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Dynamic Field Measurements of Submicron Particles from Diesel Engines

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We present new tools and a complete setup with which the submicron particles, emitted from combustion processes, can be measured and classified according to their chemical nature even in the field. Diesel engines are the predominant source of these particles in the industrialized countries. The setup comprises an exhaust conditioning part including means for precipitation of the coarse particle fraction, dilution, and removal of volatile material. The submicron particles are detected with three different sensors: one for particle number concentration (condensation particle counter, CPC), one for the particle "Fuchs"-surface (diffusion charger, DC), and one that responds specifically to the carbonaceous particles (photoelectric aerosol sensor, PAS). These sensors possess a short response time so that transients such as those occurring in the free acceleration mode may be observed as well. Experiments on a conventional engine test bench demonstrate the tools. The test results are highly reassuring. Correct handling of the volatile fraction is essential to avoid severe artifacts from gas to particle reactions particularly in exhaust from engines equipped with particle traps.

Introduction

The public is increasingly concerned about the health impact of ultrafine particles from diesel engine exhaust. Diesel-powered vehicles such as passenger cars and most all trucks produce considerable densities of ultrafine particles in the air where people live. However, a significant number of engines are also used in off-road applications, e.g., in electrical power generation, ships, and construction work (*1*). If these engines are operated in areas with reduced air exchange, such as tunnels, serious problems may occur.

Table 1 shows typical concentrations for the most important pollutants in diesel exhaust and the corresponding Swiss limits for working areas. To meet the regulations for the ambient air in such areas, the exhaust gases have to be diluted by forced ventilation. It is evident that the required dilution is completely dominated by the particle emissions. Considering a typical exhaust volume of diesel engines of 6 $m^3\ kW^{-1}\ h^{-1}$, a minimal dilution air volume of the order of 750 000 m^3/h is required for a 100-kW diesel engine to keep the particulate pollution of ambient air in tunnels below the legal limits. Beside technical problems, this causes tremendous costs so that only a reduction of particle emissions can solve the problem. Progress in engine construction already has significantly reduced the emissions; however, this is by far not sufficient. Other techniques such as particle traps or fuel additives have to be applied.

TABLE 1. Diesel Engine Emissions and Limits[a]

	CO (mg/Nm^3)	NO_x (mg/Nm^3)	SO_2 (mg/Nm^3)	particles (mg/Nm^3)
diesel engine emissions	1000	3000	350	250
MAK for working areas	35	30	5	0.2
required dilution factor	28	100	70	1250

[a] Typical values for engines used in construction sites.

Therefore, emissions from off-road diesel engines and means for their reduction have been studied (*2*) in the framework of a program called VERT (*V*erminderung der *E*missionen von *R*ealmaschinen im *T*unnelbau).

Limits for working places are given for the elemental carbon (EC) concentration in Germany (*3*) and for the total carbon (TC) concentration in Switzerland (*4*). The reference method for the determination of these concentrations is coulometric analysis (*5*).

The emission limits, on the other hand, were up to now given by total mass (total particulate matter, TPM) determined by gravimetric analysis from filter samples taken at a fixed temperature (52 °C). At this temperature, the volatile fraction is mainly in the condensed, i.e., the particulate, phase.

The fact that different quantities are used for emission limits and working place limits means that it is hardly possible to estimate working place concentrations from emission values, even if the dilution is well-known. This problem increases dramatically if particle traps are used. Good traps have an efficiency of the order of 99% for particles down to diameters of some 10 nm. The EC fraction is therefore reduced by this factor. However, as the particle trap is close to the engine where the exhaust temperature is still high, much volatile material passes the particle trap in the gas phase and condenses when the exhaust gas cools. At the 52 °C for the gravimetric sampling, this material appears as particles. Particle trap efficiencies in terms of gravimetric analysis are therefore much lower, 90% or less. The ratio TPM/EC before and after the trap is completely different and depends significantly on the temperature. The very high volatile fraction after the trap enhances the temperature dependence and makes a reliable measurement of TPM concentrations at working places or ambient air measurements hardly possible when particle traps are used. So far the problems of the particle mass measurement have been discussed from the point of view of reliability and reproducibility. More importantly, one has to ask which particles are relevant for public health.

Recent research indicates that the submicron fraction that can penetrate into the alveolar region is of crucial importance (*6, 7*). This result leads to a reduction of the size limit from PM 10 to PM 2.5, but PM1 is already in discussion.

Another approach is to change from mass to number or surface concentration. This automatically gives more weight to the very small particles, which mainly determine the number concentration but are not very relevant for the total mass.

These considerations have a significant impact on techniques for particle measurement as methods are required to determine the small particle fraction and to get relevant information on the volatile particle fraction. It is not clear

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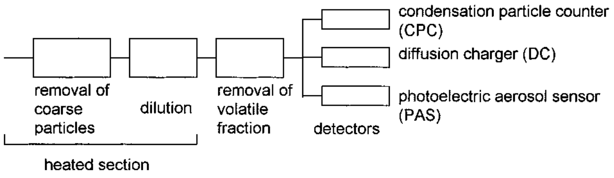

FIGURE 1. Setup for field measurements.

how regulation will develop in the future, whether particle mass in the small size range will be limited, or the number concentration will be limited, and how the problem with volatile material will be treated. According to recent findings, the solid fraction of the submicron particles is highly relevant to human health. In any case, adequate instrumentation is needed to monitor the particles in the laboratory and in the field in a simple way.

The instruments should (a) be sensitive to the submicron fraction and (b) allow you to distinguish between soot, volatile fraction, and particles different from soot that might arise from fuel additives or other fuel contaminants.

Beside test bench measurements, it is required to have a means for periodical control of particle emissions of diesel engines and—if particle traps are used—of the trap characteristics. The measurement should be such that emission and working place/ambient air values can be compared, i.e., the same quantities should be measured in both cases, preferably with the same methods.

Whereas laboratory technologies are available to some extent, field measurements still pose considerable problems. In the following, we present a technique to quantify particulate emissions in the field and in the laboratory.

Elements of the Field Measurement System

Figure 1 shows a schematic diagram of the proposed setup. In the first step, the coarse fraction has to be removed. This is necessary mainly for working place measurements where considerable amounts of dust may be present, while engine emissions usually do not contain many coarse particles.

Dilution is required not only to obtain concentration levels that are adequate for the subsequent detectors but also to prevent problems with condensation of vapors when the exhaust gas cools. While the coarse particle precipitator and the dilution have to be heated, the subsequent parts may be operated at ambient temperature. Note that the volatile fraction can be removed by a thermodesorber.

Useful detectors are (a) the condensation particle counter (CPC) to measure the number concentration; (b) the unipolar diffusion charger (DC) followed by an aerosol electrometer, which yields information on the surface concentration; and (c) the photoelectric aerosol sensor (PAS), which allows you to distinguish between soot and non-soot fractions. These components will now briefly be described.

Coarse Particle Precipitation. As already mentioned, the precipitator for coarse particles is mainly required for working place applications where substantial dust concentrations may occur. Just for this purpose a heated system is not really required. Nevertheless, it is favorable to have a heatable precipitator that can be used also for emission applications (for example, in combustion of solid fuels such as coal or wood) without running into problems with condensation of volatile material.

The coarse fraction can be precipitated readily by an impactor or a cyclone having a cutoff diameter of a few micrometers. Cyclones can be operated also at high dust concentration as they possess a large storage capacity for the precipitated material.

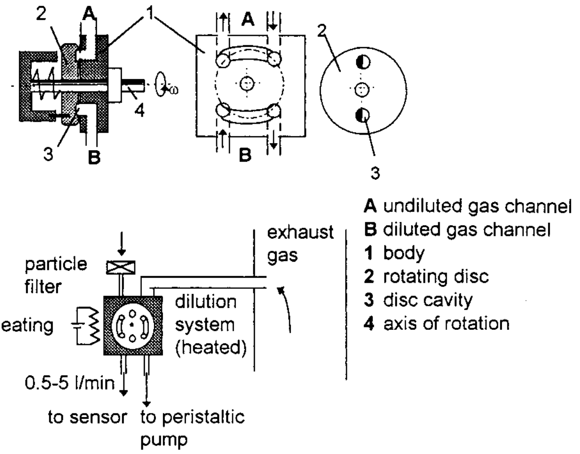

FIGURE 2. Dilution system.

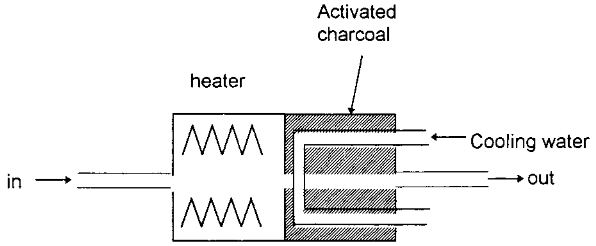

FIGURE 3. Thermodesorber.

Dilution. In engine test bench applications, dilution tunnels are used (constant volume samplers, CVS, or minitunnels as the AVL smart sampler complying with the demands of the European 13 operation points test according to ECE R49). These are very large and expensive devices that by no means can be used in field measurements. In other common dilution methods such as injector type systems, the dilution factor depends on the pressure at the input, i.e., in the exhaust pipe of the engine to be measured. As this pressure usually changes during operation, this diluter is very problematic. A simple and effective way for dilution of submicron particles is described by Hüglin et al. (*8*); see Figure 2. A rotating disk containing a number of cavities transports a well-defined amount of gas from the input channel, where the undiluted gas flows, to the output channel, where dilution gas flows. The dilution ratio is determined by the speed of rotation, the number and volume of the cavities, and the flow rate of the dilution air. However, it is independent of the flow rate of the undiluted gas. In particular, pulsations from the engine are not transferred to the diluted side. This system allows stable dilution, adjustable from 1:10 to 1:10000. It is small and can be mounted close to the exhaust pipe, making long heated tubes unnecessary and avoiding or at least reducing artifacts such as coagulation in the sampling tube. The current design can be used with temperatures up to 150 °C; a design for higher temperatures is being examined. The performance of the diluter has been tested in the size range from a few nanometers to 1 μm. For larger particles, impaction losses are to be expected; however, this has not been examined so far.

Thermodesorber. The thermodesorber (Figure 3) to remove volatile material contains a heated section where the material is vaporized. It is followed by a water-cooled section with walls consisting of activated charcoal. There the volatile material is absorbed to prevent re-attachment to the particles as the temperature drops. Some care has to be taken to design the thermodesorber such that recondensation of volatile material can be neglected. A series of test measurements prove that this is the case in the design used here (for more details, see Burtscher et al. (*9*)).

Further test measurements show that particle losses in the thermodesorber are less than 5%. The losses of the whole

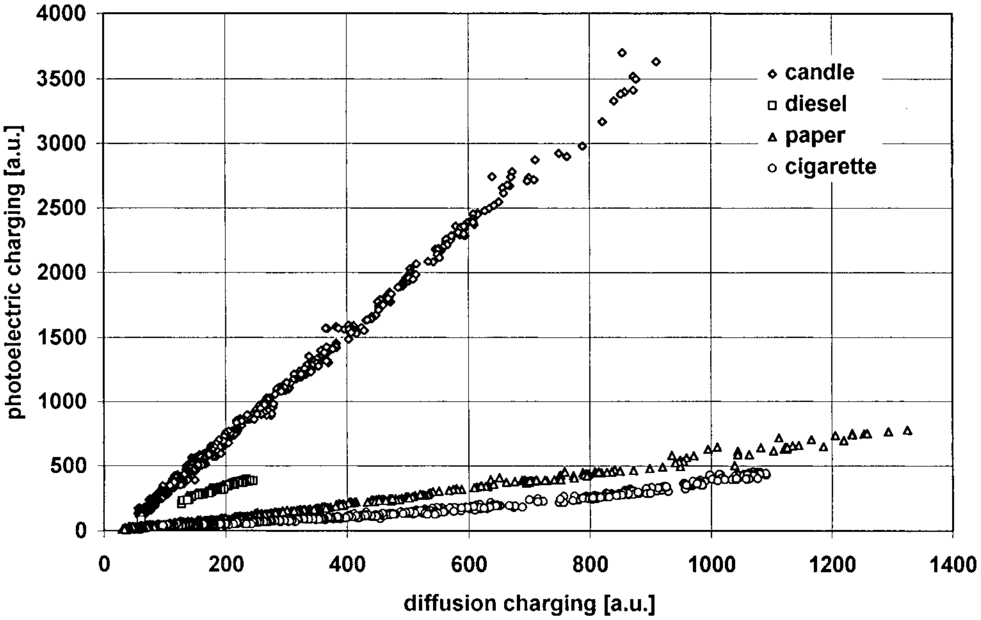

FIGURE 4. PAS signal versus diffusion charging for different kinds of combustion.

system are mainly determined by diffusion losses in the tubes. At the present flow rates and tube length, the losses are on the order of 10% for the 10 nm particles and lower for larger ones.

Detectors. *Condensation Particle Counter (CPC).* Condensation particle counters (*10*) are suitable to determine the particle number concentration down to very small particles in the nanometer size range. For the measurements described below, a TSI 3025 CPC has been used. This is a relatively expensive and delicate instrument that is of limited use in field measurements. For future applications, it is planned to apply a simpler and more rugged device based on the same principle.

Diffusion Charger (DC). In the diffusion charger, particles are charged by the attachment of ions of one polarity, created by an electrical corona discharge. In the subsequent aerosol electrometer, the current produced by the charged particles is measured. The attachment of ions to particles depends on the particle size but not significantly on their composition (*11*). In the free molecular limit, the attachment coefficient is proportional to the square of the mobility diameter d, i.e., diffusion charging is a measure of the particle surface assuming spherical particles. In general, the attachment coefficient scales with the Fuchs-surface (*12*), which is derived from the attachment coefficient for neutral atoms or molecules. So, when talking about surface here, we assume this definition not the BET surface. When using ions instead of neutral species, care has to be taken that the ion concentration is low enough to prevent errors due to the repelling Coulomb potential in multiple charging.

Photoelectric Aerosol Sensor (*PAS*). Whereas diffusion charging is more or less material independent, photoelectric charging, i.e., the emission of electrons from the particle upon irradiation with UV light, is sensitive to chemical surface properties. In a number of studies, it has been shown that this method responds to soot (*13*).

The first step in photoelectron emission is the absorption of a photon. This step is proportional to optical absorption, i.e., to the aethalometer signal or more generally to the total number of light absorbing atoms, that is to the mass of the aerosol. The probability that the photoelectron can escape from the particle is proportional to the probability with which it reaches the surface that is proportional to the surface area. Depending on which of these processes is dominant, the PAS signal is proportional to the surface or the mass. The work function depends on the chemicals at the surface; hence, the probability of overcoming the surface barrier potentials depends on the chemicals adsorbed at the surface. Therefore, the PAS signal also depends on the surface chemistry.

If the photoelectric charging probability scales with the particle cross section, i.e., the square of the mobility diameter, looking at the ratio of photoelectric charging to diffusion charging eliminates geometry and concentration. What remains is chemical information, i.e., information on the chemical nature of the surface and the bulk of the particle. This technique was used by Amman et al. (*14*) to characterize volcanic aerosol. In the case of combustion particles, this allows you to distinguish between particles arising from different combustion processes. In Figure 4, the PAS signal is plotted versus DC signal for different aerosols (*15*). If the slope is constant, which actually is the case for most aerosols except cigarette smoke, the particles do not change during the experiment. The magnitude of the slope is characteristic for the source from which the particles were emitted. In this way, source attribution of particles is possible. It was shown that the PC/DC ratio is the same for diesel aerosol all over the globe; hence, the calibration factors are universal and do not depend significantly on the individual engine (*15*).

Test Bench Results

The system described above has been compared in a large number of measurements on a engine test bench with the following: (a) scanning mobility particle sizer (SMPS) measurements, which yield the particle size distribution (*16*); (b) aethalometer measurements, which is the measure of optical absorption and thus is sensitive to the black carbon concentration (*17*); (c) gravimetric and coulometric analysis.

The test bench is operated with a dilution tunnel (AVL smart sampler) downstream and an adjustable dilution unit as described above upstream from the particle trap. This setup makes possible the simultaneous measurement on both sides of the trap. The diesel engine is a 105-kW Liebherr TDI engine type 914 T for construction machines, and the particle trap is a SHW sinter-metal filter. The two PAS are operated simultaneously while the SMPS measurements are done alternately upstream and downstream from the trap. Figure 5 shows the setup used for these measurements.

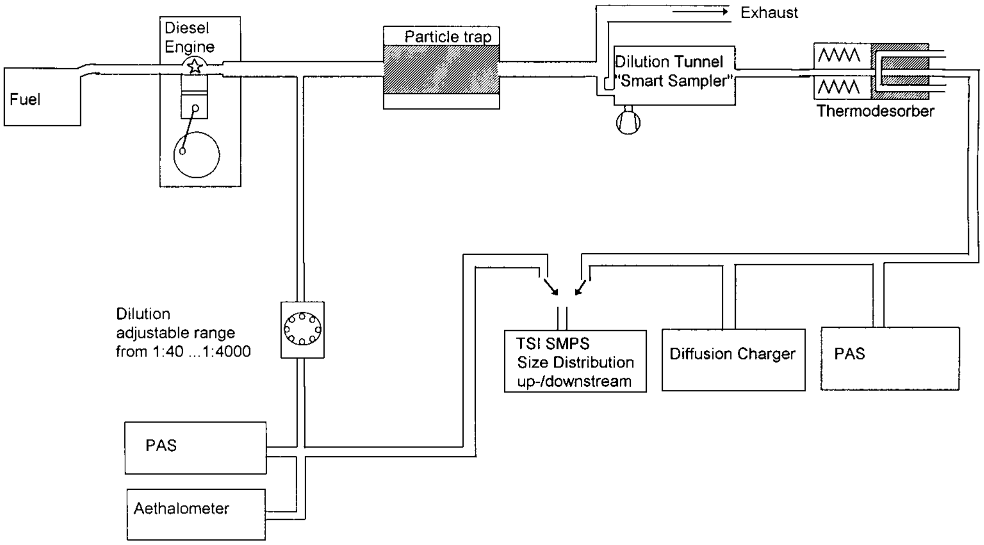

FIGURE 5. Setup of the test bench measurements.

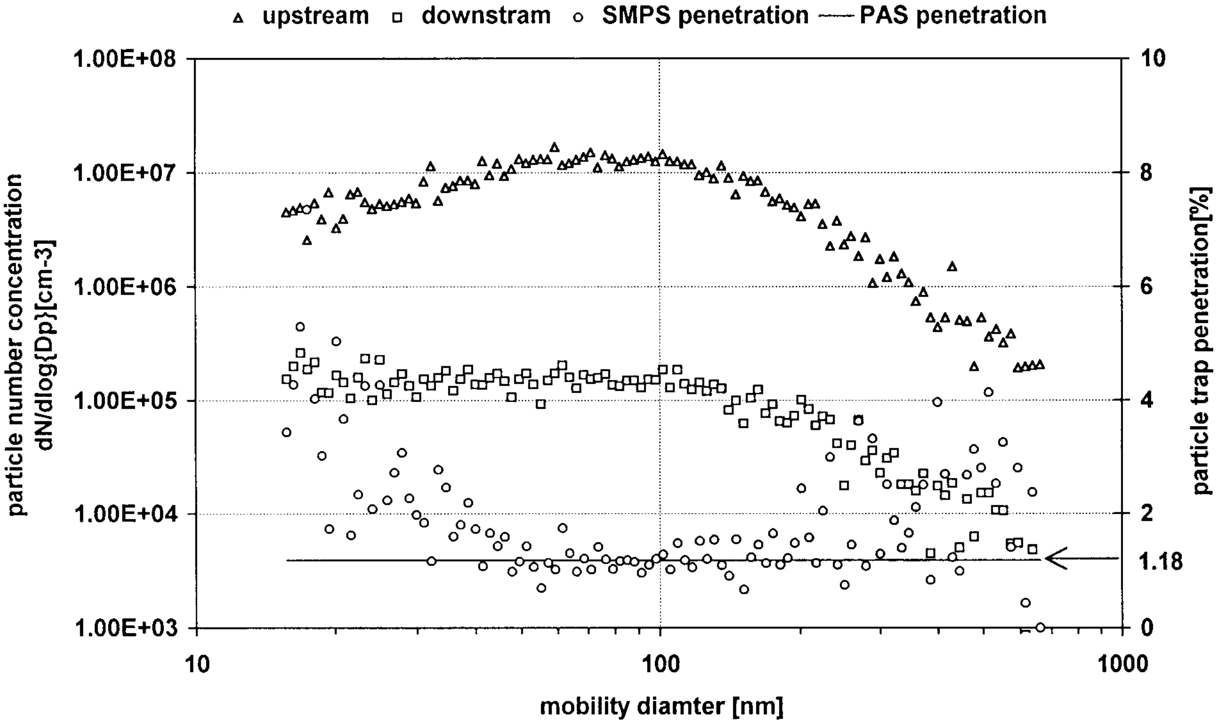

FIGURE 6. Size distribution of particles in the emissions of a heavy-duty diesel engine upstream and downstream from the particle trap. The trap penetration is also given.

Figure 6 shows a typical example of a size distribution before and after a sinter-metal particle trap, determined by a SMPS measurement, and the trap penetration. This shows that the particle trap efficiency is very high and does not significantly vary with particle size. Also plotted in the same graph is the ratio of the PAS signal upstream and downstream from the particle trap. This integral value for the particle trap penetration agrees with the SMPS result. The engine was operated in steady-state conditions at 1400 rpm and 50% of the rated torque. Similar results for the particle trap penetration within ±20% variation are obtained at the three additional operating conditions of 1400 rpm/100% torque, 2000 rpm/ 50% torque, and 2000 rpm/ 100% torque. The good agreement between the two different observations demonstrates that the PAS provides an integral information on the penetration characteristics of the particle trap in the submicron size range.

In certain operation conditions (high temperature in the trap), high concentrations of very small particles are found after the trap, in some cases much higher than upstream. These particles are mostly ultrafine H_2SO_4 droplets formed from SO_3 in the cooling phase downstream from the trap (*18*). SO_3 is generated in most traps and catalysts from SO_2 when the temperature in the trap is above approximately 460 °C. Additionally, these particles can be caused by condensation of volatile material, passing the trap in the gas phase and then condensing as the exhaust gas cools. That these particles are volatile can easily be proven by varying the temperature in the thermodesorber, as shown in Figure 7. The engine is driven on full load whereby a temperature of >500 °C is reached in the trap. The number concentration of the volatile particles is more than 2 decades higher than that of the soot particles which penetrate the trap. At higher temperatures in the desorber, the volatile species evaporate

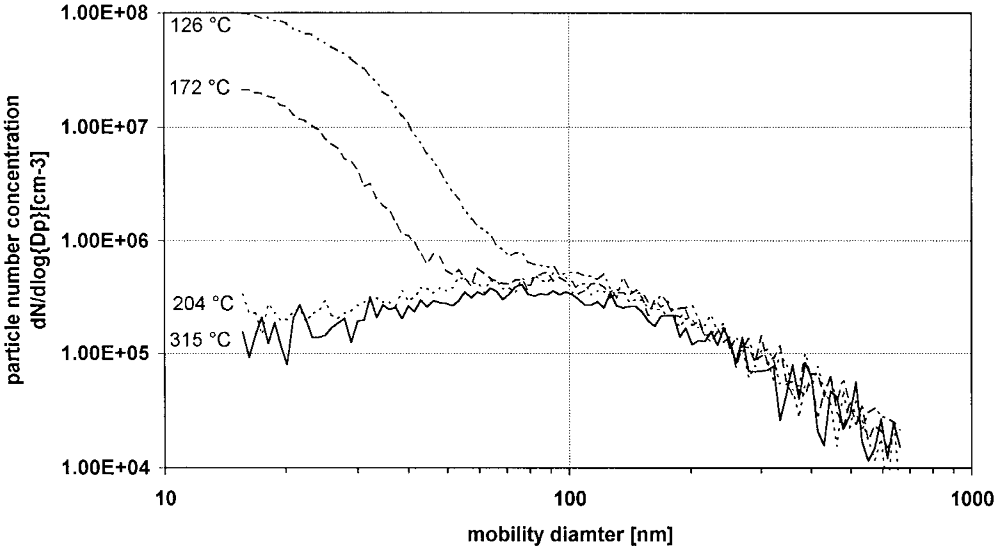

FIGURE 7. Size distribution downstream from the particle trap at different temperatures of the thermodesorber.

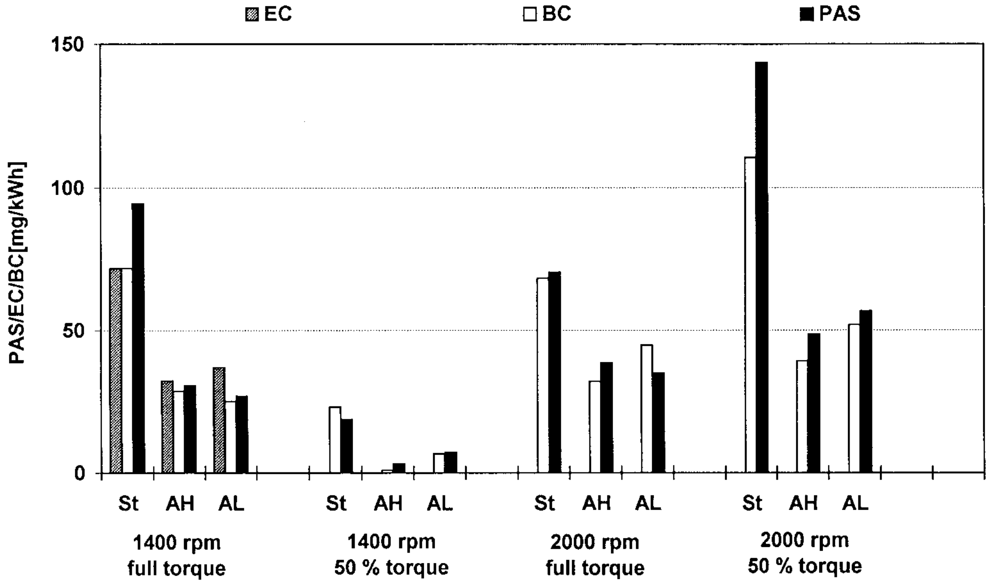

FIGURE 8. Comparison of EC and BC concentration and signal of the PAS for various operation points and fuels (St = standard fuel, AH = additive with rated dosing, AL = additive with 50% of rated dosing).

and are retained in the desorber. The thermodesorber is therefore a very important tool to distinguish between nonvolatile particles from the engine and volatile particles formed in the trap as well as to evaluate true penetration characteristics of the traps.

Within the VERT project, it has been found that in all tested diesel particle traps H_2SO_4 droplets with mobility diameter up to 50 nm and number concentration up to 10^8 cm^{-3} were formed when the temperature in the trap exceeded ≈460 °C

The volatile material may also be distinguished from the primary C particles by using the ratio of PAS and DC signals. Whereas the PAS signal is only sensitive to the carbonaceous solid part but not the volatile material, the DC measures the total surface concentration. Therefore, the PAS signal remains unchanged if the volatile material is removed by increasing the temperature of the thermodesorber; the signal from the diffusion charger strongly decreases.

The next plot (Figure 8) shows a comparison between PAS signal, EC concentration determined by coulometric analysis, and black carbon concentration (BC) measured by the aethalometer for various steady-state operation conditions using standard fuel and fuel containing two types of additives. First, this shows that the benefit of the additives for particle reduction is quite limited. Much effort has been taken to find additives that efficiently suppress soot emissions; however, up to now the main incentive to use additives has been to assist regeneration of particle traps. Second, the good correlation between PAS signal and EC as well as BC concentration indicates that the PAS monitors the carbonaceous particulate fraction in diesel exhaust. This is valuable because it is particulate EC that is limited at working places.

Some of the legal emission tests on combustion engine emissions are performed in transient operating conditions, e.g., drive cycles on roller dynamometers. For gravimetric or coulometric analysis, filter samples are taken over the whole drive cycle. The short time response of the PAS allows dynamic measurements, yielding detailed information in which part of the cycle emissions are high or low. If the analyzer of the SMPS is set to one particle size, the subsequent CPC can also track the time dependence of the particle concentration.

Figure 9 illustrates the PAS signal in comparison with the number concentration of 100 nm soot particles of a TDI diesel

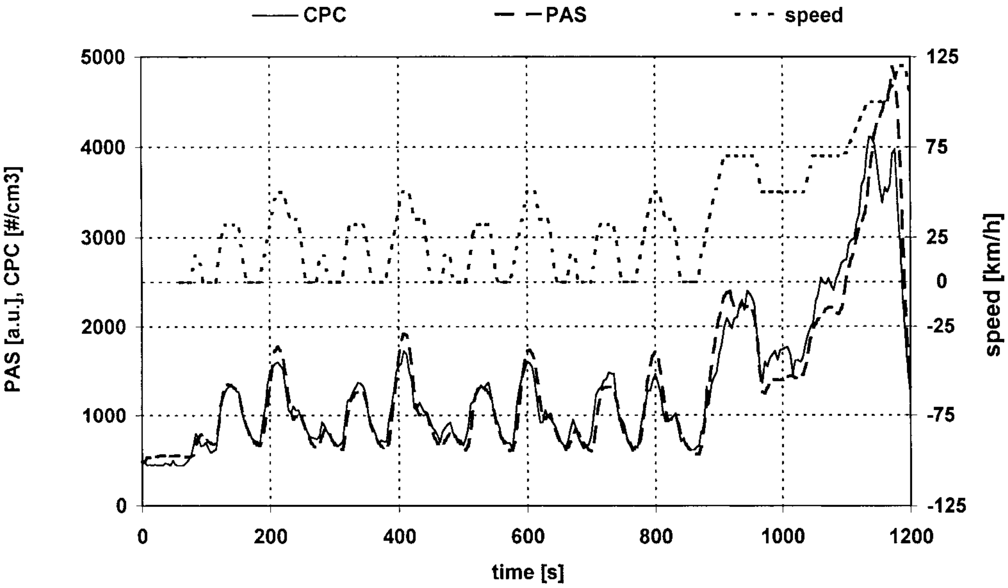

FIGURE 9. Transient ECE−EUDC driving cycle, measured by the PAS, and the particle concentration at the outlet of a mobility analyzer set to 100 nm.

passenger car in an ECE−EUDC driving cycle on a roller dynamometer. SMPS measurements show that the mean mobility diameter of the particles is approximately 100 nm, independent of the load condition. An excellent correlation is observed between the number concentration at 100 nm diameter and the signal of the PAS. This shows that photoelectric charging is tightly related to the concentration of particles in the submicron range where most of the soot particles are found.

Discussion

The last example demonstrates that photoelectric charging is adequate to track submicron particle emissions in transient operation conditions. Measurements on a test bench or a roller dynamometer are very expensive and, therefore, cannot be used for periodical tests of engine emissions or particle trap characteristics. A simple technique uses free acceleration (*19*). Even if this method yields much less detailed information, it may be sufficient for field tests, provided that an adequate measurement technique exists. The high time resolution of the PAS and DC allows us to perform such measurements in the field. As in the last example, comparison of PAS results with 100 nm concentrations shows a good agreement. Doing the measurements upstream and downstream of a particle trap yields good information on the trap characteristics. The sensitivity of PAS and DC is high enough to determine also particle concentrations at working places.

The proportionality between PAS signal and EC concentration is explained by the fact that the first step in photoelectric charging is the absorption of a photon, which is proportional to the number of absorbing atoms. However, as the fractal dimension of the aggregates often is of the order of 2 and the primary particle size varies only little, the mass also scales with d^2, which is yet another reason the surface-sensitive PAS and EC are proportional.

The new dilution unit replaces the bulky dilution tunnels and is adjustable to a wide range of dilutions. It furthermore is portable, easy to use, and easy to maintain. The removal of the volatile particles, for instance, in a thermodesorber, is required to obtain results that are reproducible and can be interpreted. The latest results indicate that the thermodesorber may be replaced by a high enough dilution with preheated dilution air.

The combination of PAS and DC provides relevant information on the chemistry, source, and surface concentration without the need of the more complicated size classification. If a size determination is required, a promising approach is the electrical low-pressure impactor ELPI (*20*). The EPLI is a commercial instrument that is rugged enough for field use.

In this paper, results from one engine are presented. On the basis of our decade long research on diesel particles, we do not expect that these results are different with another engine. However, a program to study the universality of the relations is in progress where the influence of engine type, age of the particles, and interaction of the particles with other gaseous pollutants is being investigated. First results are available from the study of fresh diesel particles on motor ways in or near major cities around the globe. The results indicate universal validity of the calibration factors (*15*).

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