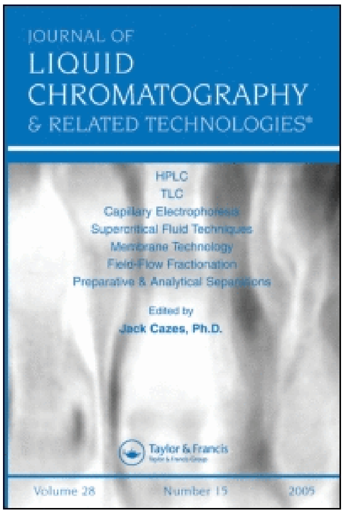

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Analysis of Soot Particles Emitted from a Modern Light Duty Diesel Engine Running in Different Operating Conditions using Field Flow Fractionation and Granulometric Techniques

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Abstract: Soot particles emitted from a light duty (LD) Volkswagen diesel engine running at different operating points (speed and torque levels) are analyzed for mean size determination using a laser-based three Wavelength Extinction Method (3-WEM). For this reason, collected soot samples are suspended using an appropriate sample preparation technique with optimized conditions of sonication as it revealed its effect on the soot mean particle size measured by 3-WEM.

An online Scanning Mobility Particle Analyzer (SMPS) is also used to measure soot emission at identical engine operating points. Size values obtained from SMPS are lower than those of suspended soot samples obtained from 3-WEM. The size discrepancies are mainly related to the required sample preparation procedure employed for 3-WEM measurements. The engine operating points affect, differently, the size measurements obtained from SMPS and 3-WEM.

Sedimentation Field-Flow Fractionation (SdFFF) is used for density determination of soot samples based on size measurements of fractions collected at peak maxima

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of fractograms using the off-line hyphenation with 3-WEM. It is assumed that a size dependent separation of soot particles occurred with a uniform particle density over the whole size distribution. An average density value is used for the conversion of soot fractograms to size distributions. Discrepancies are also found with size distribution profiles obtained from SMPS for the same engine operating points, due to the sample preparation procedure employed for SdFFF measurements.

Keywords: Field-Flow Fractionation, Online-scanning mobility particle sizer, Three Wavelength Extinction Method, Soot particles

INTRODUCTION

Particulate emissions generated by combustion draw significant attention worldwide[1] not only due to increasingly tighter environmental legislation, but also due to very recent findings correlating mortality rates in cities[2] with concentrations of fine particles smaller than approximately 2.5 microns, most of which come from combustion sources. The emitted soot particles can cause serious health problems by penetrating and delivering coated chemicals into human respiratory systems.[3,4] Current regulations are mainly concerned with the total emitted soot, not the sizes of the particles. Although the size of soot particles is not regulated by national or international laws, yet its importance has increased in the last years with the upcoming discussion of health effects caused by small particles. Diesel engines are considered to be the major source of the particulate emissions. There are two types of diesel engines: light duty (LD) 4 cylinder engines used for passengers cars, and heavy duty (HD) engines used in buses, trucks, construction equipment, etc. The soot amount in automobile exhaust is mostly composed of fine carbonaceous particles that are coated with a mixture of various toxic chemicals, such as polycyclic aromatic hydrocarbons (PAH). Soot particles have irregular shapes (usually in chain forms) formed by aggregation of several primary spherical particles.[5] There has been an increasing number of studies on soot particle formation emitted from LD diesel engines as well as HD diesel engines,[6–8] showing a higher health risk exposure with the decrease in the average particle size of the soot emission.

A number of methods have been tested for the size analysis of soot particles in the automobile exhaust. The on-line methods included the Electrical Aerosol Analyzer (EAA),[9,10] Time-Of-Flight Mass Spectrometry (TOF-MS),[11] Scanning Mobility Particle Sizing (SMPS),[12] and Long Path Multi-wavelength Extinction (LPME).[13–15] The off-line methods included the cascade operator,[16] electric low-pressure impactor,[10] Scanning Electron Microscopy (SEM), and Photon Correlation Spectroscopy (PCS).

Sedimentation Field-Flow Fractionation (SdFFF), operated at multi gravitational field, is useful for size determination for high-resolution separation and characterization of a large variety of colloids.[17] The potential of SdFFF for off-line size analysis of diesel soot particles has already been shown.[18–20]

SdFFF uses a thin (usually 50–500 μm thickness) ribbon-like flow channel that provides a well-defined parabolic laminar flow profile. The separation mechanism of colloids is described as "Brownian" in which an external multi gravitational field is applied perpendicularly to the flow axis and forces the sample particulate species to migrate toward the accumulation wall of the channel. An equilibrium layer is established as a result of a counteraction between the external field-driven migration and the diffusion of sample components away from the accumulation wall. Parabolic flow carries sample components down the channel. The down-stream migration velocity of a sample component depends on the thickness of the component's layer. Features and merits of SdFFF as a sizing tool have been described in detail elsewhere.[21,22] One of the merits of SdFFF is that, in the Brownian mode, particulate species with a uniform density are separated according to their size. Smaller particles are eluted before larger particles. In this way, narrow fractions of particles can be collected and be submitted to further analysis for chemical composition, shape, and more. Therefore, SdFFF has been hyphenated, off- or on-line, with different techniques like Electron Microscopy (EM), light scattering analysis,[23] and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).[24]

The purpose of this study is first to analyze the variation of the collected amount and the average sizes of soot particles emitted from a modern LD Volkswagen (VW) diesel engine running at different operating points using SMPS and a three Wavelength Extinction Method[25,26] (3-WEM). SdFFF is used to determine the soot density and size distributions based on results obtained by off-line hyphenation with 3-WEM. An FFF elution profile (fractogram) is a direct representation of the size distribution and can be directly converted to the size distribution assuming that particles with a uniform density are separated according to their size.

EXPERIMENTAL

VW Diesel Engine

A 4 cylinder diesel engine, i.e. LD VW Euro III TDI 85 kW engine with a displacement volume of 1.9 L was used. It is equipped with specific modern features like: i) variable geometry toroidal (VGT) technology that enables the power pistons to rotate in a perfectly circular chamber with the drive shaft at its geometric center; ii) exhaust gas recirculation (EGR) for recycling a part of the exhaust gas to minimize the NOx concentration at low speed and torque; iii) pump unit injection (PUI). Engines with PUI systems have one pump for each fuel injector oppositely to the common rail systems that possess only one pump for all fuel injectors. Therefore, higher injection pressures are reached (2,000 bar) and the fuel droplets are, consequently, smaller. The combustion is cleaner and the soot concentration is reduced in comparison with engines with common rail. The engine is installed on a test bed and coupled to a 220 kW Schenck Dynas dynamometer (Darmstadt, Germany). The engine speed and torque levels can be adjusted by an engine controller. The diesel fuel used has a sulfur content of 45 ppm, octane number 55, specific gravity (15/4°C) 0.851 and 10% distillation residue 0.08 w%.

Exhaust Dilution and Soot Collection System

For the soot collection, the engine pipe is connected to a dilution system (Fig. 1). The exhaust gas emitted from the pipe is sucked by the first injector through a heated hose (200°C) inside a first dilution tunnel made of electropolished stainless steel tubing with 5 cm in diameter and 70 cm in length. This injector ensures a rapid mixing of the exhaust gas with the conditioned ambient air so-called dilution air which is generated by a compressed air regulator. The dilution air is purified by passing through an activated carbon bed air filter. The filtered air has an ambient room temperature of 20 to 30°C. The rapid dilution and collection of soot are to avoid a possible particle aggregation via nucleation, adsorption, and condensation. The dilution ratio needs also to be constant as the particle size distribution and the composition of adsorbed organic materials could vary with the dilution ratio.[27,28] A flow controller is used to assure a constant volume sampling of the first dilution tunnel. This means that the sampling volume is always constant and independent of the exhaust gas flow or velocity.

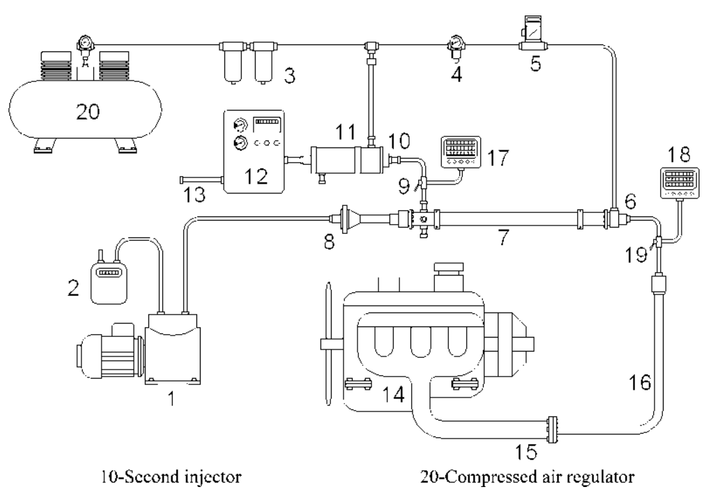

Figure 1. Scheme of the dilution system for soot collection and SMPS analysis.

At the end of the first dilution tunnel, a filter holder is installed. Teflon coated glass fiber filters, called Pallflex with 70 mm in diameter, are used for the soot sample collection. Each filter is conditioned in a cabinet drier at 40°C for at least 2 hours before both the pre- and post-collection weighing and then kept for 24 hours in a dessicator (Fig. 2). The exhaust particles enter the first dilution tunnel where particles are mixed with the clean air. They continue to travel down the filter holder equipped with the Pallfex filter, where they are deposited. The average sampling time for each collected sample was approximately 2 hours. One sample was collected per engine operating point. In total, 6 soot samples were collected while the engine was running at 6 different operating points. An operating point means that the engine was running at certain speed and torque constant levels, during which the concerned soot sample was collected. The engine speed and torque levels are listed in Table 1. The soot quantity, obtained at each engine operation point, is calculated by weighing the Pallflex filter before and after collection. The air pump in Fig. 1 is installed to suck the gas (exhaust gas mixed with dilution air) in the first dilution tunnel. The flow meter measures the total gas volume of the pump. Thus, the whole gas volume in the first dilution tunnel can be measured for a certain operation time. The soot concentration (mg/m^3) in the first dilution tunnel can be then determined by the ratio of the collected soot mass and the measured gas volume.

A first CO_2 analyser, installed at a 3-way valve between the first and the second dilution tunnels, is used to measure the CO_2 concentration in the dilution system. Another CO_2 analyzer is also installed at the engine exhaust in order to measure the CO_2 concentration in the exhaust gas. The dilution ratio is then determined from the CO_2 concentrations in the engine

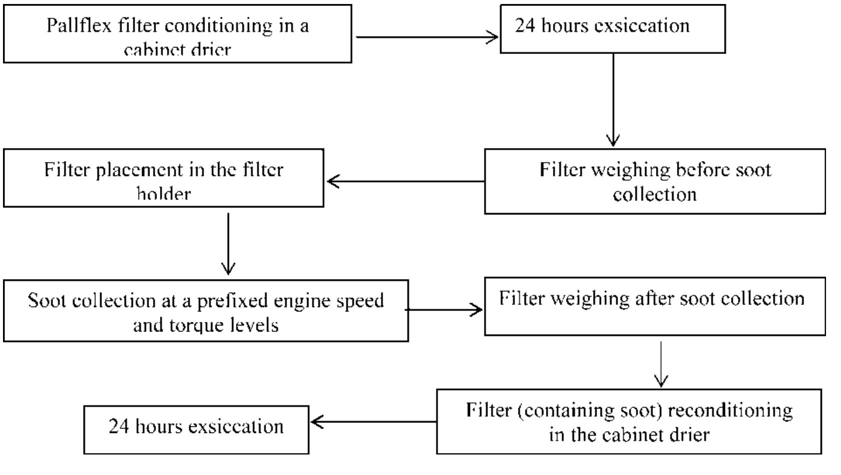

Figure 2. Schematic diagram of the soot collection procedure.

Table 1. Soot samples collected at different engine speed and torque levels

Sample	Speed (rpm)	Torque (Nm)	Sampling time (hour)	Soot emission ($\pm$0.8 mg)	Soot emission per hour (mg/h)	Soot concentration in the exhaust gas (mg/m^3)	Soot concentration in the first dilution tunnel (mg/m^3)	Dilution factor[a]
1	1800	80	1.92	30.84	16.06	37.5	3.83	9.8
2	1800	180	1.89	9.523	5.04	10.1	1.02	9.9
3	2400	80	1.87	9.391	5.02	12.4	1.19	10.4
4	2400	180	1.90	7.693	4.05	9.8	0.97	10.1
5	3000	80	1.88	18.894	10.05	22.6	2.21	10.3
6	3000	180	1.89	8.595	4.55	10.2	1.04	9.9

[a]The dilution factor is the ratio of the soot concentration in the exhaust gas to the one in the dilution system.

exhaust and in the dilution system. The dilution ratio inside the first dilution tunnel was kept constant at approximately 1:10 during the soot collection. The total soot concentration in the exhaust gas is calculated by multiplying the dilution ratio with the soot concentration in the first dilution tunnel. Table 1 shows the sampling times for each collected soot sample and the amount of particulate matter collected, as well as the measured soot concentrations in the exhaust and dilution system.

Even though the soot concentration in the first dilution tunnel is 10 times reduced, it remains considerably high for online SMPS size measurements. Therefore, a second dilution tunnel is added to reduce the particle concentration according to the SMPS counter requirements. The second tunnel (Fig. 1) is also equipped by another injector that ensures the exhaust gas dilution by the conditioned ambient air. The dilution ratio was also kept constant for each size measurement at the same engine operating points that were applied for the collection of soot samples.

Sample Preparation for 3-WEM and SdFFF Measurements

Already described suspension techniques[19,28] were employed to prepare soot samples for off-line size analysis by FFF, dynamic light scattering (DLS) and EM. The method applied in this study is derived from those previously used with some modifications regarding the quantity of organic reagents and the type of surfactant used. The same soot sample preparation technique was used for both SdFFF and 3-WEM measurements. The sampling technique consists of the following four steps: 1) recovery of sampled soot particles from Pallflex filters; 2) extraction of soluble organic compounds from soot particles; 3) dispersion in an adequate solvent; 4) sonication and vortexing for the particle dispersion.

For the soot recovery from filters, ethanol was chosen, for it is highly efficient in the total soot mass recovery after a short period of time. The collection filter is bath-sonicated for about 15 min in 10 mL of ethanol (99.9%). 15 min are largely sufficient for complete recovery from the Pallflex filters. The second step is to remove the organic components adsorbed on soot particles because earlier studies indicated that they might promote the aggregation of soot particles.[28] In this step, the mixture of ethanol and soot particles obtained in the first step is mixed with 10 mL of n-hexane in a separatory funnel. Shaking the funnel for 20 min resulted the extraction of organic compounds by n-hexane. The extraction procedure is repeated 2 times. After the removal of n-hexane, 5 mL of water containing 0.1% (w/v) SDS (sodium dodecyl sulfate) and 0.02% (w/v) NaN_3 are added to the mixture of ethanol and soot particles. At the beginning, the mixture is bath-sonicated for approximately 10 min for the dispersion of particles. The same mixture is heated afterwards on a stirring hot plate at 70°C for complete removal of ethanol. Finally, water containing soot particles is sonicated, at different cumulative time intervals ranging from 10 to 110 min, by a sonic dismembrator, Fisher model 500 (Fisher Scientific Co., Schwerte, Germany), and vortexed using a vortexmixer (Fisher Scientific Co., Schwerte, Germany). The flask containing the suspended soot is placed in a cool thermostatic water bath to prevent the heating of the suspension under intensive sonication. The sonication effect on the average particle size is explored by 3-WEM further in this report.

Three Wavelength Extinction Method (3-WEM)

The 3-WEM measurement principle is based on the integral extinction of three laser beams of different wavelengths, focused in one laser beam and directed through particle loaded fluids (aerosols or suspensions). 3-WEM allows the analysis of particle collectives with a diameter range from 0.015 to 7 μm approximately. Particles in the measurement volume attenuate the light beam in consequence of scattering and absorption according to the Mie Theory.[29] The 3-WEM measurement principle and system are detailed elsewhere.[5,26,30]

The measurement unit (Fig. 3) is manufactured by Wizard Zahoransky KG (Todtnau, Germany). It is technically derived from LPME[15] technique. The unit includes a sensor head containing three laser diodes of different wavelengths (674, 844, and 1324 nm in its standard version) combined in one focused beam. The light is released at the measurement locations and

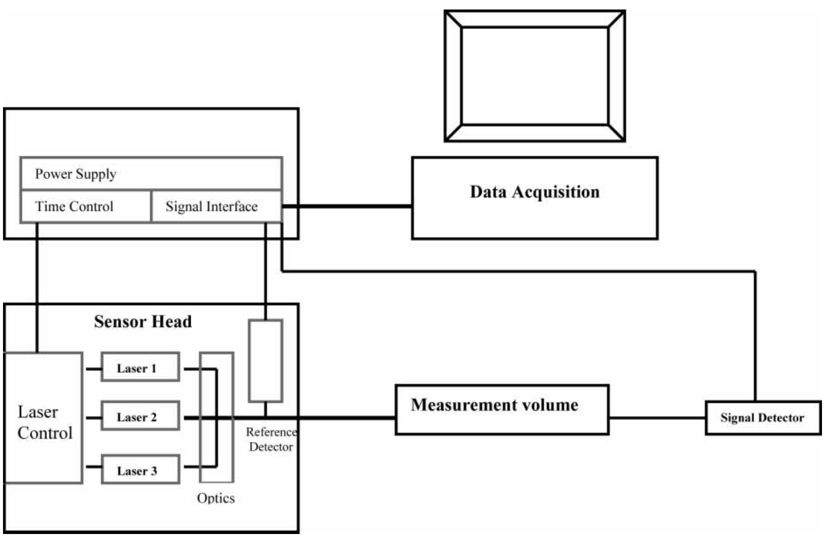

Figure 3. Schematic description of the 3-WEM measurement unit. The components are described in the text.

directed through the particle collective by the optics of the emitter part of the sensor head. On the other side of the measurement volume, the attenuated light beam is collected and directed to the photo-detector which is in the receiving part of the sensor head. The spectral attenuation of the three wavelengths is captured by the detector. A fast algorithm allows the on-line display of the measurement data. Two parameters "measured diameter" and "volume concentration C_V" are displayed in the operator's selected time intervals. The internal data acquisition rate is in the kHz range. The finally displayed data points represent averaged data values, i.e., at a speed of 1 Hz. These data are stored for later post analysis and documentation.

A cuvette (Postnova, Landsberg/Lech, Germany) of 1 cm optical path length with 2 mL volume was used for the 3-WEM measurements of soot suspensions. Once the cuvette is filled by the concerned soot suspension, it is placed in the 3-WEM measurement chamber for size analysis. The cell volume is purged after each measurement and flushed with distilled water until it is totally clean. Zero measurements are performed before each analysis to assure the cell cleanliness by filling it only with the carrier phase.

Off-Line Hyphenation of 3-WEM with SdFFF

The 3-WEM-SdFFF hyphenation is used to determine the average particle sizes of soot fractions collected at peak maximum of the SdFFF fractograms. These size values are used for the calculation of the soot density of the suspended soot samples by FFF related equations,[31] assuming a uniform density over the whole size distribution.

Fractions are collected by means of a RediFrac fraction collector (Amersham Biosciences, Sweden). Each fraction volume is reduced approximately to 200 μL by a 10 min/3,500 *g* centrifugation. After concentration, sonication (3 min) and vibration (2 min) were applied to the remaining 200 μL to prevent a possible aggregation. Another microcuvette with 1 cm optical path length and a reduced volume capacity of 160 μL (Postnova, Landsberg/Lech, Germany) was used for fraction size analysis. Each fraction was then injected into the microcell inlet by a 250 μL micro syringe until the cuvette volume was completely filled. The microcuvette containing the solute is sonicated afterwards for 2 min to prevent erroneous results caused by an eventual air bubble formation inside the cell due to the injection procedure. After drying the cell glasses by an antistatic cloth, the optical cell is placed in the 3-WEM measurement chamber for analysis. The cell volume is purged after each measurement and flushed with distilled water until it is totally clean. Moreover, zero measurements are done before every fraction analysis to assure the cell cleanliness by filling it only with the carrier phase.

Online Scanning Mobility Particle Sizer (SMPS) and Transmission Electron Microscope (TEM)

The SMPS used in this study is a Model 3080 manufactured by TSI Inc. (MN, USA). It consists of a scanning mobility analyzer (SMA), a condensation particle counter (CPC), and a computerized control with a data acquisition system. The unit enables measurements of particle number distribution in the size range from 0.01 to 1 μm using the electrical mobility detection technique. Particles coming from the second dilution channel pass through a radioactive source bipolar ion neutralizer. This brings the level of the particle charge distribution to a minimum Boltzmann's distribution. The aerosol then enters the mobility section close to its inner surface. Clean sheath air flows close to the central rod. When a voltage scan is applied to the rod, charged particles move in the radial direction inward or outward, depending on their polarity. Particles with the right polarity and electrical mobility exit through holes at the bottom of the central rod. The entire system is automated and data analysis is performed by an IBM-compatible computer system with customized software. The time response of the SMPS for a size distribution measurement is 1 to 2 min.

A Hitachi model H-600 (Tokyo, Japan) TEM was used for electron microscopy of soot particles in aerosol and in suspension.

SdFFF System

The SdFFF separation device used in this study was already technically described.[30,32,33] The separation channel is made up of two polystyrene plates, one described as the depletion wall and the other called the accumulation wall, separated by a Mylar band in which the channel is cut. The channel length, width, and thickness are 78.0, 1.6, and 0.0250 cm, respectively. The system void volume, which includes the connections tubing, injection and detector volumes, was 3.43 ± 0.07 mL ($n = 15$), measured using acetone 1% (v/v).

Polystyrene plates and the Mylar band are sealed into a centrifuge basket. The channel-rotor axis distance is 13.8 cm. Two rotating seals, drilled to allow external diameter Peek® tubing to fit in, are used to permit the mobile phase to flow along the rotating axis into the channel. A Knauer HPLC pump, Type 364.00 (Knauer, Berlin, Germany), was used to produce the carrier liquid flow. The carrier liquid is doubly distilled and deionized water containing 0.1% (w/v) SDS and 0.02% (w/v) NaN_3. An injection device, Rheodyne 7125 (Cotati, CA, USA), chromatographic valve was used for the sample injection. A V-100L switching valve (Upchurch Scientific, Oak Harbour, NJ, USA) was also used for diverting the flow off the channel during the stop-flow injection. The sample introduction was performed via the

Rheodyne valve whose injection loop volume was set to 50 μL for all suspensions.

The elution signal for detection was recorded at 254 nm by a Postnova UV-visible detector type S3120 (Postnova, Landsberg/Lech, Germany). The detector signal was processed using a data acquisition and automation system built with LabVIEW (National Instruments Inc., USA), especially designed for the SdFFF device.[30] The rotation speed was recorded on-line during the run by means of a digital tachometer type RM-1501 (Prova instruments, Taiwan, China) via infrared link.

RESULTS AND DISCUSSION

Soot Emission

The amount of soot emitted per hour was measured at each selected level of speed and torque (Table 1) from the amount of soot deposited on the Pallflex filters and the corresponding collection time. It is noticed that the Particulate Matter (PM) emission decreased with an increasing torque at a constant engine speed. At 1,800 rpm, an increase in the torque from 80 to 180 Nm resulted in a decrease in the PM emission by 68%. At both 2,400 and 3,000 rpm, the same increase in the torque resulted in a decrease in the PM by 19% and 55%, respectively. The highest decrease percentage in the PM emission with an increasing torque is at 1,800 rpm. However, the PM emission seems less affected by the torque at 2,400 rpm.

The PM emission also decreased with an increasing engine speed at a low torque level. An increase in the engine speed from 1,800 to 2,400 rpm resulted in a decrease in the PM amount by 69% at 80 Nm torque and 20% at 180 Nm. An increase from 1,800 to 3,000 rpm resulted in a decrease in the PM amount by 37% at 80 Nm torque and 10% at 180 Nm. The decrease percentage in the PM emission with an increasing speed at high torque is not as significant as that at low torque.

The variation observed in the PM emission with the different engine operating points is specifically attributed to the engine specifications used for this study. The same engine operating points applied on another engine type will surely lead to a different variation in the PM emission.

Sonication Effect on 3-WEM Size Measurements

It was found that the average soot particle size measured by 3-WEM is considerably influenced by the amount of sonication applied to the suspension during the sample preparation.

One of the soot samples from Table 1, collected at 2,400 rpm/80 Nm, was used for this purpose. It was suspended by the carrier containing 0.1% SDS (w/v) and sonicated by the sonic dismembrator for different time intervals ranging from 10 to 110 min. After each sonication, a 3-WEM particle size measurement of the soot suspension was performed. An example of the obtained 3-WEM size data is presented in the same way as it was displayed by the unit during the measurements. Figure 4 shows, respectively, time resolved profiles of the three laser spectral attenuation, measured particle diameter, and volume concentration measurements of the suspended soot sample sonicated for a period of 30 min. The measured particle diameter and volume concentration profiles are presented in this study on the same chart. In normal cases, each of the profiles is displayed by the 3-WEM system on two separate charts. The curves tend to have constant values, due

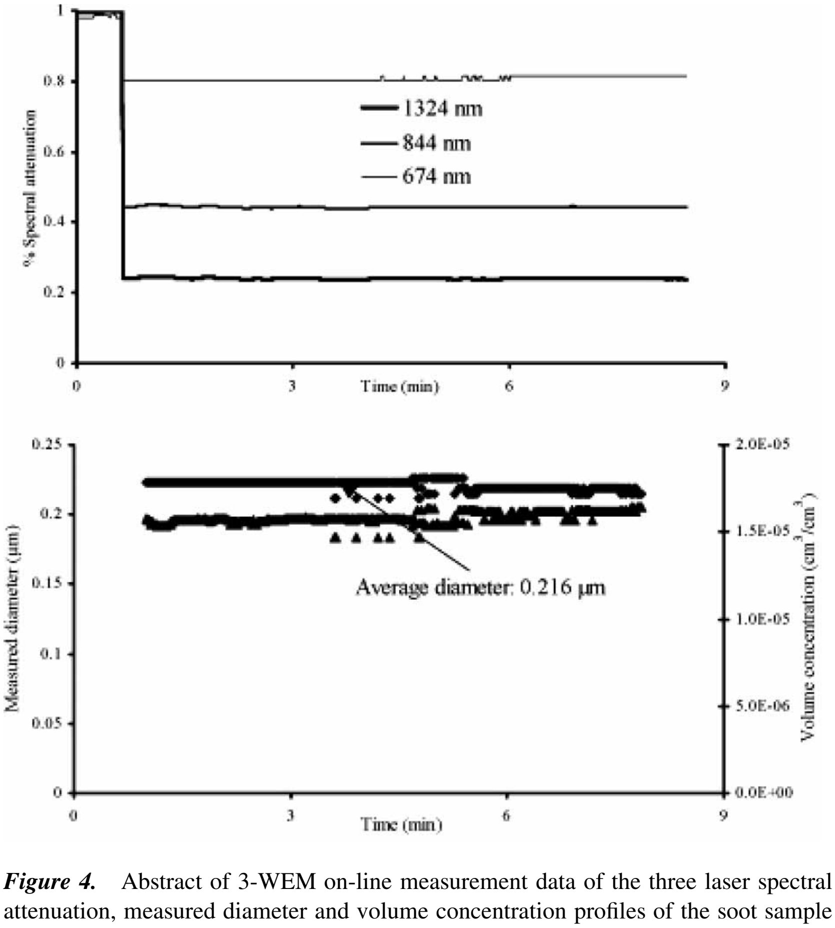

Figure 4. Abstract of 3-WEM on-line measurement data of the three laser spectral attenuation, measured diameter and volume concentration profiles of the soot sample collected at 2,400 rpm/80 Nm, suspended and sonicated for a period of 30 min. The average particle diameter 0.216 μm is calculated by averaging the data of the particle diameter profile.

to an appropriate particle suspension stability. The measured data constancy is also a direct indication of the measurement accuracy.[26,30] The average diameter values summarized in Table 2 were calculated by averaging the data of the particle diameter profiles of each suspended soot sample like the ones shown in Fig. 4.

It was noticed that an increase in the sonication from 10 to 110 min resulted in a decrease in the mean particle size by 44%, respectively. After 90 min sonication, the particle size seemed to be no longer affected by the sonication. It is thought that the sonication disaggregated suspended soot particle agglomerates until they reached a certain stage where hydrocarbon chains resisted against the breaking forces applied by the sonication.

Sonication Effect on SdFFF Particle Retention

SdFFF was also used to observe the sonication effect on the retention of soot particles inside the FFF channel. The same soot sample taken at 2,400 rpm/80 Nm was explored for both 3-WEM and SdFFF analyses.

An exponential field programming[34] for SdFFF analysis was applied with an initial field of 600 *g* (1,972 rpm), a predecay time of 5 min, and a final field of 29.60 *g* (439 rpm). The stop flow time was 15 min and the flow rate was 1.2 mL/min. The particles were injected into the channel at 0.2 mL/min flow rate). Figure 5 shows fractograms obtained of the soot sample taken above at cumulative sonication times. It was found that the retention time also decreases with an increasing sonication time (Table 2). An increase in the sonication from 10 to 110 min resulted in a decrease in the retention time by 25%. The retention time became unaffected by the sonication after 90 min sonication, which was also confirmed by a particle size

Table 2. Sonication effect on mean particle diameter measured by 3-WEM, and on retention time at peak maximum of SdFFF elution profiles

Sonication time (min)	Mean diameter (nm) measured by 3-WEM	Retention time[a] at peak maximum (min)
10	233	33.14
30	216	30.79
50	191	29.13
70	167	26.34
90	135	24.41
110	131	24.91

[a]Retention time inside the channel (excluding the void time of the tubing, injector and detector ~0.22 min).

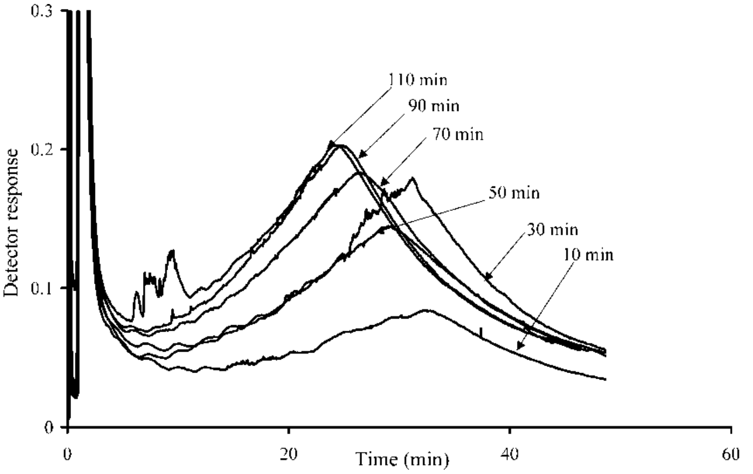

Figure 5. SdFFF elution profiles of a suspended soot sample collected at 2,400 rpm/ 80 Nm and sonicated at cumulative time intervals ranging from 10 to 110 min. Carrier phase: doubly distilled and deionized water containing SDS 0.1% (w/v). Elution conditions: initial field strength, 600 *g* (1972 rpm); final field strength, 29.60 *g* (439 rpm); predecay time, 5 min; stop flow time, 15 min; flow rate, 1.2 mL/min.

stability obtained by 3-WEM measurements. Based on this experimental finding, all remaining soot samples were sonicated for a period of 90 min. In this way, an optimized estimation of the suspended soot particle size is assured to be obtained once measured by 3-WEM.

Granulometric Analysis

3-WEM Size Analysis of Suspended Soot

The collected soot samples from Table 1 were suspended according to the previously described sample preparation technique and sonicated for 90 min before 3-WEM analysis. 3-WEM was used to perform size measurements for two purposes: i) to analyze the effect of the engine operating points on suspended soot samples, where measurements were done by a normal cuvette of 2 mL volume capacity and 1 cm optical path length; ii) to determine the soot density using FFF related equations by measuring the average particle size of soot fractions collected at peak maximum of SdFFF fractograms, where measurements were performed via a microcuvette of 160 μL volume capacity and 1 cm optical path length (see Experimental section). The second purpose is discussed in detail in a further section.

For the first purpose, 3-WEM size measurements of the suspended soot samples are presented in Table 3. Results showed that an increase in the engine speed at 80 Nm torque yielded a decrease in the mean size from 1,800 to 2,400 rpm and an increase from 2,400 to 3,000 rpm. However, the same increase in the engine speed at 180 Nm did not influence the mean size significantly.

The increase in the torque resulted in the decrease in the mean size by 18% at 1,800 rpm, 4% at 2,400 rpm and 15% at 3,000 rpm. The size variation with torque and speed is thought to be related to the variation of the soot PM amount emitted at different engine operating points, i.e., the PM amount decreased with an increasing torque at a constant engine speed (Table 1), and it was practically stable with an increasing engine speed at 180 Nm. Thus, the mean particle size increased with an increasing PM amount in suspension mainly due to agglomeration. Therefore, the size variation obtained by 3-WEM cannot describe the real size variation at different engine operating points because of the sample preparation procedure.

Online Size Analysis by SMPS Compared to 3-WEM

On-line size measurements of soot particles emitted at each engine operating point (Table 1) were made by SMPS without any prior sample preparation. Size distribution profiles were established in Fig. 6 and the corresponding average particle sizes were determined.

A comparative diagram (Fig. 7) shows the mean particle sizes obtained by both 3-WEM and SMPS. The size measurements were repeated 3 times by each technique. The standard deviations obtained were around 3% for 3-WEM and 2% for SMPS.

The 3-WEM size data are significantly higher than the SMPS data. Soot particles in suspension tend to aggregate and form agglomerates which sizes

Table 3. Mean particle diameters of diesel soot measured by 3-WEM and SMPS

Soot sample[a]	3-WEM mean particle size of soot suspension (±4 nm)	SMPS mean diameter (±2 nm)
1 (1800/80)	169	66
2 (1800/180)	141	71
3 (2400/80)	138	55
4 (2400/180)	135	66
5 (3000/80)	161	53
6 (3000/180)	140	64

[a]Samples 1 to 6 correspond to the engine operating points (speed and torque levels) at which soot samples were measured.

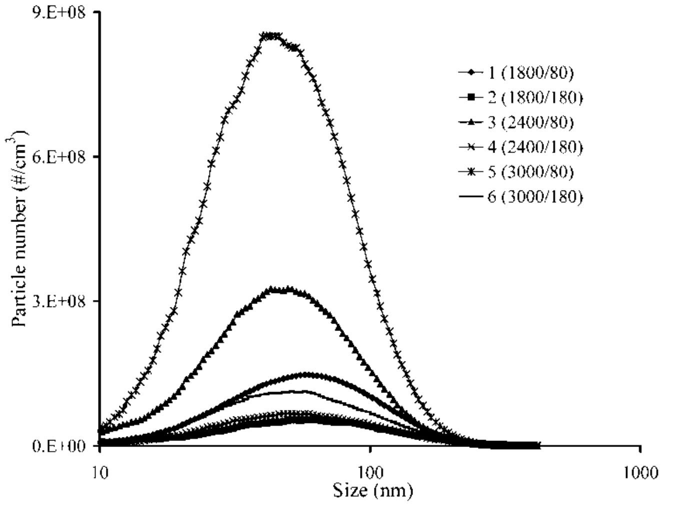

Figure 6. Size distribution profiles of soot particles emitted at different engine operating points (Table 1) determined by SMPS.

exceed the original size. A TEM picture (Fig. 8A) taken from the suspended soot sample collected at 2400 rpm/80 Nm shows a clear agglomeration of the soot particles which form bigger aggregates where primary particles are difficult to distinguish. Another TEM picture (Fig. 8B) of soot particles was taken from the diluted exhaust gas at the second dilution tunnel (Fig. 1) while the engine was running at 2,400 rpm/80 Nm. It reveals a lower agglomeration tendency where primary particles could be easily distinguished. This explains why the average size of suspended soot particles exceeds the size of those in the exhaust. The role of the sample preparation for soot suspension is mainly to limit a massive agglomeration of suspended soot that could lead to large aggregated particles and yields high average sizes.

The decrease in size obtained by 3-WEM, which is yielded by the increase of the torque (at a constant engine speed), is contradicted by SMPS where the resulting mean particle size seems to increase with an increasing torque at a constant engine speed. SMPS shows also a decrease in the mean size with an increasing engine speed at a constant torque level. This is not the case for 3-WEM where the mean size decreases with an increasing engine speed from 1,800 to 2,400 rpm and it increases from 2,400 to 3,000 rpm at a low torque level. The major factor that plays a role in these discrepancies between 3-WEM and SMPS data is the sample preparation procedure employed for 3-WEM measurements. For 3-WEM, the size variation at different engine operating points is more related to the variation in the collected soot amount that influenced the mean particle size in suspension. A good estimate of the real size variation in the emitted soot amount with

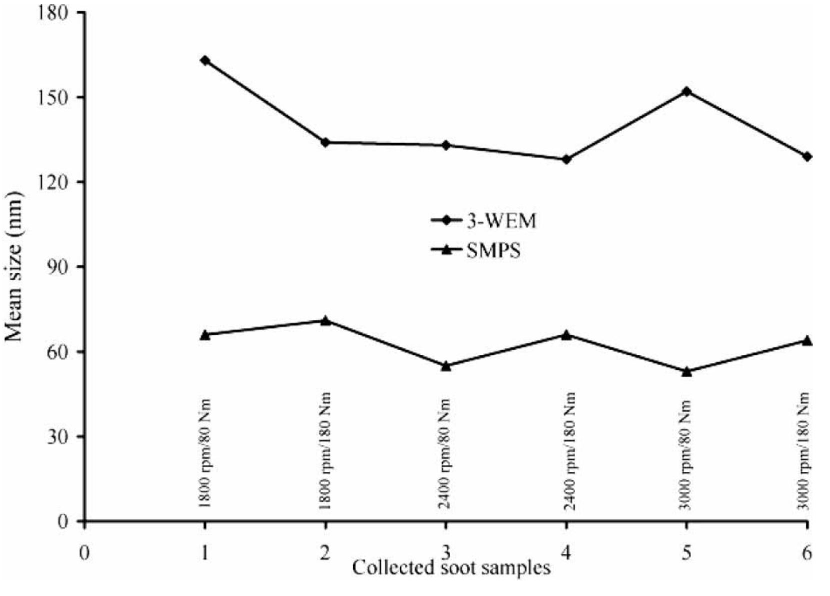

Figure 7. Mean sizes of soot particles emitted at different engine points determined by 3-WEM and SMPS.

the different engine operating points can only be described by on-line techniques such as SMPS.

SdFFF Analysis

Density Analysis

The suspended soot samples, collected at different engine operating points (Table 1), were analyzed by SdFFF. An exponential field decay identical to the one used previously was applied. The stop flow time and the flow rate were, respectively, 15 min and 1.2 mL/min. The particles were also injected into the channel at 0.2 mL/min flow rate.

Figure 9A shows fractograms of the six soot samples analyzed by SdFFF. Fractions from each fractogram were collected for 4 min durations at the peak maximum. Then, they were submitted for size analysis using the off-line SdFFF/3-WEM hyphenation procedure described in a previous section. The 3-WEM average particle size and the retention time at peak maximum, together with the channel void time, are used to determine the soot density using FFF related equations.[31] As shown in Table 4, the density values obtained in this study range from 1.41 to 1.76 g/cm^3. The differences in density among soot samples are relatively small.

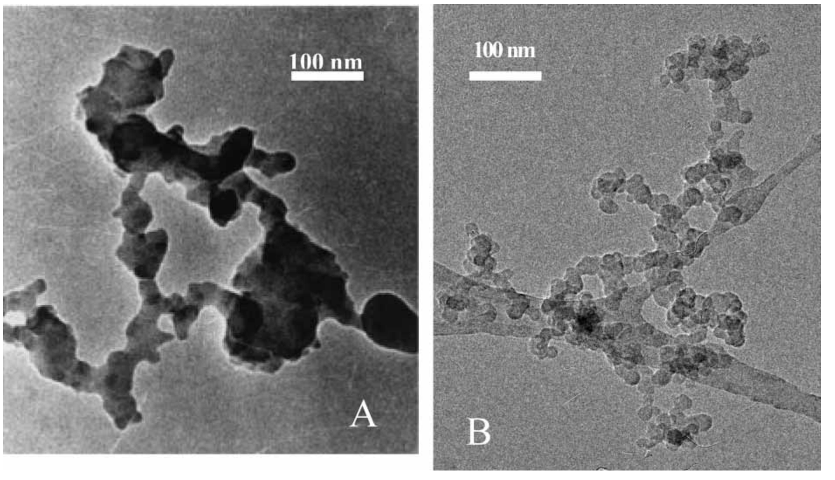

Figure 8. TEM pictures taken from a suspended soot sample collected at 2,400 rpm/80 Nm (A) and soot particles (B) from the diluted exhaust gas while the engine was running at 2,400 rpm/80 Nm.

The soot density was previously determined by Lee et al.[19] using FFF equations. They measured the particle size of collected fractions at peak maximum using PCS to determine the density. They obtained an average density value of 1.3, which they used for the determination of size distributions obtained from soot fractograms assuming a constant density over the whole range of the size distribution of the soot samples. The obtained average density value of 1.6 in this study is slightly higher, due to three possible reasons: i) soot particles emitted by a different type of diesel engine; ii) collection and sample preparation lead to a heavier soot mass in suspension; iii) soot analysis performed by another SdFFF separator which have differentiated the average particle size and the retention time values necessary for the density determination.

The 3-WEM size measurements that were made on the suspended soot samples (Table 3) and on the collected soot fractions (Table 4) from SdFFF fractograms (Fig. 9A) are in good agreement. This could be explained by the fact that 3-WEM is a particle sizing technique that provides the average size over the entire particle population. Therefore, size values of the whole suspended soot samples (Table 3) are slightly higher due to a wider size distribution than the one in the collected soot fractions.

Size Distribution Analysis

The average density value of 1.60 obtained in the previous section is used for all soot samples for the determination of the size distribution profiles. The FFF elution profiles (fractograms) from Fig. 9A are converted to the corresponding

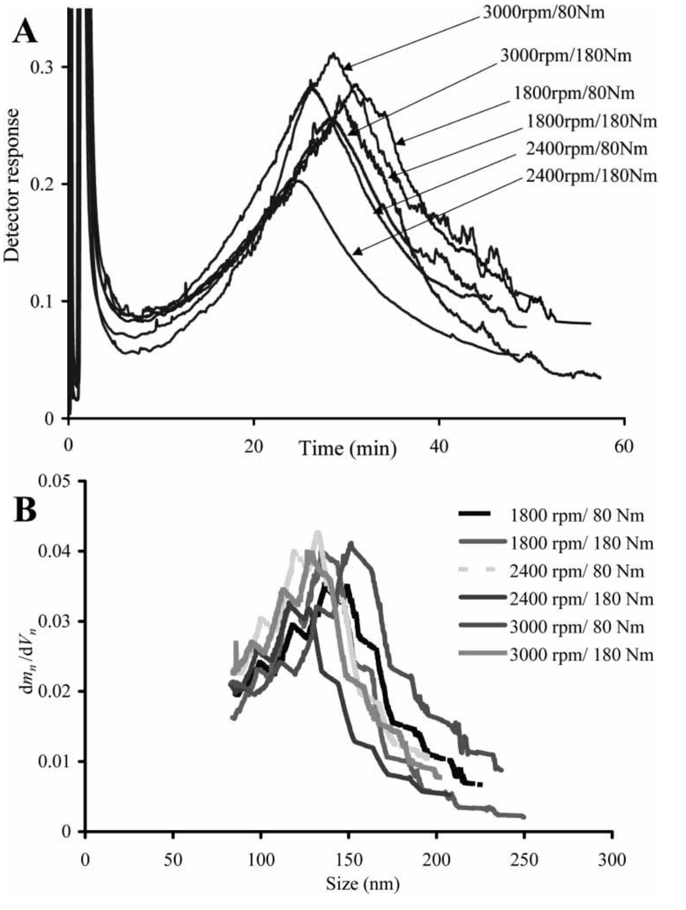

Figure 9. SdFFF elution curves (A) of collected soot samples from Table 1. Elution conditions: initial field strength, 600 g (1,972 rpm); final field strength, 29.60 g (439 rpm); predecay time, 5 min; stop flow time, 15 min; flow rate, 1.2 mL/min; sonication time, 90 min. Fractions collected at peak maximum during 4 min for 3-WEM size measurements. Size distribution profiles (B) of the collected soot samples converted from SdFFF.

size distribution by assuming the detector signal is proportional to the mass concentration, dm_n/dV_n, where m_n and V_n are the mass and volume of the nth slice of the FFF elution profile.[19–21] The size distribution can be obtained by plotting the relative mass, dm_n/dd_n versus the diameter d_n, where $dm_n/dd_n = dm_n/dV_n \times \delta V_n/\delta d_n \propto$ detector signal $\times\ \delta V_n/\delta d_n$. The equivalent spherical particle diameter d_n corresponding to a given volume V_n is determined by FFF equations. Figure 9B shows size distribution profiles obtained from the fractograms shown in Fig. 9A. It is observed that there is perturbation in the profiles, due to the direct proportionality

Table 4. Density of suspended diesel soot determined by SdFFF using retention times and 3-WEM size values of collected fractions at peak maximum

Soot sample	t_r (min)[a]	density (g/cm^3)	3-WEM mean particle size at peak maximum[a] ($\pm$4 nm)
1 (1800/80)	31.00	1.46	163
2 (1800/180)	29.01	1.68	134
3 (2400/80)	26.25	1.61	133
4 (2400/180)	25.03	1.76	128
5 (3000/80)	28.51	1.41	152
6 (3000/180)	28.15	1.70	129

[a]Retention time inside the channel (excluding the void time of the tubing, injector and detector ~0.22 min).

between the detector signal and the mass concentration dm_n/dV_n, due to the dependence of the signal on the particle size as the light attenuation is mostly due to the scattering rather than absorption.

The SdFFF measurements were repeated 2 times for each suspended soot sample, and the standard deviation was less than 3%. The variation of the SdFFF size distributions is different than the one of the SMPS size distributions for the same engine operating points. The main discrepancy between SMPS and SdFFF data is the sample preparation procedure employed for SdFFF measurements.

CONCLUSION

Soot emitted from a modern LD VW diesel engine running at various operating points was analyzed by three different techniques: 3-WEM, SMPS, and SdFFF. The 3-WEM was used for size analysis of soot suspended according to the sample preparation method elaborated in this study. Furthermore, 3-WEM is fast, easy to operate and requires no measurement calibration by standard material. 3-WEM size measurements showed that suspended soot is subject to a size reduction under the effect of sonication.

The size discrepancies obtained between SMPS and 3-WEM are related to the measurement principles: i) SMPS is an on-line technique that directly measures the size of the soot particles without any prior sample preparation. It describes better the size variation at different engine points; ii) 3-WEM is an off-line technique that requires sample preparation before the analysis. Thus, the related size values are higher than those obtained by SMPS due to a higher aggregation tendency as was shown by TEM comparison. The variation in the average particle size of soot in suspension is mostly related to the variation in the amount of the collected PM at each engine operating point.

SdFFF is used in this study for the determination of soot density in suspension, as it is assumed that a size dependant separation of soot particles occurred with a uniform density over the whole size distribution. The determination of the density using FFF related equations requires the soot mean particle size at peak maximum with its corresponding retention time to be known. Therefore, fractions of soot samples analyzed by SdFFF were collected at peak maximum for size measurements using the off-line hyphenation procedure of 3-WEM with SdFFF.

The density values calculated by FFF equations showed a small variation among soot samples. An average density value is used for the conversion of soot elution profiles to size distributions. Mean particle size values are needed for the density determination were obtained from 3-WEM by fraction collection from SdFFF fractograms at peak maximum. The SdFFF size distributions are different from the ones obtained from SMPS for the same engine operating points. The main difference is related to the sample preparation procedure employed for SdFFF measurements.

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