, H. *Diesel Prog. N. Am.* **1987**, *41*, 1079–1083.
- (17) Pierson, W. R.; McKee, D. E. *J. Air Pollut. Control Assoc.* **1978**, *28*, 604–607.
- (18) Japar, S. M.; Szkarlat, A. C.; Pierson, W. R. *Sci. Total Environ.* **1984**, *36*, 121–130.
- (19) Waggoner, A. P.; Weiss, R. E.; Ahlquist, N. C.; Covert, D. S.; Will, S.; Charlson, R. J. *Atmos. Environ.* **1981**, *15*, 1891–1909.
- (20) Hansen, A. D. A.; Rosen, H.; Novakov, T. *Sci. Total Environ.* **1984**, *36*, 191–196.
- (21) Hansen, A. D. A.; Novakov, T. *Global Biogeochem. Cycles* **1988**, *2*, 41–45.
- (22) Bodhaine, B. A. *J. Geophys. Res.* **1995**, *100*, 8967–8975.
- (23) Wolff, E. W.; Cachier, H. *J. Geophys. Res.* **1998**, *103*, 11033–11041.
- (24) Hansen, A. D. A.; Rosen, H. *J. Air Waste Manage. Assoc.* **1990**, *40*, 1654–1657.
- (25) Hansen, A. D. A.; McMurry, P. H. *J. Air Waste Manage. Assoc.* **1990**, *40*, 894–895.
- (26) Allen, G. A.; Lawrence, J.; Koutrakis, P. *Atmos. Environ.* **1999**, *33*, 817–823.
- (27) Lavanchy, V. M. H.; Gäggeler, H. W.; Nyeki, S.; Baltensperger, U. *Atmos. Environ.* **1999**, *33*, 2759–2769.
- (28) Moosmüller, H.; Arnott, W. P.; Rogers, C. F.; Chow, J. C.; Frazier, C. A.; Sherman, L. E.; Dietrich, D. L. *J. Geophys. Res.* **1998**, *103*, 28149–28157.
- (29) Arnott, W. P.; Moosmüller, H.; Rogers, C. F.; Jin, T.; Bruch, R. *Atmos. Environ.* **1999**, *33*, 2845–2852.
- (30) Truex, T. J.; Anderson, J. E. *Atmos. Environ.* **1979**, *13*, 507–509.
- (31) Faxvog, F. R.; Roessler, D. M. *J. Appl. Phys.* **1979**, *50*, 7880–7882.

- (32) Killinger, D. K.; Moore, J.; Japar, S. M. In *Laser Probes for Combustion Chemistry*; ACS Symposium Series 134; Crosley, D. R., Ed.; American Chemical Society: Washington, DC, 1980; pp 457–462.
- (33) Japar, S. M.; Szkarlat, A. C. *Combust. Sci. Technol.* **1981**, *24*, 215–219.
- (34) Japar, S. M.; Szkarlat, A. C. *SAE Tech. Pap. Ser.* **1981**, No. 811184.
- (35) Roessler, D. M. *Appl. Opt.* **1982**, *21*, 4077–4086.
- (36) Faxvog, F. R.; Roessler, D. M. *Aerosol Sci. Technol.* **1982**, *1*, 225–234.
- (37) Japar, S. M.; Moore, J.; Killinger, D. K.; Szkarlat, A. C. In *Light Absorption by Aerosol Particles*; Gerber, H. E., Hindman, E. E., Eds.; Spectrum Press: Hampton, VA, 1982; pp 275–278.
- (38) Roessler, D. M. *Appl. Opt.* **1984**, *23*, 1148–1155.

Received for review June 19, 2000. Revised manuscript received November 30, 2000. Accepted December 4, 2000.

ES0013935