U. Matter
Eidg. Technische Hochschule ETH
Zürich
Switzerland

Formation of volatile Particles in Traps

Volatile and Nonvolatile Particles in Exhaust of Diesel Engines with Particulate Traps

U. Matter[1], H.C. Siegmann[1], M. Kasper[1], and H. Burtscher[2]

[1]Laboratorium für Festkörperphysik, ETH Hönggerberg, CH-8093 Zürich, Switzerland

[2]Fachhochschule Aargau, CH-5210 Windisch, Switzerland

Abstract

Two different types of diesel particulate traps are compared with respect to their influence on the spontaneous nucleation of volatile material downstream of the trap. This nucleation leads to nanoparticle emissions of considerable number concentration. One of the trap is built up of catalytic active sinter-metal, the other of non catalytic active silicon carbide (SiC). With both traps volatile nanoparticles are observed when a threshold temperature of the exhaust in the trap is exceeded.

These nanoparticles are investigated by a) a thermodesorber with adjustable temperature in the heating zone to evaluate the evaporation temperature of the nanoparticles and b) by analyzing SO_4 and total particulate mass downstream of the trap. In operating conditions where volatile nanoparticles are emitted, the SO_4-concentration is appr. 5 % of the total mass. The particles consist mainly of volatile material. Varying the thermodesorber heating temperature shows that the volatile material evaporates at appr. 100°C. Therefore it can be concluded that the volatile nanoparticles consist of high diluted sulfuric acid. The threshold temperatures (exhaust temperature in the trap) for the emission of volatile nanoparticles is appr. 300 °C in the SiC-trap and appr. 460 °C in the sinter-metal trap. This indicates that the characteristics of the trap have significant influence on the nucleation process.

Introduction

Spontaneous nucleation of volatile material may lead to the appearance of nanoparticles in the exhaust of combustion engines. Such gas to particle reactions are attracting considerable interest because they are a major disturbing factor in the legal evaluation of the emissions from diesel engines.

In various studies and experiments, (Kittelson et al., 1998, Shi et al., 1998) interrelations have been established between these condensation phenomena and the experimental conditions at which the exhaust gases were sampled. It turned out that the main factors are the residence time as well as the temperature in the tail pipe, and the degree to which the exhaust gases are diluted. In the VERT-project and subsequent studies (Mayer et al., 1998, Matter et al., 1999), nanoparticle formation has been observed exclusively downstream of particle traps and oxidation catalysts. It must be concluded that some properties of these aftertreatment devices have a significant influence on the formation of particles in the gas to particle reactions. In the present work, we now investigate in more detail the conditions for nanoparticle formation from the gas phase for two different types of diesel particulate traps.

Experimental setup

The measurements were carried out at the engine test bench of the Berner Fachhochschule Biel-Nidau, the setup is described in fig. 1. A Liebherr heavy duty 105 kW turbo charged diesel engine type 914 T for construction machines is operated in continuous load conditions according to ISO 8178. Standard diesel fuel acc. to EN590 KO with sulfur content lower than 50mg/100g and a sulfur free synthetic DEA fuel have been used to examine the influence of sulfur on the emission of volatile nanoparticles.

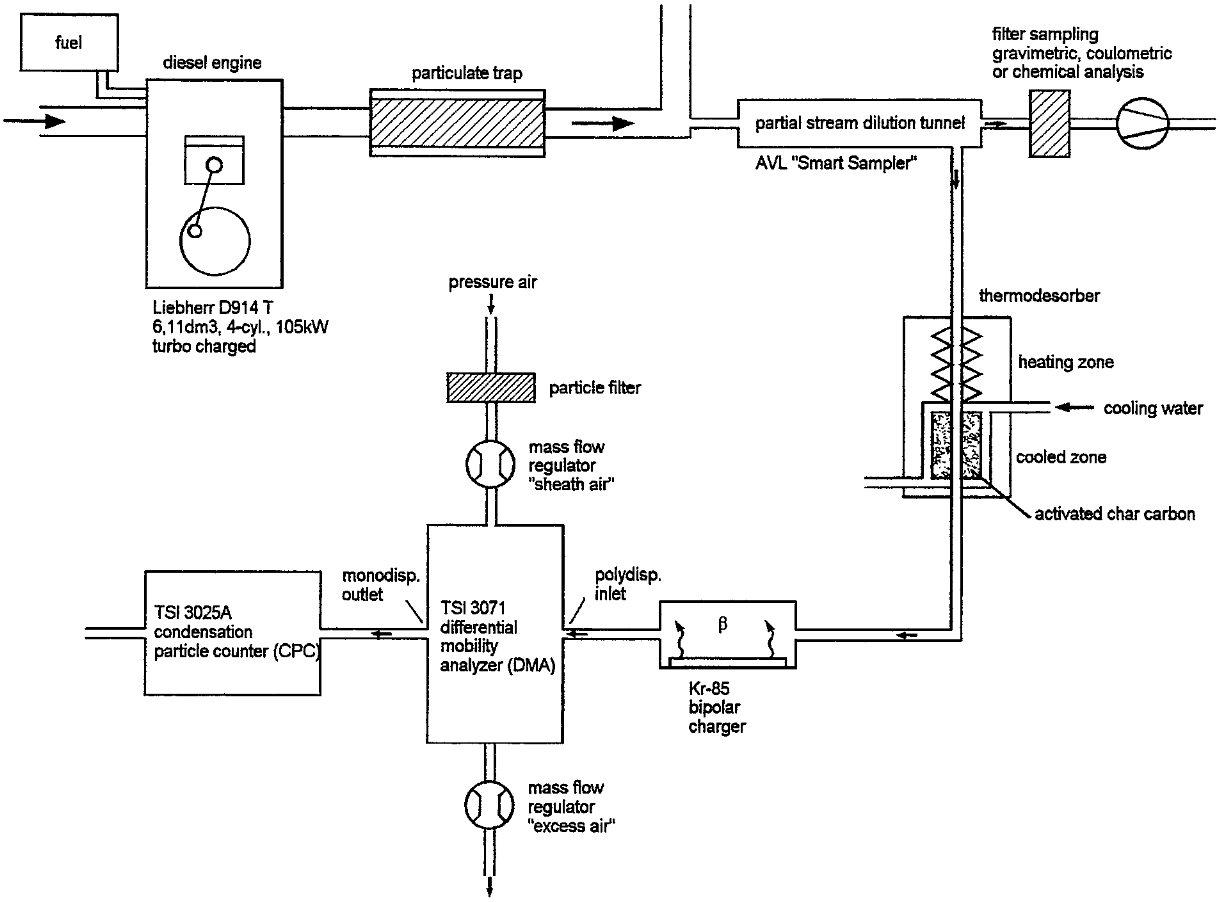

Fig. 1, Experimental setup

The two investigated traps, a sinter-metal and a SiC-trap, are introduced between the engine and an AVL "Smart Sampler" partial stream dilution tunnel. Filter samples for gravimetric mass- and SO_4—analysis with an undiluted mass flow of 0.4 g/s and a dilution of 1:5 were taken. The dilution ratio for the fine particle measurement varied between 1:6 and 1:16, depending on the operation conditions of the engine. The dilution factor in the tunnel is calculated from the CO_2- concentration in the diluted and the undiluted gas.

A TSI SMPS-system (Scanning Mobility Particle Sizer) is applied to measure the particle size distribution in the mobility diameter range of 16 — 700 nm (Wang et al., 1990). For some of the measurements a thermodesorber (Baltensperger, 1997) was connected between the dilution tunnel and the SMPS-system. This device consists of an entrance zone which can be heated to a regulated temperature from ambient until 330 °C. The gas stream then traverses a cooled zone with activated charcoal behind a fine grid where vapors of evaporated volatile particles are captured. The thermodesorber is operated in two modes. a) Using a constant temperature $T \cong 300$ °C. In this case the SMPS-system analyses only the nonvolatile particle fraction which is of interest for the evaluation of the trap penetration characteristics; b) measuring at variable temperature which allows us to determine the evaporation temperature of volatile particles.

Measurements

Penetrations of particulate traps are evaluated by measuring the particle size distribution of the diesel engine downstream of the trap and without trap. The penetration is evaluated as the ratio of the particle number concentration with and without trap respectivly at continuous load conditions. Usually the following 4 operation points according to ISO 8178 are measured:

1 = 2000 rpm/100 % torque (105 kW)
2 = 1400 rpm/100 % torque (88 kW)
5 = 2000 rpm/50 % torque (52.5 kW)
6 = 1400 rpm/50 % torque (44 kW)

Fig. 2 shows a result without thermodesorber and a sinter-metal trap at ISO point 5 with 52.5 kW load and an upstream exhaust temperature of appr. 320 °C. The 2 distributions are typical for carbonaceous soot particles from diesel engines and show the excellent filtration characteristics of the sintermetal trap: 99% of the particles are removed over the entire size range investigated.

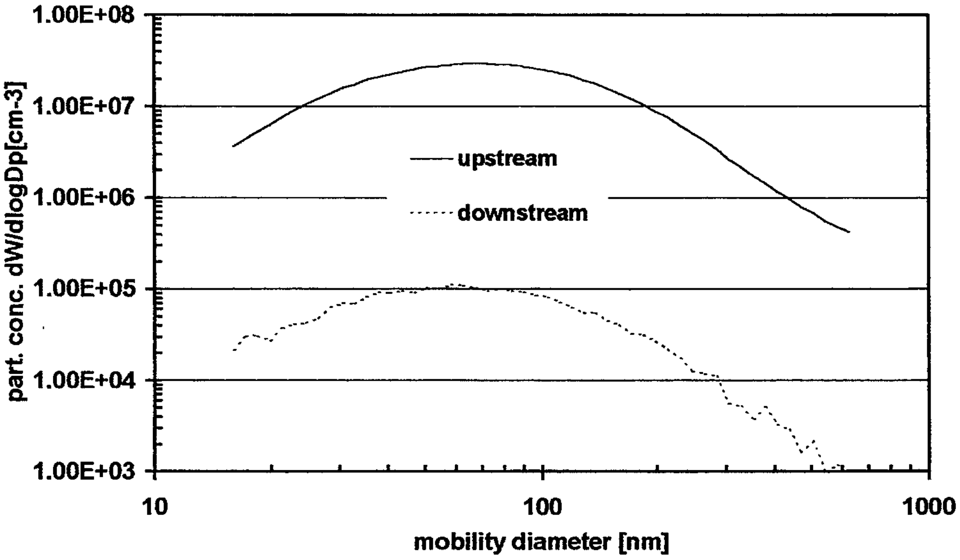

Fig. 2 Particulate emissions up- and downstream of the sinter-metal trap at 2000rpm/ 50% torque (ISO point 5) upstream exhaust temperature appr. 320°C

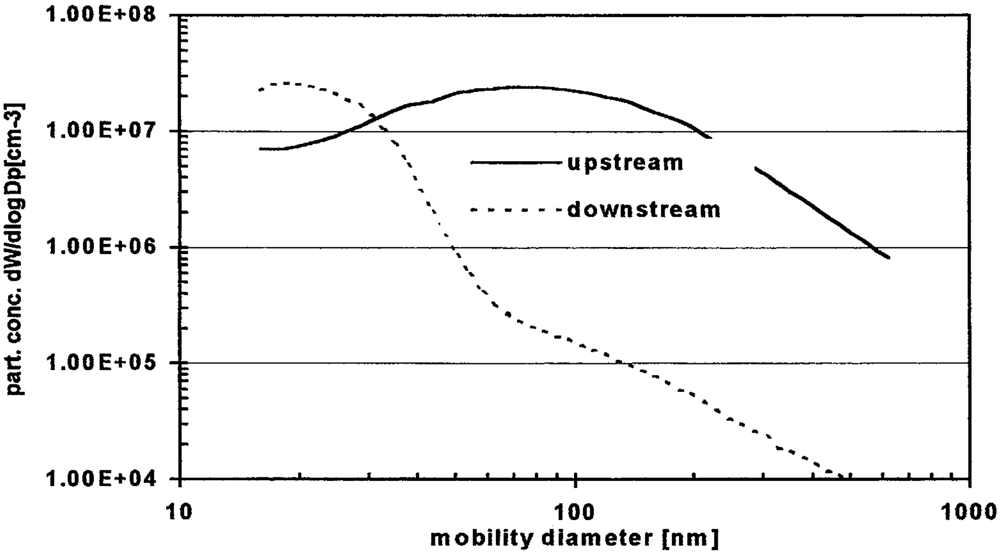

Fig. 3 Particulate emissions up- and downstream of the sinter-metal trap at 2000rpm/ 100% Torque (ISO point 1) upstream exhaust temperature appr. 470°C

In fig. 3 the size distributions are shown for ISO point 1 with 105 kW load and an exhaust temperature of appr. 470 °C. The distribution downstream of the trap is completely different to that at ISO point 5. Its shape is dominated by a high number concentration of nanoparticles at appr. 20 nm. These nanoparticles are emitted as soon as the exhaust temperature rises above appr. 460 °C and disappear when the temperature decreases below appr.450 °C.

The thermodesorber is introduced to examine whether these ultrafine nanoparticles are volatile. In fig. 4 the size distributions downstream of the trap are shown at ISO point 1 for several thermodesorber temperatures. These diagrams illustrate clearly that the nanoparticles below 60 nm are volatile droplets which start evaporating at appr. 150 °C.

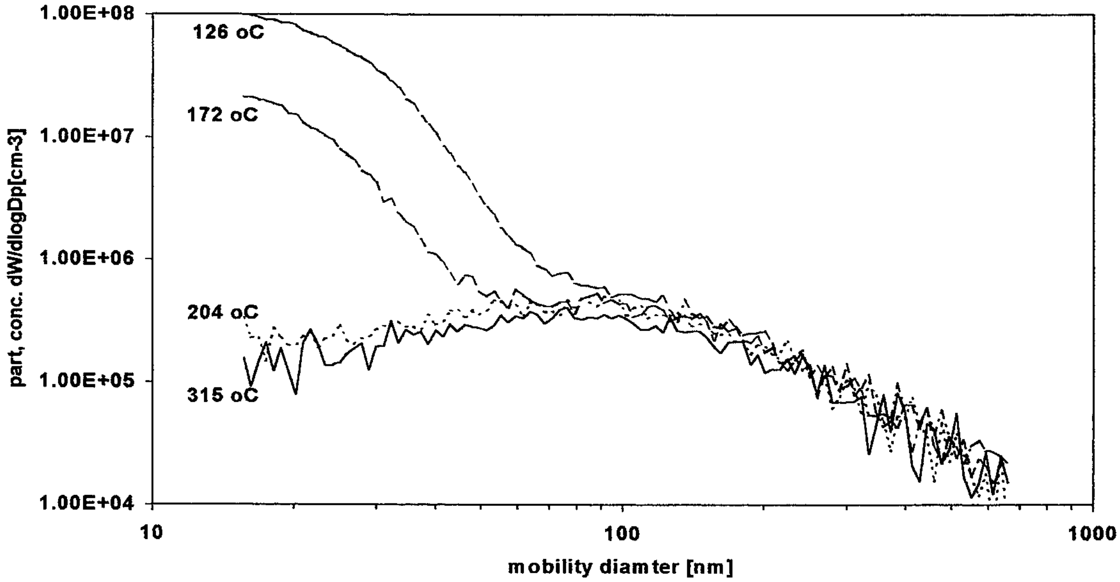

Fig. 4 Size distribution downstream of the sintermetal trap on 2000rpm/ 100% torque (ISO point 1) with thermodesorber at variable heating temperatures

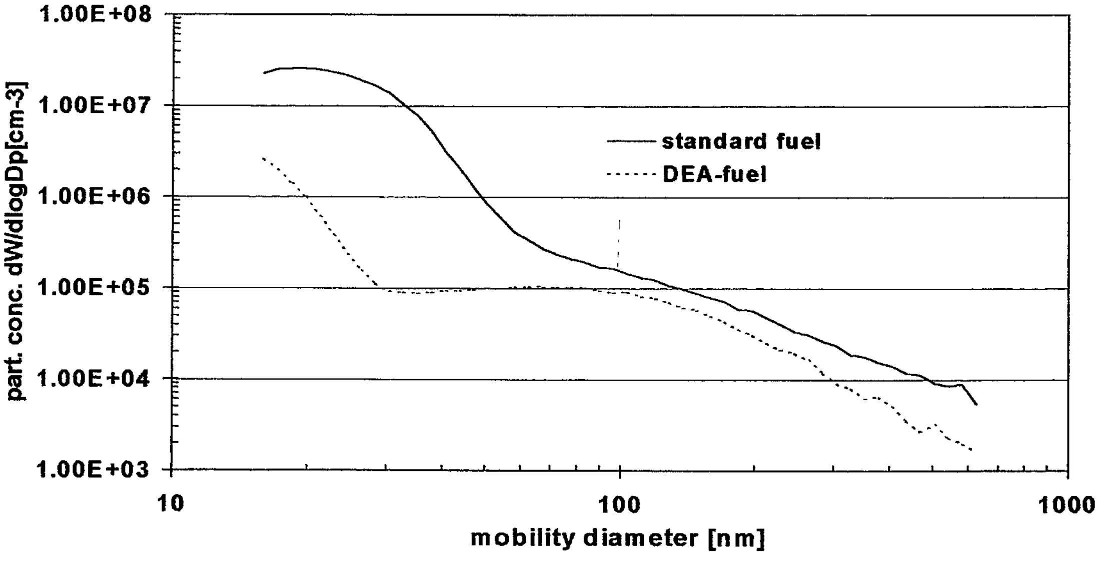

Fig. 5 Size distribution downstream of the sintermetal trap on 2000rpm/ 100% torque (ISO point 1) with 2 fuels of different sulfur content

It is known that oxidation catalysts can be origin of sulfuric acid droplets as a result of catalytic oxidation of SO_2 to SO_3 on the catalytic surface (Gairing et al., 1994). The influence of the sulfur content in the fuel is therefore examined. ISO point 1 downstream of the trap is measured without thermodesorber comparing the nanoparticle emission with standard fuel EN 590 (S typically 300 ppm) to the emission with a synthetic sulfur free DEA fuel (S < 5 ppm). The difference in the nanoparticle concentrations as illustrated in fig. 5 support the hypothesis that the nanoparticles are mainly sulfuric acid droplets.

While chemical reactions leading to sulfuric acid droplets have to be expected in the catalytically active sinter-metal trap, this is not the case for the catalytically non active SiC trap.

traps	**sinter-metal**	**SiC**
material	Ni/Cr/Fe	SiC-ceramic
penetration	10^{-2}	10^{-3} - 10^{-4}
cell density	< 100 cpi	200 cpi
relative surface	1	4
min. temp. for volatiles	450 – 470 °C	300 – 320 °C
catalytic properties	yes	no

Table 1 Specifications for sinter-metal- and SiC-trap

Table 1 shows some data for the two filters. The SiC-trap has an exceedingly low penetration for solid particles if measured with thermodesorber heated to 300 °C thus suppressing the condensation of particles.

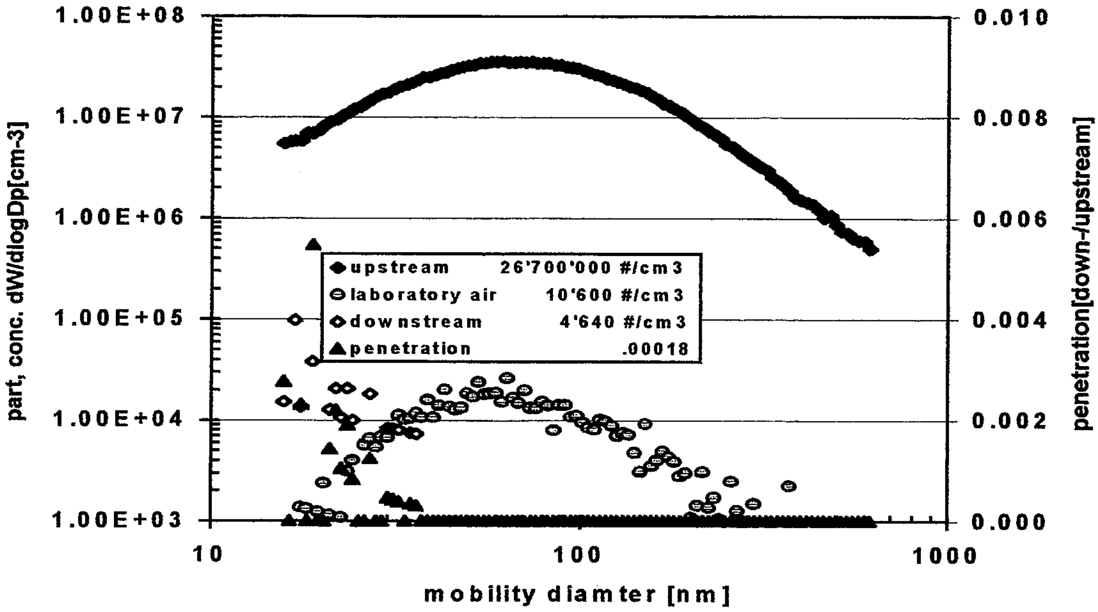

Fig. 6 Solid particle emission up- and downstream of the SiC-trap on 1400rpm/ 50% torque (ISO point 6) measured with thermodesorber at 300°C

Fig. 6 illustrates one of these tests in which penetrations from 10^{-3} to 10^{-4} have been observed. The particle number concentration downstream of the trap is by one to two decades lower compared to the ambient laboratory air.

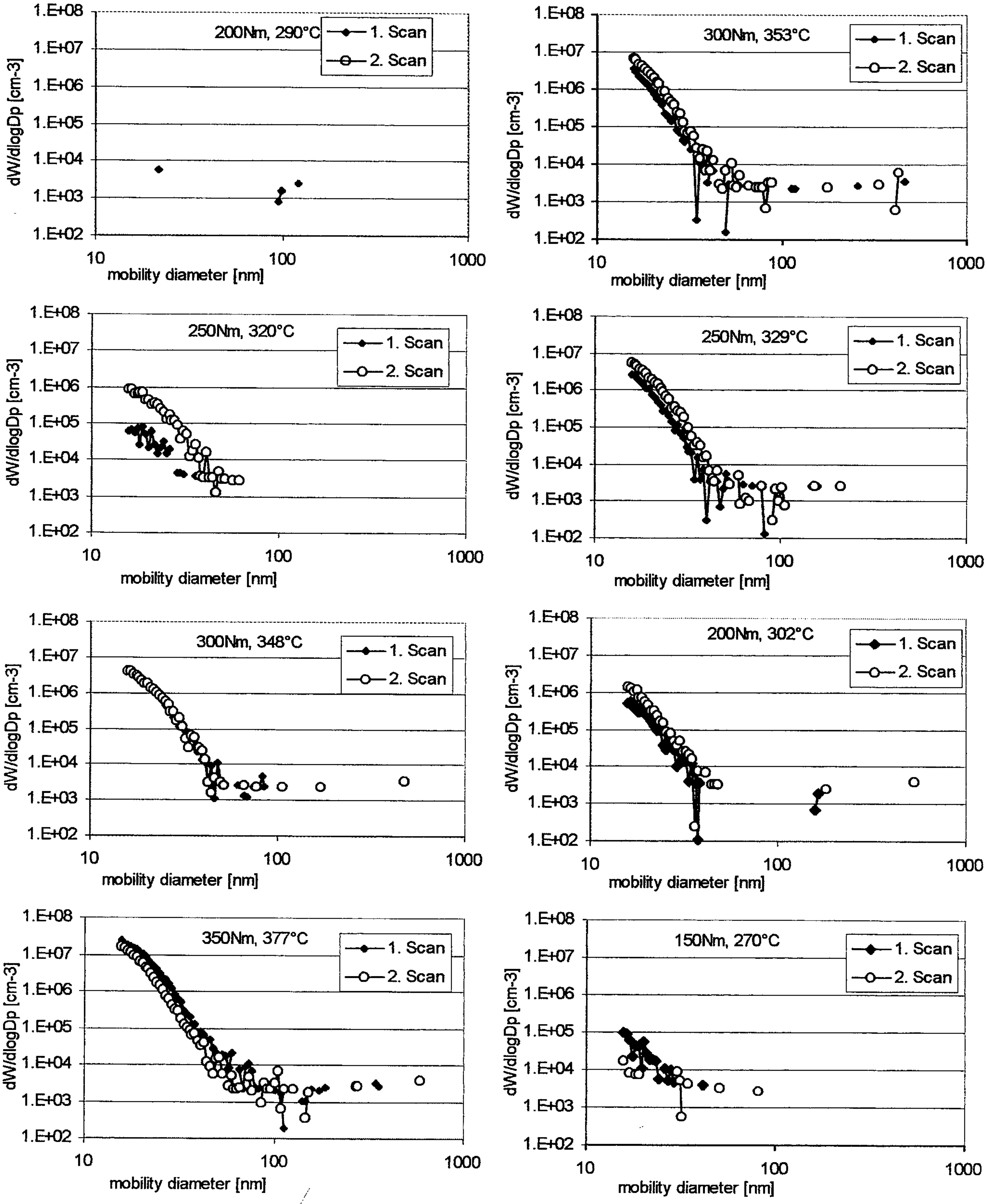

Fig. 7 Particle emission downstream of the SiC-trap on 1400rpm at variable exhaust temperatures and torques

Measurements without thermodesorber reveal that the SiC-trap emits volatile nanoparticles as well, and that this phenomenon appears already at an upstream exhaust temperature above appr. 300 °C. To examine the reproducibility of the relation between the upstream

Legal gravimetric mass measurement (VRV, 1992) calls for sampling volatile and nonvolatile material in the exhaust at a temperature of 52 °C. Since the mass of the solid particles penetrating the trap can be neglected it must be concluded that the legally determined gravimetric particulate mass downstream of the SiC-trap consists mainly of nanosize droplets of low concentration sulfuric acid.

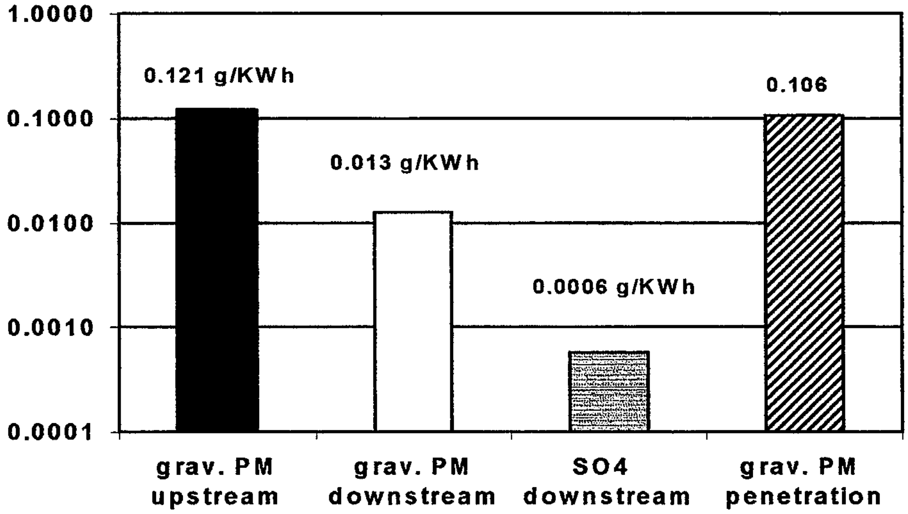

Fig. 9 Gravimetric and chemical SO_4 analysis on the SiC-trap at 2000rpm/ 100% torque (ISO point 1)

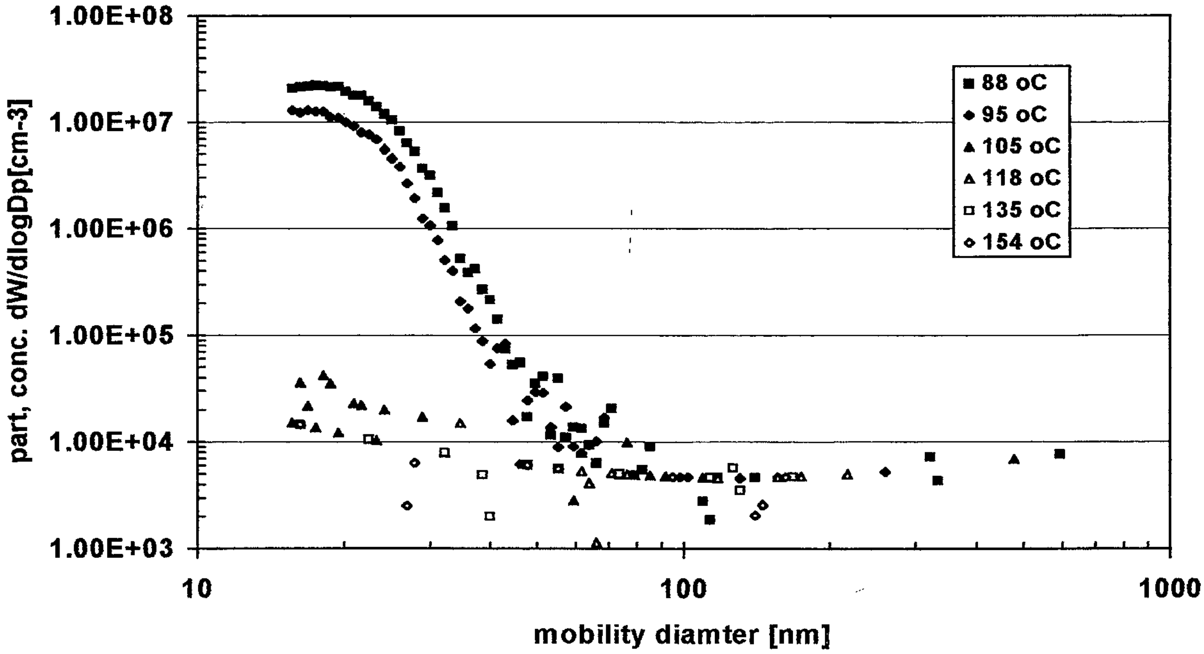

Fig. 10 Particle emissions downstream of the SiC-trap at 2000rpm/ 100% torque (ISO point 1) with thermodesorber at variable temperatures

exhaust temperature and the onset of particle formation, the diesel engine is operated in a narrow band above and below the threshold temperature for the emission of volatile particles. The variation of the exhaust temperature is done by increasing and decreasing the torque in small steps at a constant speed of 1400 rpm.

Fig. 7 illustrates how the nanoparticles in the lower size range appear at rising and disappear at decreasing temperatures.

In fig. 8 the total number concentration is plotted versus the upstream exhaust temperature. The concentration increases and decreases over more than two decades in a narrow temperature range around appr. 300 °C and shows a hysteresis. It is not examined whether the hysteresis is due to the chemical reaction mechanism in the trap itself, or to the time lag between trap and exhaust gas temperature. There is no possibility to measure the temperature inside the trap. Therefore it is probable that the time interval of appr. 15 min, chosen between the measurements of the particle spectra are not sufficient to establish the equilibrium trap temperature

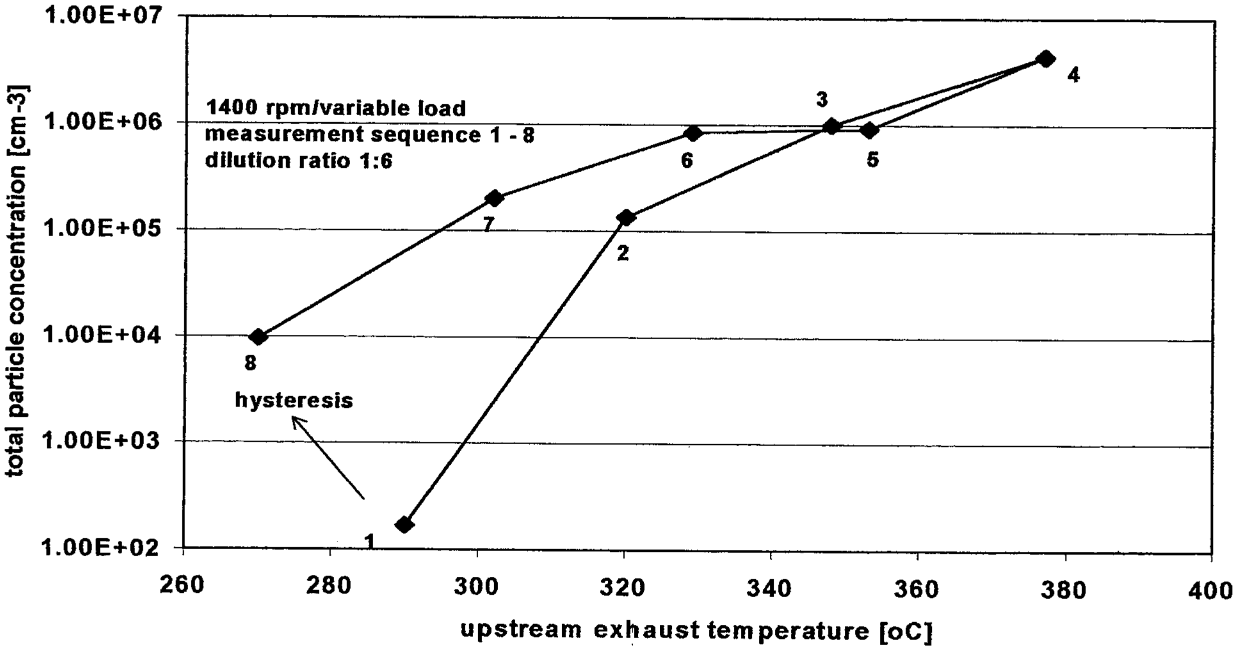

Fig. 8 Particle emission on SiC-trap on 1400rpm, total number concentration versus exhaust temperature

To obtain additional information about the nature of the volatile nanoparticles the gravimetric mass is compared to the total sulfate (SO$_4$)concentration downstream of the trap (see fig. 9). This analysis is carried out at the full load ISO point 1 which is clearly above the threshold temperature for the emission of volatile nanoparticles.

Additionally the evaporation temperature is evaluated by measuring the size distribution with the thermodesorber at variable temperatures. The distributions in fig. 10 reveal that the volatile nanoparticles evaporate at appr. 100 °C.

Two significant observations can be deduced from fig. 9 and fig. 10

- The penetration evaluated from gravimetric mass measurement up- and downstream of the trap is only appr. 10^{-1} or a factor of 50 worse than that obtained by the measurement of only the solid particles (fig. 6).
- The SO$_4$-concentration in the particles downstream of the trap is appr. 5% of the total mass. Hence this material consists mainly of liquid droplets evaporating at appr. 100 °C.

Conclusions

Investigations of two different particle traps show that the formation of volatile nanoparticles may occur under certain operating conditions. In many experiments within VERT- and subsequent projects this phenomenon has been observed on most of the tested traps.

The comparison of the two traps shows a significant difference in the threshold temperature above which the gas to particle reactions set in. This threshold is appr. 300 °C for the SiC-trap and appr. 460 °C for the sinter-metal trap (see fig. 11). This result indicates that not only the sampling conditions but also the trap construction and the filter material have an influence on the formation of nanoparticles in gas to particle reactions after the trap.

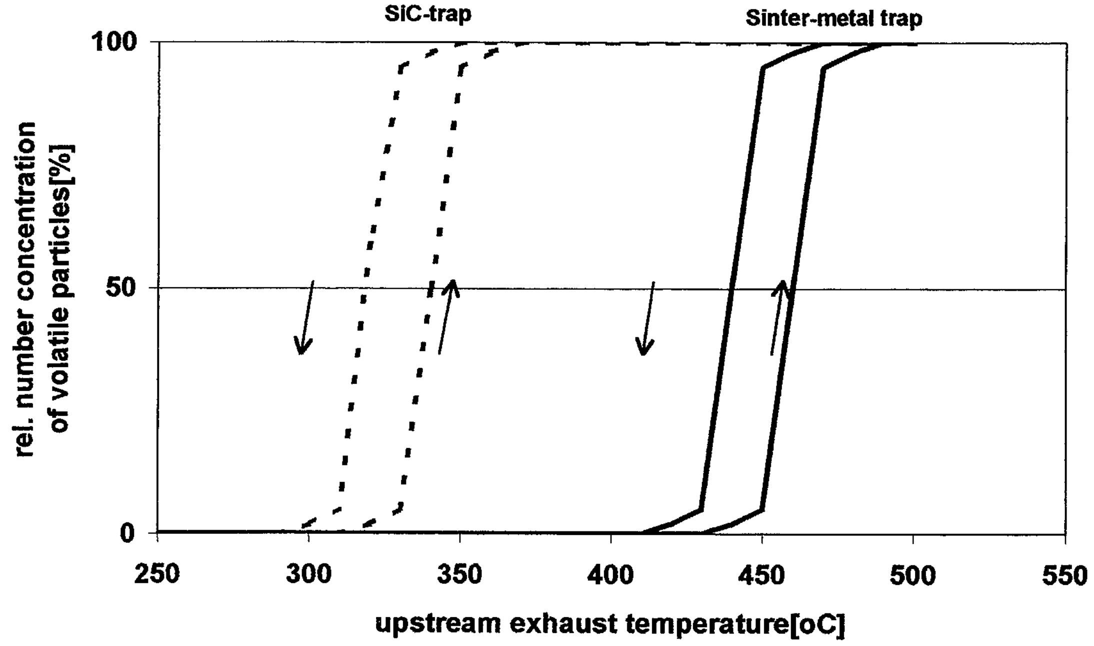

Fig. 11 Comparison of the rel. number concentration on 2 different traps at 2000rpm versus exhaust temperature

Chemical analysis of filter samples and the evaporation temperature of the volatile droplets indicate that the droplets consist mainly of water with very little sulfuric acid. The procedure of the legal gravimetric particulate matter measurement on combustion engines includes these droplets in the sampled and measured mass. Depending on the sulfur content of the fuel these volatiles which pass the trap in the gas phase contribute significantly to the particulate mass measured downstream of trap. Traps with excellent efficiency for solid particles have been tested where the gravimetric test yielded even negative penetrations due to this phenomenon (Mayer et al., 1999).

Therefore it must be discussed whether the legal gravimetric test in its present form is still suitable to qualify low emission diesel engines with particulate traps for two reasons.

- Clearly, as numerous medical, epidemiological, and toxicological studies have shown, human health is affected by the non-volatile carbonaceous fine particles emitted from diesel engines, while the probability of adverse health effects from the volatile particles consisting mainly of water is very low. Therefore, the two species of particles should at least be measured separately to efficiently protect public health. This is not possible in the present legal gravimetric test.

For a given aftertreatment device, the result of the gravimetric test mainly depends on the sulfur content of the fuel and not on the performance of the combustion engine nor on the one of the exhaust aftertreatment. Therefore gravimetric analysis examines mainly the quality of the fuel. However, the sulfur content of the fuel can be determined much more simply than by measurement of the ultrafine droplets formed in the exhaust. Therefore, the present legal procedure is also a vaste of public money.

Acknowledgements

We thank

Urs Baltensberger from Paul Scherrer Institute Villigen for SO4 ion chromatography analysis

Jan Czerwinski from Berner Fachhochschule Biel for supplying the diesel test bench

Andreas Mayer from TTM Niederrohrdorf for valuable support and promotion.

References

Baltensperger U. (1997) Analysis of Aerosols, *Chimia* **51**, 686-689

Gairing, M. et al. (1994) Einfluss von Kraftstoff-Eigenschaften auf die Abgas-Emissionen moderner Dieselmotoren. *MTZ Motortechnische Zeitschrift* **55/1**, 8.

Kittelson D., and Abdul-Khalek I. (1998) Nanoparticle Formation during Exhaust Exhaust Dilution, *Proceedings of "Second International ETH Workshop on Nanoparticle Workshop"*, Aug. 07. 1999, **chap. 15.**

Matter U., Siegmann H.C.,Burtscher H. (1999) Dynamic Field Mesurement of Submicron Particles from Diesel Engines, *Environ. Sci. Technol.* **33**, 1946-1952

Mayer, A., Czerwinski, J., Matter, U., Wyser, M., Scheidegger, Kieser, D., and Weidhofer (1998) VERT: Diesel Nano Particulate Emissions: Properties and Reduction Strategies, *SAE International*, **980539**, Febr. 1998, 127 – 138

Mayer A., Matter U., Scheidegger G., Czerwinski J., Wyser M., Kieser D., Weidhofer J. (1999) Particulate Traps for Retro-Fitting Construction Site Engines VERT: Final Measurements and Implementation, *SAE Technical Paper* **Series 1999-01-0116**

Shi J. P., Harrison R. M., Brear F. (1998) Ultrafine Particle Formation During Diesel Exhaust Dilution, *Proceedings of "Second International ETH Workshop on Nanoparticle Workshop"*, Aug. 07. 1999, **chap. 16.**

VRV Schweizerische Verkehrsregelnverordnung (1992),Wartung und Nachkontrolle von Motorwagen betreffend Abgas und Rauchemissionen, Art 59a vom 22.11.1992

Wang S.C., and Flagan R.C. (1990) Scanning Electrical Mobility Spectrometer, *Aerosol Science and Technology* **13** p. 230-240.