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Volker Scheer, Ulf Kirchner, Roberto Casati and Rainer Vogt
Ford Forschungszentrum Aachen

Birgit Wehner, Sabine Philippin and Alfred Wiedensohler
Institute for Tropospheric Research

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ABSTRACT

Vehicle exhaust particles from diesel passenger vehicles were studied in terms of volatility and chemical composition. Condensation of semi-volatile compounds leads to particle growth during exhaust dilution and cooling. The particle growth was observed to be particle surface related. At higher vehicle speed and load some of the semi-volatile material forms nucleation particles that are dominating the particle number concentration. The nucleation mode is completely volatile at 180°C and consists mainly of sulfate. The amount of organic material is smaller. The organics/sulfate ratio is larger for the soot mode indicating an earlier condensation process of organics before they are incorporated in the nucleation process. Under typical atmospheric dilution conditions most of the semi-volatile material is present in the soot mode. The semi-volatile material evaporates at temperature between 130°C and 180°C. Thermal treatment using a thermodenuder enables complete evaporation of the nucleation particles, however not all material from the soot particles is removed.

INTRODUCTION

Ambient particulate matter (PM) is under public discussion because of its potential adverse effects it may have on human health as has been found within several epidemiological studies. Also a correlation between mortality and particle size was indicated [1,2]. Particles from diesel exhaust are a source contributing to ambient PM. Black carbon is also under discussion because of its influence on the radiation budget of the atmosphere, which is not only due to the black carbon but also linked to associated components [3,4]. Particles are described typically by their physical characteristics like particle size, number, surface or mass concentration and/or their chemical composition. The latter is determined typically from the bulk mixture and represents an average over all particles although it might vary significantly with size depending on the process of particle formation.

Diesel exhaust particles consist of fractal-like agglomerates of carbon particles and some semi-volatile components like H_2SO_4 and organic species that might condense on the surface of the carbon particles or nucleate to form new very small particles during the dilution and cooling process as schematically shown in Figure 1. Here we study the size dependent composition of semi-volatile compounds and the concurrent processes of condensation on existing particles and nucleation to form new particles within the exhaust from diesel passenger cars. Volatility studies using a volatility tandem DMA (VTDMA), a combination of a thermodenuder (TD) with two scanning mobility sizers (SMPS) and mass spectrometric measurements with an aerosol mass spectrometer (AMS) were compared to determine the composition of semi-volatile particle components.
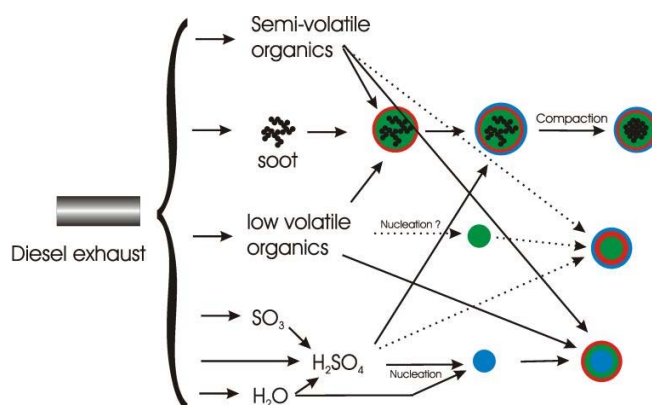

Figure 1: Simplified schematic mechanism of the condensation and nucleation process during diesel exhaust dilution and cooling. Blue: volatile (H_2SO_4); red: semi-volatile organics (unburned fuel); green: low-volatile organics (lube oil).

EXPERIMENTAL

CHASSIS DYNAMOMETER MEASUREMENTS

The tests were performed on a 48" (1.22 m) diameter concrete role ("Compact Rolle", AVL, Kiel, Germany) with max. 186 kW break power, max. speed 200 km h^{-1}, and loss compensation. For the experiments two different Diesel passenger cars were used: vehicle #1: model year 2000, 1.8 L, 66 kW (90 hp), vehicle #2: model year 2002, 1.8 L, 74 kW (100 hp) car with common rail direct injection technique. Both cars were equipped with a turbo charger, exhaust gas recirculation, and oxidation catalyst. For both vehicles the inertia weights were 1360 kg and emission levels were EURO III. For all tests a fuel with 360 ppm sulfur content was used.
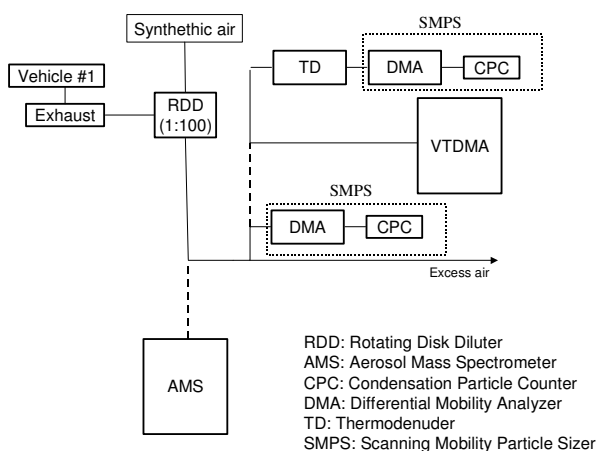

RDD: Rotating Disk Diluter
AMS: Aerosol Mass Spectrometer
CPC: Condensation Particle Counter
DMA: Differential Mobility Analyzer
TD: Thermodenuder
SMPS: Scanning Mobility Particle Sizer

Figure 2: Setup of emission test with vehicle #1 for volatility measurements with VTDMA and TD/SMPS or measuring chemical composition using an AMS

RDD: Rotating Disk Diluter (1:30)
TD: Thermodenuder
AMS: Aerosol Mass Spectrometer
CPC: Condensation Particle counter
DMA: Differential Mobility Analyzer
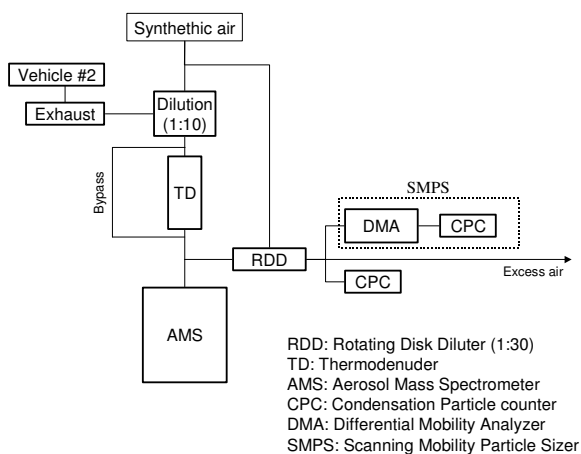SMPS: Scanning Mobility Particle Sizer

Figure 3: Setup of chemical composition measurements with vehicle #2

Vehicles were operated at constant speed, and warmed at selected speed for at least 10 minutes. The sampling configuration of the instruments is shown in Figures 2 and 3. Dilution ratio for the rotating disc diluter was maintained by setting of rotation speed as given by the instrument's manual. Primary dilution ratio, as used in the second set-up (Figure 3), was measured by the ratio of CO_2 before and after dilution. For some experiments additional filter samples were taken from a full flow dilution tunnel.

COMBINED VTDMA AND TD/SMPS MEASUREMENTS

A combined setup using a VTDMA and a TD/SMPS setup was used to examine the size and temperature dependent volatility of diesel exhaust particles after dilution with a rotating disc diluter (MD19-2E, Matter Engineering AG) at tailpipe (Figure 2). While the VTDMA measures the volatility of particles with certain selected sizes the TD/SMPS setup measures the whole particle size distribution with two SMPS before and after thermal treatment by a thermodenuder (TD). The number size distribution between 10 and 400 nm of the ambient aerosol was measured using an SMPS system (3934L, TSI Inc.). To measure the corresponding non-volatile number size distribution of this ambient aerosol, a second SMPS system (3934U, TSI Inc.) was placed downstream of a TD [5]. This TD consisted of two units: a heating section to remove the volatile material at temperatures up to 300°C, and a cooling section filled with active carbon to adsorb evaporated gas phase compounds to prevent re-condensation. The non-volatile number size distributions of the ambient aerosol were measured using TD/SMPS system with TD heating at four different temperatures (80, 130, 180, and 280°C). A more detailed explanation about the TD as well as its calibration is given in [5]. The non-volatile cores of certain particle diameters were measured using a VTDMA system, which is an in situ technique that evaporates volatile compounds at temperatures between 25 and 280°C. It contains eight parallel heating columns, each of them can be hold at a different temperature. This system allows switching fast between the temperatures [6]. In this study, 25, 80, 130, 180, and 280°C have been used. The VTDMA-technique consisted of three steps. In the first step, quasi-monodisperse particles from a polydisperse aerosol were "selected" with a DMA and counted using a Condensation Particle Counter (CPC, TSI Model 3010). In the second step, the quasi-monodisperse particles were passed through a heating unit where all volatile compounds (e.g., nitrate, sulfate) were volatilized at a specific temperature between 25 and 300°C. Operation above 350°C might result in artifacts due to burning or charring of organic matter in the particles [7]. In our current study, we therefore chose a maximum temperature of 280°C, where sulfates and most of the volatile organic carbon evaporate [6]. In the third step, the resulting number size distribution of the non-volatile particles and the corresponding number size distribution at ambient 25°C were measured by using a second DMA/CPC combination. The resulting volatility size distribution was normalized by the maximum of the initial size distribution (size distribution at 25°C), thus a

maximum initial size distribution had a value of 1. The non-volatile number and volume fractions were then derived from these volatility number size distributions using the assumption of spherical particles for the volume calculation. In general, the size distribution obtained at a temperature of 280 °C differed compared to the initial size distribution, indicated by a shift in the initial mode (measurement at 25 °C) towards smaller particle diameters or by a multimodal structure characterizing the non-volatile particle composition. Because the lower detection limit of the VTDMA system was 10 nm due to the CPC detection limit (TSI-3010), non-volatile particles and cores smaller than 10 nm could not be measured using this system.

The VTDMA was used to measure four representative diameters in the Aitken and accumulation mode size ranges (30 nm, 50 nm, 80 nm, and 150 nm). The measured size distributions were corrected for the CPC counting efficiency and particle losses due to thermophoresis and diffusion in the VTDMA. Calibration curves for the VTDMA are taken from [6]. Data inversion, that is more complicated for a TDMA than for a single DMA, to obtain the real size distribution from the measured raw size distribution, was done using a special data inversion algorithm [8].

AMS MEASUREMENTS

The size-resolved chemical analysis has been carried out with the Aerodyne Aerosol Mass Spectrometer (AMS, Aerodyne Research, Inc.). Particles with aerodynamic diameters between 20 and 1500 nm are sampled from ambient pressure through a 100-μm pinhole. Subsequently, the aerosol particles are focused onto a narrow beam and are separated from the gas. The particles are flash-vaporized on a hot surface (approx. 500 °C). At this temperature, the volatile and semi-volatile (= non-refractory) parts of the particles evaporate. Black carbon, which is a major compound of soot, is not evaporated. Since the evaporation and ionization processes are separated and linear, the quadrupole mass spectrometer can be calibrated and used for quantitative detection of aerosol components like sulfate, nitrate, ammonium etc. The instrument can be operated in two modes:

1) The mass spectrum (MS-) mode: The particle beam is continuously analyzed and the whole mass range (typically up to m/z = 300) of the spectrometer is scanned with a repetition rate of 3 Hz. This mode is used for total chemical composition measurement.

2) The time-of-flight (ToF-) mode: The particle beam is chopped by a chopper wheel rotating at 100 Hz and the mass spectrometer is set onto specific masses, e.g. 48 (SO^+) and 64 (SO_2^+) for sulfate. By triggering the reading of the ion signal with the opening of the chopper, the mass loading of the individual species can be measured as a function of particle time-of-flight and thereby as a function of particle size. For more details of the AMS see [9,10,11].

Here, we focus on the sulfate and organic components of the exhaust particles. Sulfate mass loadings are inferred from the ions SO^+, SO_2^+, SO_3^+, HSO_3^+, and $H_2SO_4^+$ (m/z = 48, 64, 80, 81, 98). Organics are inferred from various mass peaks that are known not to originate from inorganic species like sulfate, nitrate ammonium, chloride etc. Typical ion signal from organics molecules appear at the ion series $C_nH_{2n-1}^+$ and $C_nH_{2n+1}^+$.

Since the acceleration of the particles in the aerodynamic lens takes place in the free molecular regime, the measured diameter is not the usual aerodynamic diameter. The Cunningham correction in the free molecular regime is proportional to the inverse of the volume equivalent diameter (D_v), which leads to a linear dependence on density and shape factor. This so-called "vacuum-aerodynamic diameter", D_{va}, is therefore related to the volume equivalent diameter D_v by equation 1:

$$D_{va} = D_v \, \rho_p/\rho_0 \, \chi^{-1} \tag{1},$$

where ρ_p is the density of the particle, ρ_0 is the unit density (=1g cm^{-3}), and χ is the dynamic shape factor [12].

AMBIENT MEASUREMENTS

In order to compare laboratory data obtained from a single vehicle with the ambient atmosphere measurements were carried out at two sites: a) at a highway site, which is a parking lot adjacent to the German highway (Autobahn) A4 north of the German city of Aachen (near the border of the Netherlands and Belgium); b) at a rural site about 3 km downwind from the highway 0.6 km next to the small village Dürwiß (Blausteinsee, Germany).

For one campaign in August 2000 at the highway site the VTDMA and TD/SMPS were mounted in the Ford Mobile Laboratory (FML) [13], and the aerosol inlet was about 3 m above ground. Parallel measurements of the meteorological parameters (wind speed, wind direction, temperature and relative humidity) and other parameters, such as trace gases (O_3, NO_x, NO, CO) were taken. No measurements were done during this measurement campaign at the rural site.

For a second campaign in February 2002 the AMS was installed in the FML instead of the VTDMA and TD/SMPS and measurements were done at both sites.

CAR CHASING MEASUREMENTS

Chemical composition measurements from laboratory tests were compared with those under real atmospheric dilution conditions by car chasing experiments. These were constant speed tests carried out on a 4km oval test track following vehicle #2 closely (~10m distance) by the FML, which sampled SMPS, AMS, CPC, NOx and CO2 data. The test vehicle was warmed up at selected speed for at least 10 minutes. For details see [14].

RESULTS AND DISCUSSION

VEHICLE #1 EMISSION TESTS

Volatility measurements at different speeds were carried out at 50, 120, 140 km/h, and additionally at 120 km/h with an increased load of 45KW. At each speed four temperatures were selected in addition to ambient conditions. Thus, the remaining fraction was measured after heating to 80, 130, 180, and 280 °C.

A detailed comparison of particle emissions treated at different temperatures is shown in Figure 4. At 50 km/h and 120 km/h the particle size distribution remained unchanged at all temperatures pointing to a non-volatile behavior of the emitted particles. At 140 km/h the particle emissions increase from test to test and an additional particle mode appeared at sizes below 50 nm. At temperatures of 130 °C and above the additional material completely evaporates and leads to a significant decrease in particle number emission.

The 120 km/h(high load) test showed a high particle number emission rate. Thermal treatment at 130 °C led to a particle number decrease, which changed throughout the test. This points to the fact that the additional volatile material evaporated partly at 130 °C and composition might change even under steady state conditions. Thermal treatment at 280 °C resulted in a number decrease by one order of magnitude and stable residual size distribution.

The remaining non-volatile particles have a mean size of around 50 nm in all cases.

In Figure 5 the VTDMA-measurements are shown. Particles at higher speed and load show a tendency to shrink due to thermal treatment. The effect is more pronounced at higher temperature of the heating column and at smaller initial particle diameter. The influence of temperature at initially selected particle diameter and vehicle speed on particle size and number concentration is shown in more detail in Figure 6.
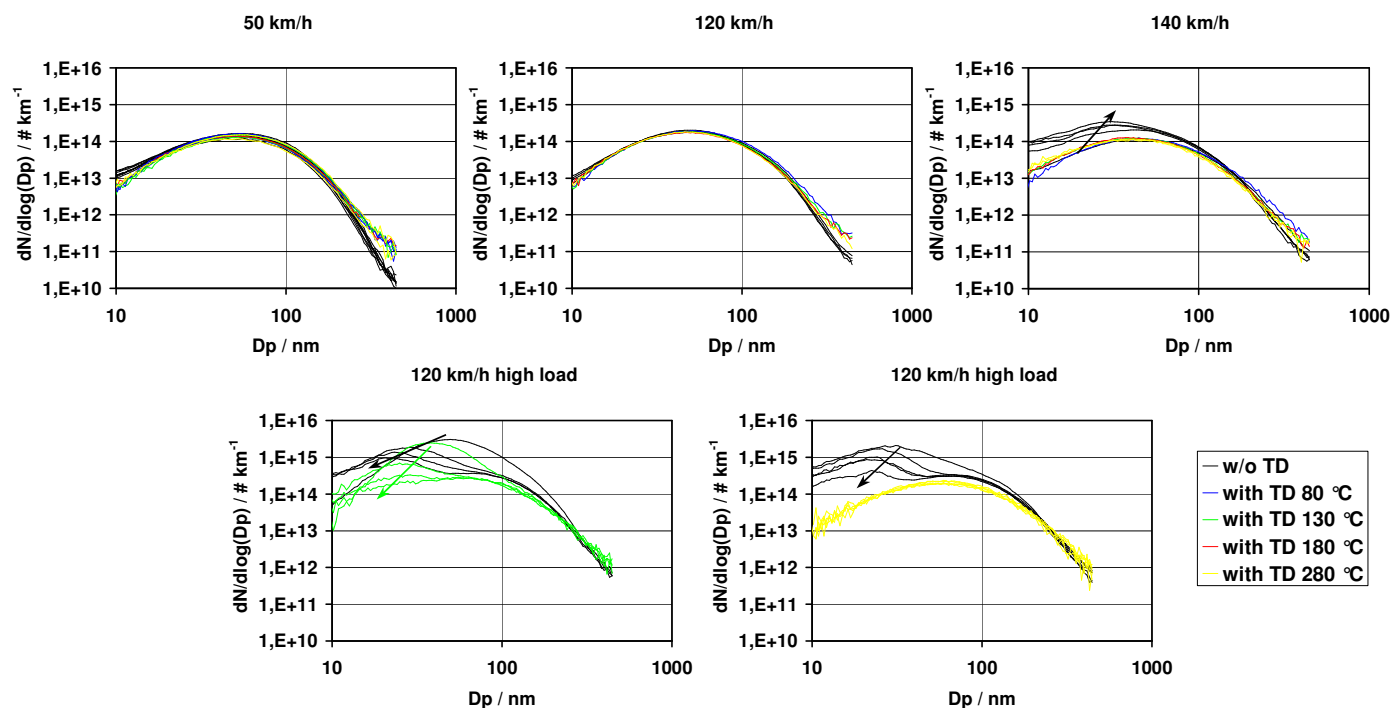

Figure 4: Particle size distribution of diesel exhaust measured at the tailpipe before (black lines) and after thermal treatment at different temperatures (80 (blue lines), 130 (green lines), 180 (red lines) and 280 °C (yellow lines)). For 50, 120 and 140 km/h tests curves are averaged while for 120 km/h(high load) individual scans are shown. At 140 km/h a second particle mode occurred and increased from test to test (black arrow). At 120 km/h(high load) the second particle mode decreased during the test (black arrow) and also some of these particles remained after thermal treatment at 130 °C and decreased during the test (green arrow).

At 50 km/h there is no significant amount of volatile material present (Figure 5). The changes in particle size observed are within the experimental error, and number concentration is not changing. At 120 km/h particle size is changing while the number concentration remains constant. This suggests the particles to be partially non-volatile with a non-volatile core and a volatile outer layer.

Higher speed (140 km/h) leads to larger changes in particle size. Additionally, the number concentration is changing for small particle sizes at temperatures above 130 °C and small particle size. This suggests the particles to consist of two different types: a partially non-volatile type (as described above) and additionally, a completely volatile type in which no solid core could be observed. This observation of two particle types is more pronounced at 120 km/h(high load) where almost all particles at 30nm are evaporated at temperatures above 130°C and also the change in diameter, measured at 80nm, is larger.

In general at 80°C there is nearly no volatile behavior observable. At 130°C the particles partly change their size, where roughly half of the volatile material is disappearing, while the particle number concentration is not reduced. At 180°C and 280°C the size change is at maximum and the particle number concentration is reduced. In this case the original size distribution is bimodal (140 km/h and 120 km/h(high load), see Figure 4). The temperature dependence is similar to the

behavior of $(NH_4)_2SO_4$ particles [6], however sulfuric acid or organic material might show a similar dependence. Chemical filter analysis, where values of 1.4, 9, 31 and 35 % sulfate content of the total PM at 50 km/h, 120 km/h, 140 km/h and 120 km/h(high load) respectively were observed, assists the theory of sulfate to be a main volatile compound. This is also in agreement with a chasing study [14] where nucleation was only present at high sulfur fuel (360 ppm S) and high load conditions, while it is not occurring using low sulfur fuel (< 10 ppm S).

The size changes ΔDp in all cases are nearly independent of the initial selected particle size. This is consistent with the assumption that the condensation process is dependent on particle surface leading to an absolute particle diameter growth that is independent of initial particle size. This is in agreement with observations of a constant size changes for emissions of a heavy-duty engine [15].

There is a slight tendency of smaller size change for larger particles. Larger soot particles are known to consist of agglomerates of carbon with a fractal structure containing some free volume within the particle. The larger the particle the more free volume is expected. It is possible that condensable material fills up some of this volume, which explains this tendency. However, the observed difference of 2 to 3 nm between 30 and 80 nm particles is relatively small.
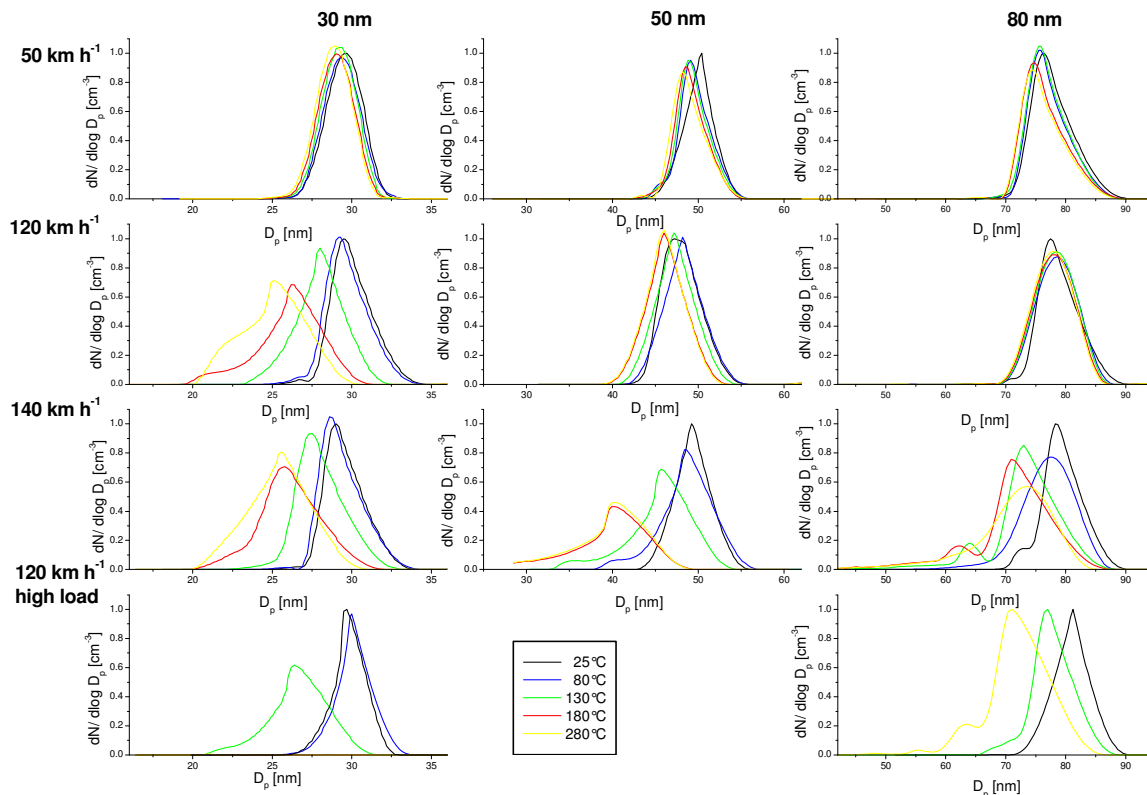

Figure 5: VTDMA measurements of Diesel exhaust particles. Standardized for initial size distribution at 25°C.
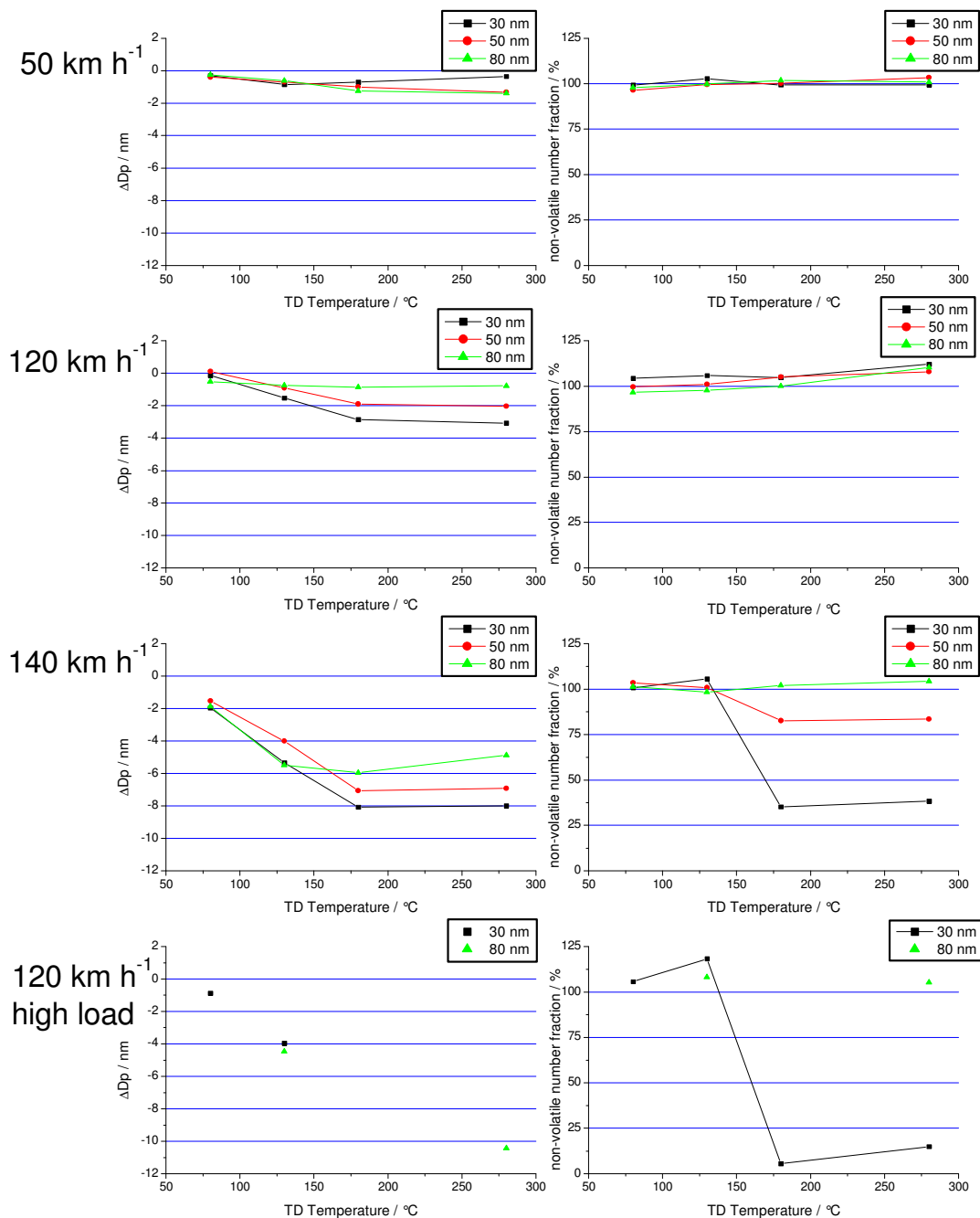
Figure 6: Dependence of diesel exhaust particle diameter (size change ΔDp) and number on thermal treatment at 80, 130, 180, and 280°C for selected initial particle sizes (30 nm black squares; 50 nm red circles; 80 nm green triangles).

To gain knowledge about the amount of semi-volatile material present at individual mobility diameter one could calculate its volume size distribution using the TD/SMPS and VTDMA results. From a constant size change it follows that the amount of condensed semi-volatiles is along with the particle surface distribution as measured by the SMPS. The volume size distribution of semi-volatile compounds from condensation on soot surface could be calculated using the 'dry' soot size distribution as obtained by SMPS measurements with TD and

calculating the volume growth by a size change that is measured by the VTDMA applying equation 2:

$$V_{(Dp+\Delta Dp)} = (1/6 \ \pi \ (Dp+\Delta Dp)^3 - 1/6 \ \pi \ Dp^3) \ N_{soot} \quad (2)$$

$V_{(Dp+\Delta Dp)}$ is the volume of semi-volatile compounds at resulting particle size after condensational growth, ΔDp is the diameter change during condensational growth, Dp is the diameter and N_{soot} the number concentration of particles at Dp of the 'dry' soot. Two examples are shown

in Figure 7a and 7b using size changes taken from VTDMA data ΔDp=2nm for 120 km/h and ΔDp=10nm for 120 km/h(high load).

Additional semi-volatile material from nucleation needs to be calculated. TD/SMPS data show that in the presence of a nucleation mode (140 km/h and 120 km/h(high load)) this mode completely disappears upon thermal treatment. This is also shown by the VTDMA data where in case of nucleation particle occurrence large fractions of small particles are completely disappearing. The semi-volatile compounds of the nucleation mode could be separated from the soot mode with lognormal fits and calculating the volume for the nucleation mode by equation 3:

$$V_{Dp} = 1/6 \; \pi \; Dp^3 \; N_{nucl} \qquad (3)$$

Where V_{Dp} is the volume of semi-volatile compounds from nucleation, Dp is the diameter and N_{nucl} the number concentration at Dp of nucleation particles. An example of the calculation for 120 km/h(high load) data is given in Figure 7b.

Although the nucleation mode is dominating the particle number concentration during the 120 km/h(high load) experiment most of the semi-volatile material is present as condensed material on the soot particles as shown in Figure 7b (middle).

How is the relation of condensed material to total volume size distribution? Assuming the particles measured to be spheres the semi-volatiles/non-volatiles ratio is decreasing with increasing particle diameter (e.g. large particles are mainly non-volatile soot). This is more complicated for soot particles known to be agglomerates of chain like structures. For example, applying the rough approach that particle volume for fractal agglomerates is related to particle diameter by Dp^{df} and assuming a fractal dimension of df=2, the semi-volatile/non-volatile ratio would be independent of particle size. However, since the fractal dimension has not been measured during these experiments a semi-volatile/non-volatile ratio could not be calculated.

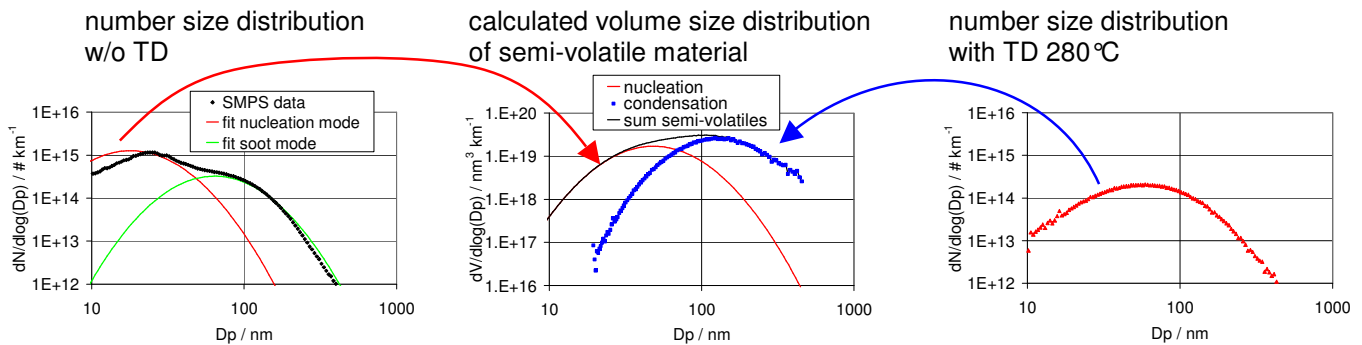a) 120 km/h
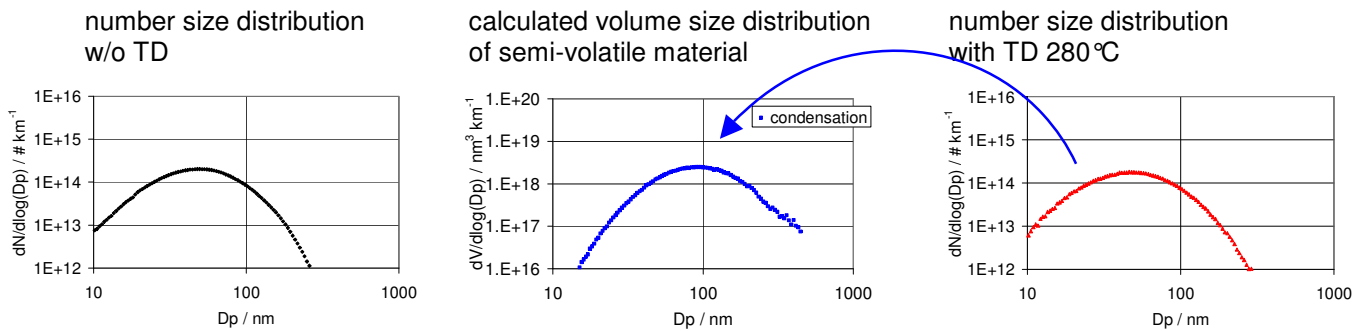
b) 120 km/h(high load)

Figure 7: Calculation of volume distribution of semi-volatile compounds from nucleation and condensation at: a) 120 km/h with ΔDp=2nm and b) 120km/h high load (45kW) with ΔDp=10nm. Red arrow indicates volume calculation of semi-volatile material from nucleation particles, blue arrow indicates volume calculation of semi-volatile material that covers solid soot after condensation onto its surface.
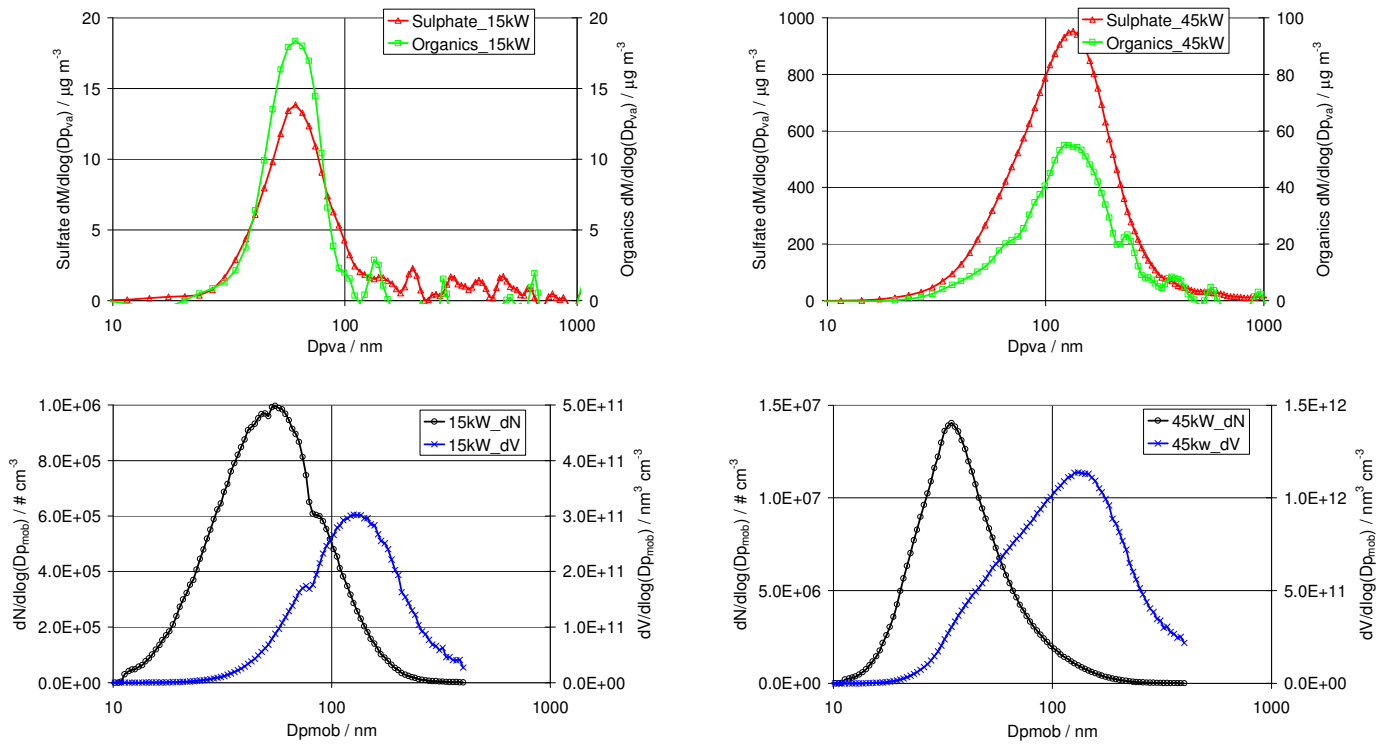
Figure 8: Size distribution of sulfate and organics (AMS) and number and volume size distribution (SMPS) of diesel exhaust particles at 120 km/h(15kW) left graphs and 120 km/h(45kW) right graphs.

Chemical composition measurements by the AMS confirm the increase of semi-volatile material with increasing speed and load (Figure 8). While the amount of organics is only slightly increasing the amount of sulfate increases strongly. The presence of organics and sulfate are well aligned across all particle sizes. Assuming the particles to be spheres this indicates that the nucleation and condensation for both classes of compounds has occurred on the same time scale. Earlier condensation of one component and subsequent coagulation processes would have lead to a shift of this component towards larger diameters. However, if the particle aggregates would have a fractal dimension of df=2, there would be no difference observable. Unfortunately the fractal dimension is not known and at the moment it is not possible to convert the AMS vacuum-aerodynamic size data into mobility data to compare the condensation to be surface related as measured by the VTDMA and TD/SMPS experiment. Qualitatively this complication is shown by the AMS measurements that at 15 kW volatile organic and sulfate modes are observed at smaller diameters than the volume size distribution calculated from SMPS data (assuming the particles to be spheres). This is partly explainable by a surface related condensation process, and additional a density and shape factor ratio ρ_p/χ , as used in equation 1, smaller than 1, because for fractal soot agglomerates the shape factor χ is larger than 1 and density ρ_p is smaller than 1 for compact soot. At 45 kW sulfate and organic modes have the same peak diameter as the volume size distribution, while surface related material would have had an occurrence at smaller sizes. This is explained by a ratio ρ_p/χ that is larger than 1, because of an increased density due to a higher sulfate content and a decreased shape factor, since the particles are becoming more spherical (schematically shown in Figure 1). Furthermore for the nucleation mode the ratio ρ_p/χ is assumed to be larger than 1, because the density of sulfate is larger than 1 and nucleation particles are spheres with a shape factor of 1, and therefore in the AMS sulfate and organics mode from nucleation and soot mode are not separated.
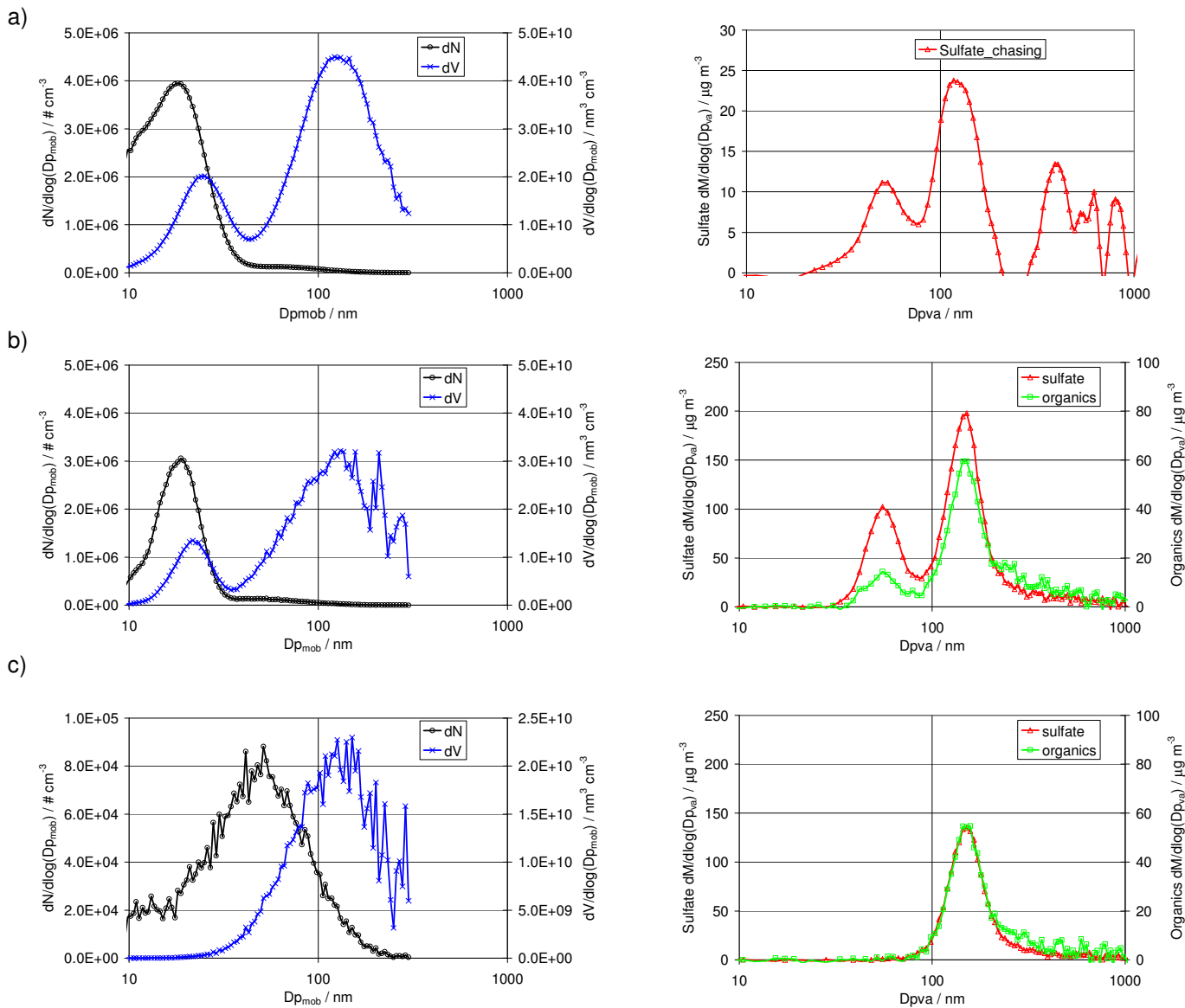
Figure 9: Size distribution of sulfate and organics (AMS) and number and volume size distribution (SMPS) of diesel exhaust particles at 120 km/h during a) chasing experiment b) chassis dyno w/o thermodenuder and c) chassis dyno with thermodenuder at 280 °C.

VEHICLE #2 EMISSION AND CAR CHASING TESTS

During the first chassis dynamometer measurements with dilution setup as shown in Figure 2 nucleation occurred only during high load and speed while in atmospheric dilution experiments (car chasing) nucleation already occurred at 120 km/h(normal load) (Figure 9a). It was decided to repeat some tests with a different diluter setup (Figure 3). This new setup applies the principle of diluting directly where the exhaust sample is taken. The experiment with this setup (Figure 9b) shows two distinct modes of particles with sulfate and organics and that there is a competition between the condensation of semi-volatiles on existing soot particles and formation of nucleation particles. In contrast to the

first test series, where the AMS could not separate the soot from the nucleation mode, the nucleation mode in this test is smaller in size and therefore the AMS is capable of separating the soot and nucleation mode. The amount of sulfate is much larger than the organics content. Furthermore the observation of different organics/sulfate ratios for the two particle modes shows, that the condensation of organics on existing soot particles is preferred and/or earlier than the incorporation in nucleation particle formation. Figure 9a and 9b show the comparison of size distribution and chemical composition data obtained from chassis dyno and car chasing experiments. Laboratory and chasing data compare very well. Thus the laboratory diluter represents very well the real-atmospheric dilution process.
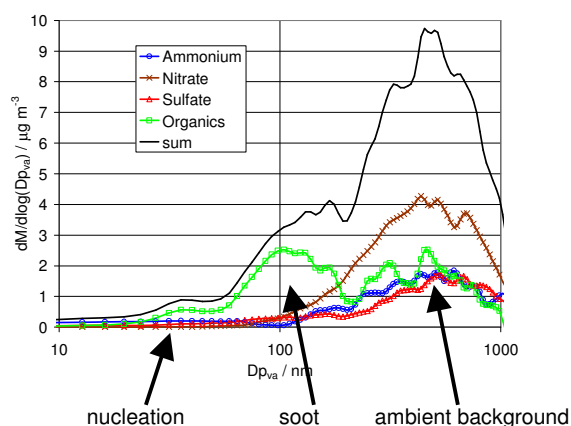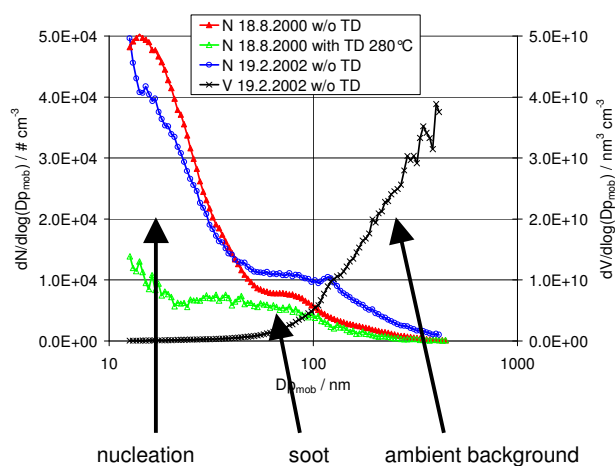
Figure 10: Comparison of TD/SMPS measurements taken August 2000 and AMS measurements taken February 2002 at a motorway A4

Thermal treatment of diesel exhaust particles with a thermodenuder at 280 °C results in a complete disappearance of the nucleation mode (Figure 9c), while within the soot mode there are still sulfate and organics present. These remaining semi-volatiles might be explained by an incomplete evaporation within the heating part and/or a recondensation within the cooling part of the thermodenuder.

AMBIENT MEASUREMENTS

Measurements carried out at a motorway (A4, near Aachen) during a campaign in August 2000 show a distinct nucleation mode together with a soot mode (Figure 10) clearly correlated with NO_x from exhaust emissions. The volatilization of nucleation particles starts at 130 °C and is complete at 180 °C [16], which is comparable to chassis dyno experiments. On the other hand a second campaign in February 2002 with AMS measurements shows that there is no sulfate associated with the nucleation particles, in contrast to chassis dyno and car chasing experiments. The possible explanation

is a lower fuel sulfur content in today's car fleet used, and the presence of heavy duty trucks that might be a source of nucleation particles with a much smaller fraction of sulfate. This observation is consistent with measurements on emissions from heavy-duty engines to be mainly organics [17,18].

CONCLUSIONS

The nucleation mode, observed in the exhaust of a diesel passenger car is completely volatile at temperatures of 180 °C and above and consists mainly of sulfate.

The organics/sulfate ratio is larger for the soot mode indicating an earlier condensation process of organics before they are incorporated in the nucleation process.

Condensation of organics and sulfuric acid on existing soot particles is related to particle surface. Under typical atmospheric dilution conditions most of the semi-volatile material is present in the soot mode. At the same time the particle number may be dominated by nucleation particles.

The volatile material evaporates completely at temperatures between 130 and 180 °C. This is comparable to motorway measurements, however AMS shows that near a motorway there is no traffic related sulfate mode but an organic mode is observed. Possibly the ambient site is dominated by emissions from heavy-duty vehicles.

The evaporation temperature between 130 °C and 180 °C leads also to the conclusion that nucleation takes place during the dilution process, since typical exhaust temperature at speed/load condition when nucleation occurs is roughly 100° above this temperature and therefore the volatile material is expected to be in the gas phase.

Thermal treatment using a thermodenuder enables evaporation of nucleation particles. However, not all material from soot particles is removed. Also recondensation on soot particles could occur.

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