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# Physical characterization of particulate emissions from diesel engines: a review

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**Abstract**

Properties of particles emitted from diesel engines and the consequences of these properties for sampling and measuring the particles are reviewed. The influence of aftertreatment devices such as particle traps and catalytic converters on particle properties is demonstrated. Based on the particle properties and results from health effect studies, requirements to metrics, and measurement systems, for example, for type approval testing, are discussed. This discussion is limited to physical properties. Special attention is given to the volatile fraction. We show that care has to be taken when designing the sampling and dilution system, because this step decisively influences what happens with the volatile material, which may remain in the gas phase, condense on solid particles, or form new particles by nucleation. If nucleation occurs, particles formed in the sampling lines may dominate the particle number concentration. A selection of systems for dilution, conditioning and measuring is shown. Systems to

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*Abbreviations:* BC, black carbon; BET, Brunauer, Emmett, and Teller; CPC, condensation particle counter; CPSA, condensation particle size analyzer; CVS, constant volume sampler; DC, diffusion charger; DIN, deutsche Industrienorm; DMA, differential mobility analyzer; EAD, electrical aerosol detector; EC, elemental carbon; EDB, electrical diffusion battery; ELPI, electrical low pressure impactor; EPA, Environmental Protection Agency; EU, European Union; FEFD, full exhaust flow dilution tunnel; GRPE, Groupe de travail de la pollution et de l'énergie (working party on pollution and energy); HC, hydrocarbon; MAAP, multi-angle absorption photometer; MASMO, mass monitor; N-MASS, nucleation mode aerosol size spectrometer; OC, organic carbon; OSF, organic-soluble fraction; PAH, polyaromatic hydrocarbon; PAS, photoelectric aerosol sensor; PFED, partial exhaust flow dilution tunnel; PM, particulate mass; PMP, Particle Measurement Program; QCM, quartz crystal microbalance; SEM, scanning electron microscope; SMPS, scanning mobility particle sizer; SUVA, schweizerische Unfallversicherung; TC, total carbon; TEM, transmission electron microscope; TEOM, tapered element oscillating microbalance; TIRE-LII, time-resolved laser-induced incandescence; UNECE, United Nations Economic Commission for Europe; VDI, Verein deutscher Ingenieure


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determine number, mass, and surface concentrations, size distributions, and carbon concentration are discussed. The discussion is focused on systems developed or adapted recently for the physical characterization of diesel particles.


*Keywords:* Diesel particulate emissions; Emissions measurement; Volatile material; Aftertreatment

## 1. Introduction

Due to their adverse health effects and their abundance in the vicinity of roads, in particular in urban areas, diesel particles have been of great concern in the past years (Lighty et al., 2000; Wichmann and Peters, 2000). Many toxicological and epidemiological studies established adverse health effects by particulate matter (PM10, PM2.5). There is increasing evidence that several health effects are associated with the ultra-fine particles with diameters below 100 nm (Brown et al., 2001). Recent research shows that they can penetrate the cell membranes, enter into the blood and even reach the brain (Oberdörster et al., 2004). Some investigations indicate that particles can induce inheritable mutations (Somers et al., 2004).

Therefore, great efforts are taken to reduce the emissions and the regulations are becoming stricter. Table 1 shows some European limits for on-road vehicles. These limits are defined in mass per distance (g/km, light-duty vehicles) or mass per energy (g/kW h, heavy-duty engines) over a defined test cycle. Limits for off-road engines are shown in Table 2. Already now, the off-road engines contribute about 50% of the total particulate emissions from combustion engines (data for Switzerland; Mayer, 2004). The main emitters are construction engines and engines used in agriculture and forestry. As the lifetime of these engines is longer than that of on-road engines, a reduction in the emissions takes more time to become effective. The relative contribution of these engines to the total particle emissions will therefore increase in the future. More information on limits and the corresponding test cycles in a number of countries can be found in www.dieselnet.com/standards.html.

Optimization of the engine combustion process has already lowered particle emissions significantly. In the future, aftertreatment devices such as catalytic converters and particle traps will become increasingly important. Detailed information on several aftertreatment techniques can be found in Steinmetz (2004). Particle traps can achieve a really dramatic reduction in particulate emissions (typically $> 99\%$ for solid particles).

The established method to measure particle emissions for type approval tests is gravimetric analysis of filter samples, taken from a full exhaust flow dilution tunnel (FEFD). As can be seen from Fig. 1 the detection limit of this method is already achieved with the Euro 4 limit and the corresponding US limits. The sensitivity of gravimetric analysis therefore has to be increased to remain applicable also for low-emission engines of the future.

However, the optimization of the engine combustion process and the application of aftertreatment devices not only reduces the emitted particle mass but also leads to significant changes in the nature of the particles, such as a relative increase in the volatile fraction. These changes have to be considered in the development of new limits and the corresponding emission metrics. Along with the insight that mainly very small particles are of importance for health effects, these changes raise the question whether *mass* still is the appropriate metric for particle emission standards.