

Time-Resolved Characterization of Diesel Particulate Emissions. 2. Instruments for Elemental and Organic Carbon Measurements

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The measurement of elemental carbon (EC) and organic carbon (OC) mass for particles emitted by diesel vehicles is currently accomplished using particle collection on filters, followed by analysis using the thermal/optical reflectance carbon analysis method (TOR) or one of its variations. Such filter methods limit time resolution to a minimum of several minutes, making it impossible to study emissions during transient operating conditions. Testing of five different measurement methods has demonstrated that fast response measurement of diesel exhaust particulate EC and OC concentrations, consistent with TOR filter measurements, is feasible using existing technology. EC mass concentrations are best measured through determination of particulate light absorption with a photoacoustic instrument or determination of light extinction with a smoke meter. The photoacoustic instrument has the better dynamic range and sensitivity, whereas the smoke meter is a simpler instrument. Fast response OC measurements cannot be made with any single instrument tested. However, a combination of real time weighing as implemented in the tapered element oscillating microbalance with the photoacoustic instrument has been shown to be capable of determining OC concentrations with good time response. The addition of a nephelometer to the OC measurement could potentially improve time resolution, freedom from interferences, and sensitivity.

Introduction

Particulate mass emitted by diesel engines consists mostly of carbonaceous material, with its two components elemental carbon (EC) and organic carbon (OC), and a typical particle size below $1\ \mu\text{m}$ with the particle mass distribution peaking at $\sim 0.1\ \mu\text{m}$ (1). The EC component does not consist of chunks of highly structured pure graphite but rather is a related, more complex three-dimensional array of carbon with small amounts of other elements. EC contains a number of

crystallites consisting of several carbon layers having the hexagonal structure of graphite (2). OC is a complex mixture of hundreds of organic compounds including numerous unidentified compounds (3).

The relative contributions of EC and OC to the total mass vary widely according to engine type, wear, and operating conditions, with EC contributions reported from 5 to 90% of the total particulate mass (4, 5). It is important to be able to quantify EC and OC contributions to diesel particulate emissions as they influence the environment in different ways due to their different optical, chemical, and toxic properties. For example, EC and OC influence radiative transfer in the atmosphere differently for the direct effect [i.e., scattering (mostly OC) and absorption (EC)] (6, 7), the semidirect effect (i.e., cloud evaporation due to absorption and heating by EC) (8, 9), and the indirect effect [i.e., acting as cloud condensation nuclei (mostly OC?)] (10–12). Carbonaceous aerosols also have a significant impact on atmospheric chemistry (13, 14), and light absorption by EC has been discussed as an indicator for aerosol toxicity (15–19).

EC and OC can be distinguished with the help of the refractory properties of EC using thermal/optical filter analysis methods, in which the optical component monitors and compensates for the pyrolysis (charring) of OC. A commonly used method is the thermal/optical reflectance (TOR) carbon analyzer developed by Huntzicker et al. (20). Our work uses a variation of this method as implemented in the DRI TOR instrument (21). Although all TOR instruments operate similarly, EC and OC are operationally defined, and the specific instrument used and details of its operation influence the split between EC and OC (22). TOR instruments perform batch analysis of particle samples accumulated on quartz fiber filters, resulting in limited time resolution and the delayed availability of analysis results. Continuous versions of the thermal method are available for ambient measurements (23–27), but their time resolution is worse than 30 min, clearly inadequate for diesel emission measurements. Therefore, thermal methods for EC/OC measurement are impracticable for the determination of EC/OC particulate emission factors as a function of speed, acceleration, and operating mode as needed for modal emission models. Modal emission modeling is essential for a more realistic description of automotive emissions, the derivation of improved emission inventories, and emission reduction through improved vehicle design and traffic planning.

To study diesel vehicle EC/OC particulate mass emissions as a 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.

Evaluation of such fast response instruments is nontrivial as neither reference measurement methods nor reference sources exist. Criteria that are used for this evaluation include (1) the degree of correlation of time-integrated results with TOR filter measurements, (2) noise and interference from nonparticulate mass sample properties, (3) time resolution, and (4) simplicity and cost.

During a recent test of five fast response instruments for the measurement of total particle mass (28), the opportunity arose to obtain TOR filter measurements of EC and OC during two Federal Testing Procedure (FTP) driving cycles. These measurements are described and analyzed in the following sections.

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In addition to the five methods evaluated here, an innovative use of a fast response heated flame ionization detector (FID) has recently been evaluated for the fast measurement of the particulate matter (PM) mass of soot and its soluble organic fraction (SOF) (29). This approach has yielded correlation coefficients of $R^2 = 0.8972$ with a conventional determination of diesel PM and of $R^2 = 0.6848$ with a conventional determination of SOF.

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 and its EC and OC components in diesel exhaust have been identified. These methods include an inertial mass measurement method [tapered element oscillating microbalance (TEOM), R&P TEOM series 1105] (30, 31) and four optical methods. The optical methods include a light scattering method [nephelometer, TSI DustTrak 8520 (DT)], two light absorption methods, one which measures light absorption of aerosol deposited on a filter [Aethalometer (AE), Anderson RTAA-800] (32, 33) and one which measures light absorption in situ [photoacoustic instrument (PA), DRI PA] (34), and a light extinction method [smoke meter (SM), DRISM]. These instruments report their measurements either as mass concentration (units of mg/m^3) or as absorption or extinction coefficients (units of km^{-1}), which are directly related to mass concentrations through an absorption or extinction efficiency. Driving-distance-based EC and OC mass emission rates can be calculated from these concentrations by considering vehicle speed and dilution tunnel flow rates. The principles of operation for the five fast response instruments have been summarized recently (28). Instrument calibration of the commercial instruments (i.e., TEOM, DT, and AE) has been performed by the manufacturer; calibrations of the photoacoustic instrument and the smoke meter come from first principles (35), with SM baseline calibration performed before and after each test run.

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, CA. A Pierburg positive displacement pump-constant volume sampler (PDP-CVS) exhaust gas dilution system was used to sample exhaust (36). A 30-cm-diameter 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 with gas temperatures at most instruments being near 300 K. The exception was the TEOM, with the TEOM sample conditioned at a temperature of 323 K. Dilution ratios in the CVS dilution tunnel were generally between 15 and 30, in some cases ranging up to 40. The aethalometer sample were diluted by additional factors of 9 for the 1996 Dodge and 16 for the 1999 Ford. Filter and instrument flows were audited using standard DRI field performance audit procedures. All measurements were corrected to a common atmospheric density (i.e., 101.3 kPa, 293 K).

Results and Discussion

Measurement Overview. Two modern diesel vehicles (direct injection, turbo-loaded engines, four-speed automatic transmission, oxidation catalyst) were operated for instrument testing according to the FTP driving cycle (37). One of these

vehicles was a 1996 Dodge Ram 2500 (vehicle weight = 3175 kg, odometer reading = 29509 km, 5.9 L Cummings engine); the other one was a 1999 Ford F250 SD (vehicle weight = 3402 kg, odometer reading = 32401 km, 7.3 L Navistar engine).

The FTP driving cycle consists of three phases: phase 1 begins with a cold start and is directly followed by phase 2, representing hot-stabilized driving, which is followed by a 10-min hot soak and phase 3, which is a repeat of phase 1, but with hot start. Normally, one filter is used per phase to determine time-integrated particulate EC/OC 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 particulate mass emissions per FTP. Sampling was switched between filters at zero vehicle velocity, that is, while the vehicle was standing still. The timing of the individual segments is shown in Figures 1a and 2a together with vehicle speed for both FTPs.

All tested vehicles were fueled with "California equivalent fuel," that is, 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 with the exception of some distillation specifications. The fuel sulfur content was 74 ppm for the 1996 Dodge and 85 ppm for the 1999 Ford.

Diesel EC/OC particulate emissions were characterized during two FTP cycles with five fast response instruments and TOR filter measurements. The filter of the TEOM was exchanged before each FTP cycle to reduce filter loading and potential interferences from semivolatile particles collected during a previous cycle. 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, making it possible to collect complete aethalometer data sets without gaps resulting from tape advances. This system splits the aethalometer sample flow into two branches; one of these has all aerosols removed by an absolute (i.e., HEPA type) filter before rejoining the other branch immediately upstream of the aethalometer inlet. The resulting dilution ratio is quantified with the help of a calibrated rotameter. The secondary dilution system introduces additional errors into the aethalometer measurements due to uncertainties in the measurement of its dilution ratio.

Interference from nonparticulate exhaust sample properties with the fast response measurements is extremely small for the DustTrak, small for the aethalometer, photoacoustic instrument, and smoke meter, and moderate for the TEOM (28). All of these interferences are small compared to particle signals observed here.

Correlation of Data from Individual Instruments with TOR EC/OC Filter Methods. The correlation of fast response measurements, time-averaged over filter sampling periods, with TOR EC and OC filter measurements indicates the degree to which any one of the five fast response instruments can serve as fast response replacement for TOR filter measurements. If the correlation is good, the values of the slope and offset can be used as calibration coefficients for the individual instruments. The results of TOR EC and OC filter measurements are shown in Figures 1b,d and 2b,d. Averaged over the FTP cycle, the TOR measurements correspond to emission rates of 29 ± 1 mg of EC/km and 35 ± 3 mg of OC/km for the 1996 Dodge and 75 ± 3 mg of EC/km and 36 ± 3 mg of OC/km for the 1999 Ford.

Three of the instruments (i.e., DT, TEOM, and AE) yield measurements with the same dimension as the TOR filter measurements (i.e., particle mass/gas volume), and units of mg/m^3 are used. This results in slopes of unit one (1) and

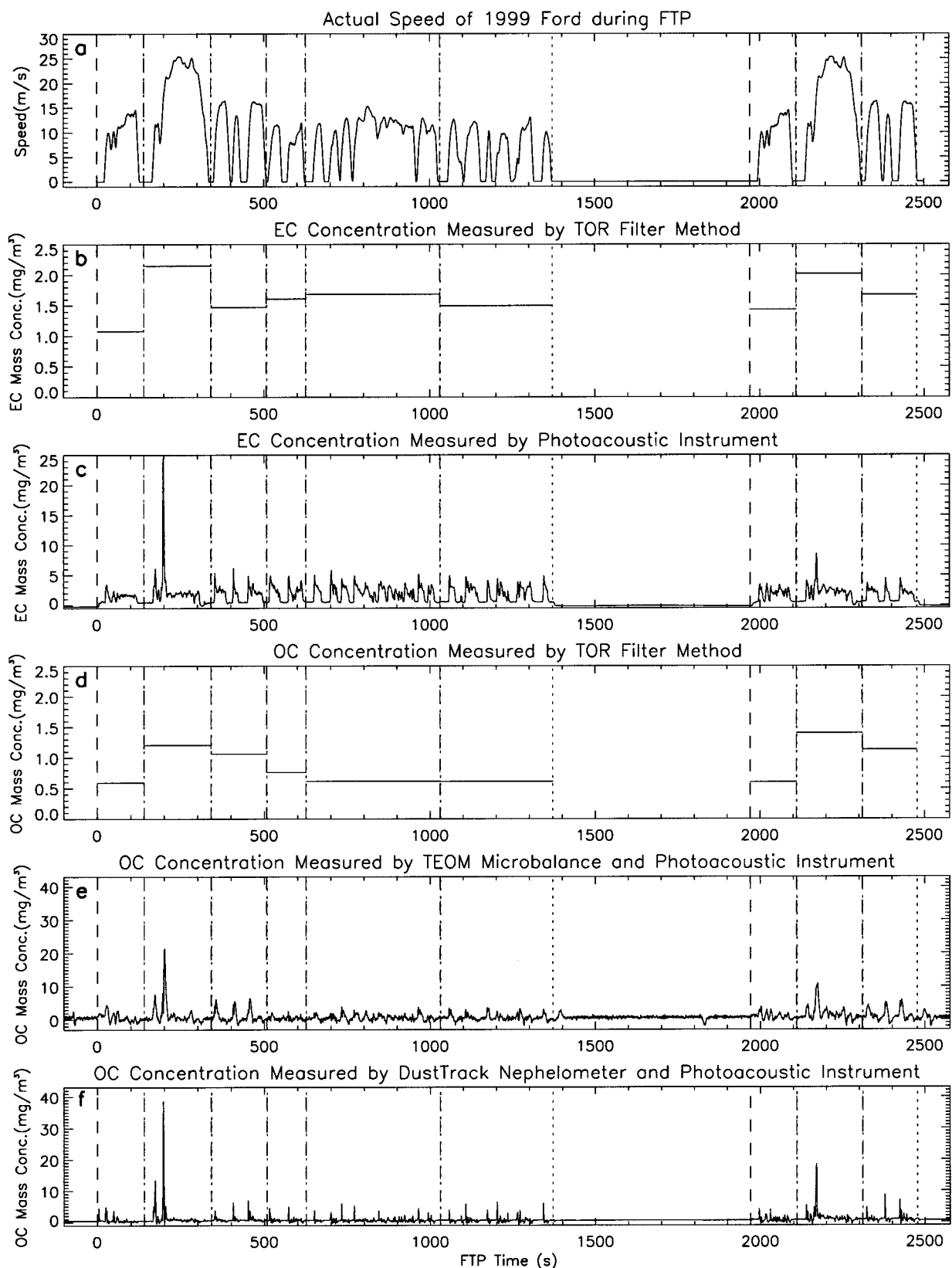


FIGURE 1. Vehicle speed, TOR filter, and fast response EC and OC concentrations for the 1999 Ford. Fast response measurements are calibrated to TOR measurements by eq 1b for EC and by eqs 2 for OC.

offsets of unit mg/m^3 . The other two instruments (i.e., SM and PA) yield measurements with dimensions of inverse distance, and units of km^{-1} are used. This results in slopes of unit m^2/g and offsets of unit km^{-1} . The slope value can be interpreted as the extinction and absorption efficiency of

the emitted particles for the smoke meter and photoacoustic instrument, respectively.

Correlation and regression coefficients calculated for TOR EC, OC, and EC + OC measurements are listed in Table 1. For EC, the best correlation with the TOR EC mass concen-

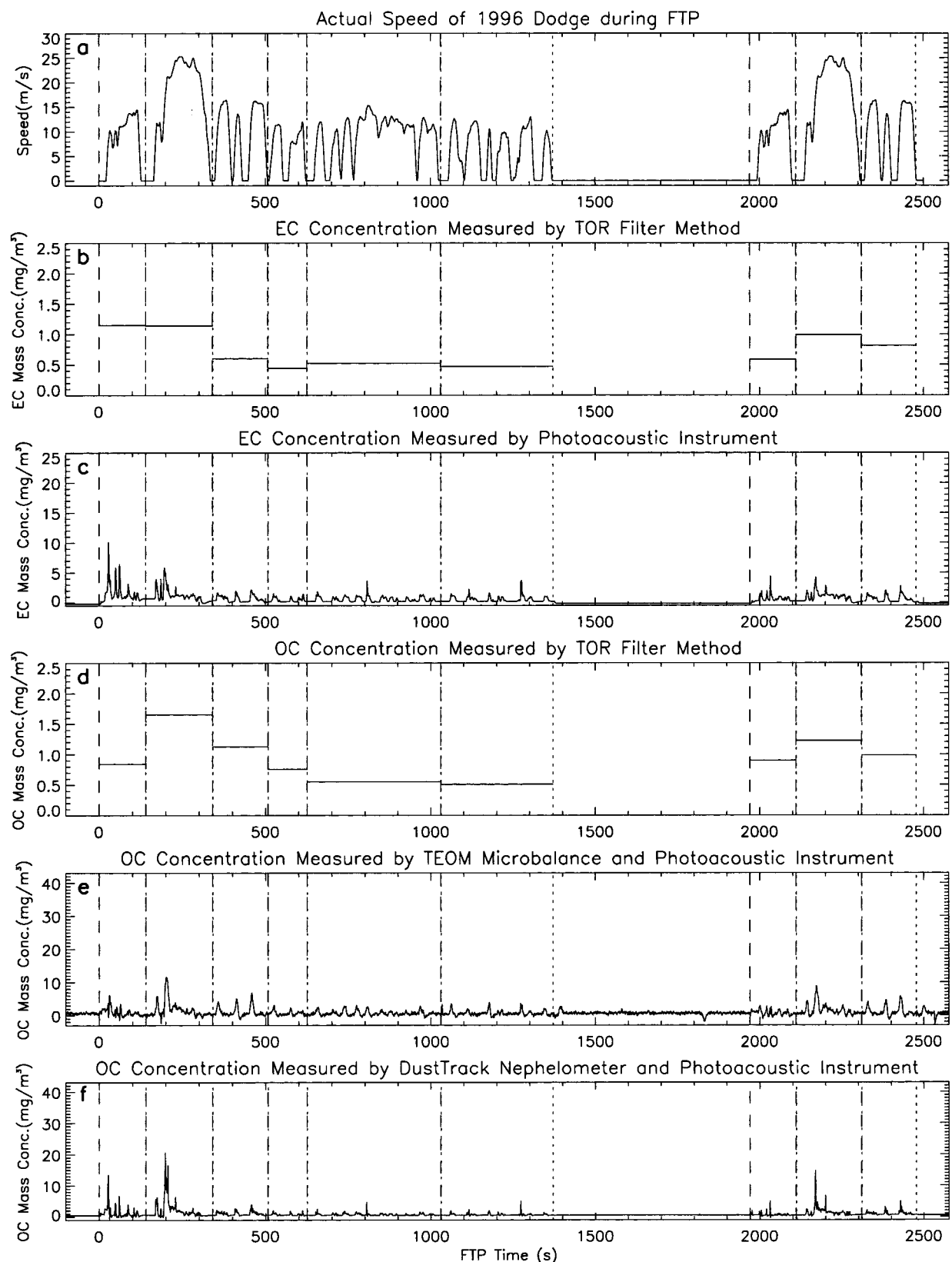


FIGURE 2. Vehicle speed, TOR filter, and fast response EC and OC concentrations for the 1996 Dodge. Fast response measurements are calibrated to TOR measurements by eq 1b for EC and by eqs 2 for OC.

tration is achieved by the absorption and extinction instruments, that is, aethalometer, photoacoustic instrument, and smoke meter ($R^2 = 0.91-0.92$). The TEOM correlation is comparable ($R^2 = 0.88$) and the DT correlation significantly

worse ($R^2 = 0.67$). For OC, measurements by the absorption and extinction instruments are essentially uncorrelated with TOR OC measurements (i.e., PA, $R^2 = 0.02$; AE, $R^2 = 0.02$; SM, $R^2 = 0.13$). The TEOM ($R^2 = 0.29$) and the DT ($R^2 = 0.41$) data

TABLE 1. Correlation of Fast Response Single-Instrument Data, Time-Averaged over Filter Sampling Periods, with TOR Filter Data^a

	TEOM	DT	AE	PA	SM
EC					
slope	1.13	1.38	1.41	8.47 m ² /g	7.05 m ² /g
offset	0.15 mg/m ³	0.50 mg/m ³	0.09 mg/m ³	1.66 km ⁻¹	0.77 km ⁻¹
R ²	0.88	0.67	0.92	0.92	0.91
OC					
slope	1.06	1.78	0.67	2.18 m ² /g	4.36 m ² /g
offset	0.52 mg/m ³	0.50 mg/m ³	1.15 mg/m ³	9.69 km ⁻¹	5.12 km ⁻¹
R ²	0.29	0.41	0.08	0.02	0.13
EC + OC					
slope	0.88	1.18	0.96	5.35 m ² /g	5.00 m ² /g
offset	-0.35 mg/m ³	-0.34 mg/m ³	-0.25 mg/m ³	0.44 km ⁻¹	-1.38 km ⁻¹
R ²	0.92	0.84	0.73	0.63	0.79

^a The TOR carbon concentration C (i.e., EC, OC, or EC+OC) can be approximated from the fast response measurements (FRM) as $C = \text{offset} + \text{slope} \times \text{FRM}$.

show some correlation with TOR OC measurements. As the correlation with TOR OC data is poor for all instruments, no single instrument can be recommended for fast response OC measurements. On the other hand, the three absorption and extinction instruments seem to be capable of measuring EC without interference from OC as shown by the very good correlation of their data with TOR EC data and the lack of correlation with TOR OC data. This is most pronounced for the photoacoustic instrument. This result comes as no surprise as light absorption measurements for particles much smaller than the instrument wavelength have a constant absorption efficiency, whereas extinction due to scattering is minimal. This is confirmed by the fact that the ratio of the smoke meter extinction efficiency (7.05 m²/g) and PA absorption efficiency (8.47 m²/g) of 0.83 about equals the inverse ratio of their operating wavelengths [i.e., 532 nm (PA) and 633 nm (SM)] of 0.84, in agreement with Mie theory if scattering extinction is negligible. Fast response EC concentrations can be calculated from data measured by these three instruments, expressing the regression results (Table 1) as

$$EC_{AE} = -0.062 \text{ mg/m}^3 + (AE/1.41) \quad (1a)$$

$$EC_{PA} = -0.196 \text{ mg/m}^3 + \frac{PA}{8.47 \frac{\text{m}^2}{\text{g}}} \quad (1b)$$

$$EC_{SM} = -0.109 \text{ mg/m}^3 + \frac{SM}{7.05 \frac{\text{m}^2}{\text{g}}} \quad (1c)$$

where EC_{AE} , EC_{PA} , and EC_{SM} are fast response EC concentrations (units of mg/m³), calculated from black carbon concentration AE (units of mg/m³), light absorption PA (units of km⁻¹), and light extinction SM (units of km⁻¹) data obtained by the three instruments. Fast response EC concentrations, averaged over the filter sampling periods, and their correlation with TOR EC filter concentrations are shown in Figure 3 for both vehicles together. The zero offset and slope of one of the regression line are obvious results of using the same data for calibration of the fast response EC measurements via eqs 1. Examples of resulting time-resolved EC_{PA} concentrations are shown in Figures 1c and 2c. Although TOR EC measurements (Figures 1b and 2b), even with nine filter samples per FTP cycle, yield little or no information about the correlation of EC emissions with vehicle speed and acceleration, EC measurements with the fast response photoacoustic instrument clearly can furnish this information. For example, for the 1999 Ford, the largest EC

TABLE 2. Correlation of Fast Response Dual-Instrument Data, Time-Averaged over Filter Sampling Periods, with TOR Filter Data

	R ²	
	TEOM	DT
AE	0.62	0.56
PA	0.82	0.74
SM	0.57	0.69

concentration is associated with the hard acceleration around 200 s, whereas for the 1996 Dodge, the largest EC concentration occurs during the first acceleration (around 25 s) after the cold start.

Both TEOM and DustTrak data correlate well with the sum of TOR EC and OC concentration (i.e., EC+OC) with correlation coefficients of $R^2 = 0.92$ and 0.84 , respectively. As the sum of EC and OC is thought to make up the vast majority of particle mass emitted by diesel engines, this corroborates an earlier result that, of the five instruments tested, TEOM and DustTrak are best suited for fast response mass measurements (28).

Although none of the fast response instruments tested is capable of OC measurements by itself, it is possible to use a TEOM or DT measurement to obtain total particle mass concentration and to subtract the EC concentration obtained with one of the absorption and extinction instruments (i.e., PA, AE, or SM), yielding OC concentration. Obviously, this concept is only applicable to samples in which the particle mass is made up nearly exclusively by EC and OC, such as samples of diesel exhaust. If the particulate mass emitted contains significant amounts of noncarbonaceous matter such as sulfate and metal ash, this noncarbonaceous mass would be reported as OC. However, for diesel vehicles in the light-duty and light heavy-duty categories, sulfate and metal ash generally make up only ~1–2% of the total PM mass (38). The concept of OC measurements with two fast response instruments has been analyzed quantitatively using multivariable linear regression between the time-integrated data of two fast response instruments and TOR OC data (39). The resulting correlation coefficients for data from all combinations of one "mass instrument" and one "EC instrument" with TOR OC data are shown in Table 2. Although all combinations yield reasonable correlation coefficients ($R^2 > 0.5$), the best correlation is obtained by the TEOM–PA combination ($R^2 = 0.82$) followed by the DT–PA combination ($R^2 = 0.74$). As it has been previously shown that TEOM and DT have different and complementary strengths as mass measurement instruments (28), these two combinations are further discussed.

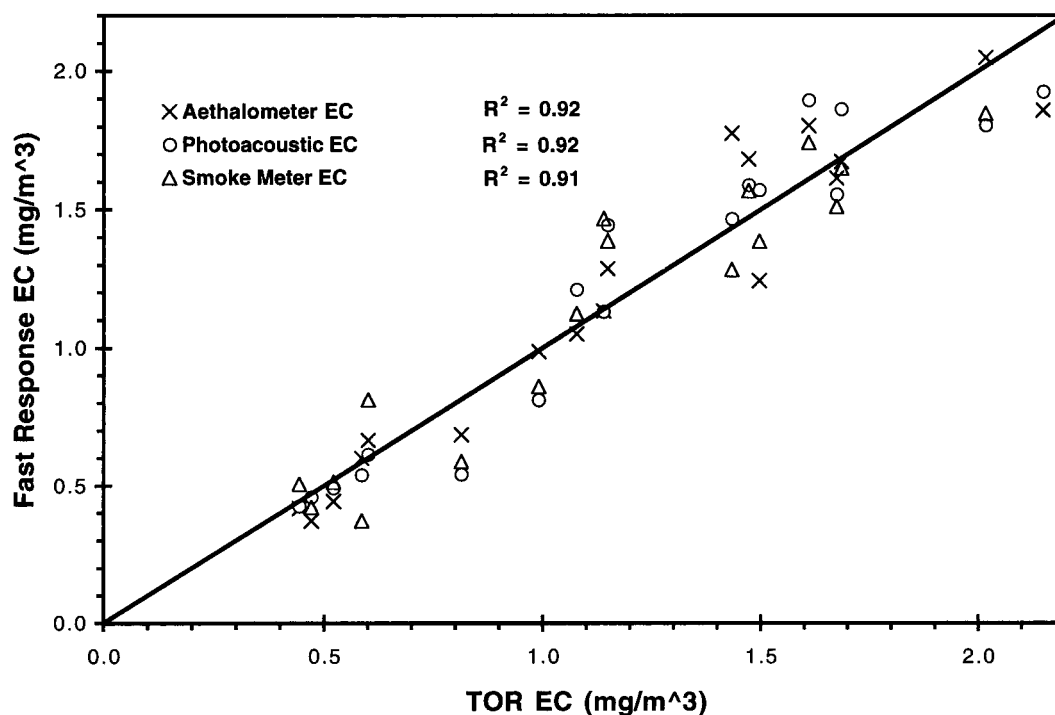


FIGURE 3. Correlation between TOR filter and fast response EC concentrations including all measurements for both vehicles. Fast response EC measurements are calibrated to TOR measurements by eqs 1. The solid line is the 1:1 regression.

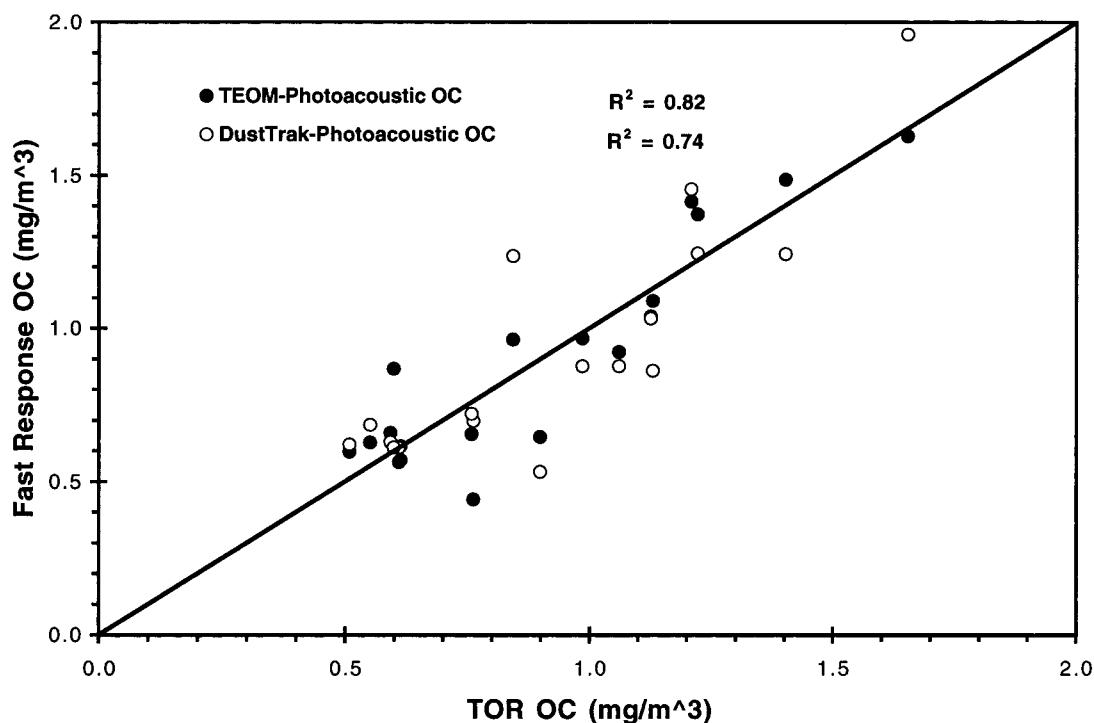


FIGURE 4. Correlation between TOR filter and fast response OC concentrations including all measurements for both vehicles. Fast response OC measurements are calibrated to TOR measurements by eqs 2. The solid line is the 1:1 regression.

Fast response OC concentrations can be calculated from data taken by these two instrument combinations, expressing the multivariable regression results as

$$OC_{\text{TEOM-PA}} = 0.684 \text{ mg/m}^3 + (1.225 \times \text{TEOM}) - (\text{PA}/7.36 \text{ m}^2/\text{g}) \quad (2a)$$

$$OC_{\text{DT-PA}} = 0.503 \text{ mg/m}^3 + (0.666 \times \text{DT}) - (\text{PA}/11.61 \text{ m}^2/\text{g}) \quad (\text{vehicle dependent}) \quad (2b)$$

where $OC_{\text{TEOM-PA}}$ and $OC_{\text{DT-PA}}$ are fast response OC concentrations (units of mg/m^3), calculated from TEOM and DT measurements of mass concentrations, respectively, and from the light absorption measurement PA (units of km^{-1}) of the photoacoustic instrument. Fast response OC concentrations, averaged over the filter sampling periods, and their correlation with TOR OC filter concentrations are shown in Figure 4 for both vehicles together. The zero offset and slope of one of the regression line are obvious results of using the same

data for calibration of the fast response OC measurements via eqs 2. Care should be taken in applying eq 2b to other vehicles as the DustTrak calibration is vehicle dependent and can be very different for older technology vehicles (28). When the results of two fast response instruments are combined to obtain a fast response OC measurement, it is important that the measurements are properly synchronized with each other and that the instrument time responses are similar. Otherwise, transient artifacts may be introduced. Ideally, two measurement methods would be integrated in a single instrument directly yielding fast response OC measurements. In lieu of this, data taken by the PA instrument have been combined with TEOM and DT data, yielding two measurements of time-resolved OC concentrations as shown in Figures 1e,f and 2e,f. Note that the TEOM has been operated with a lower time resolution (i.e., 3 s) than the other fast response instruments, resulting in less time resolution for the OC_{TEOM-PA} than the OC_{DT-PA} measurement as evident in the traces. As for fast EC measurements, the fast response OC measurements make it possible to correlate OC emissions with vehicle operation parameters such as velocity and acceleration.

Overall Instrument Evaluation. For fast response EC measurements, the three absorption and extinction instruments, that is, the aethalometer, photoacoustic instrument, and smoke meter, achieve a very good correlation of their time-integrated data with the TOR EC mass concentration. In addition, their data are essentially uncorrelated with TOR OC data, especially so for the photoacoustic instrument. With respect to other evaluation criteria, the photoacoustic instrument is more complicated than either the smoke meter or the aethalometer. On the other hand, the photoacoustic instrument has by far the largest dynamic measurement range of the three instruments, enabling it to make measurements ranging from relatively clean ambient air (33) to diesel exhaust samples from rather dirty vehicles (28). The lack of such a large dynamic range limits the sensitivity of the smoke meter and requires a secondary dilution system for the aethalometer. The use of a current commercial aethalometer is judged as being too cumbersome due to the need for secondary sample dilution. The measurement principle of choice for EC quantification is therefore either the photoacoustic instrument or the smoke meter, depending on the range of EC concentrations encountered in the sample volume.

None of the tested instruments is capable of fast response OC measurement. However, combinations of a mass instrument (i.e., TEOM or DT) with an EC instrument (i.e. AE, PA, or SM) achieve good correlations with TOR OC measurements. The instrument combination of choice is the TEOM together with the PA instrument. This instrument combination has yielded the highest correlation coefficient ($R^2 = 0.82$) and, in addition, TEOM measurements are much more independent of vehicle type than those of the DT (28). It has previously been suggested to integrate a simple nephelometer (e.g., DT) with the TEOM for particle mass measurements (28). This would combine advantages of the TEOM (e.g., vehicle-independent calibration) with those of the nephelometer (e.g., fast response, good signal-to-noise ratio, and low interference from gaseous sample properties). We believe this suggestion to be also valid for particle OC mass measurements, potentially yielding an instrument combining light scattering, inertial mass determination, and photoacoustic measurement of light absorption for the fast response measurement of OC mass concentrations.

From the measurements and analysis presented above, it can be concluded that fast response measurements of diesel exhaust EC and OC particulate mass concentrations, consistent with TOR filter measurements, are feasible using existing technology. However, it should be kept in mind that this result is based on measurements during only two FTP

cycles with two diesel vehicles. Further investigations based on these results utilizing more vehicles and test cycles are needed for the development of reliable instrumentation for diesel exhaust particulate EC and OC mass measurements.

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