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Comparing SMPS Size Distributions with DC, PAS and CPC Data

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Abstract

Diesel particle number size distributions show typical key parameters, both for ambient diesel exhaust measurements and for laboratory dynamometer experiments. Two modes dominate the size distributions in the range 5– 300 nm, a soot mode at 60 – 120 nm and an ultrafine nucleation mode at 5 – 40 nm. The concentration of the soot mode is usually directly connected to the amount of particles emitted by the source, while the presence of the nucleation mode has been shown to strongly depend on the dilution conditions of the raw exhaust prior to the particle measurement. SMPS (Scanning Mobility Particle Sizer) size number distributions have good particle size resolution, but relatively poor time resolution, with scan times of 1 minute or more. DC, PAS and CPC are real-time instruments for particle measurement with a time resolution of 10 seconds or less. The combination DC, PAS and CPC has been shown to deliver real-time key information on diesel exhaust size distributions. First, diesel exhaust plumes which contain a highly concentrated ultrafine nucleation mode can be clearly identified using the ratio of DC vs. PAS signals, in the sense of a yes/no answer. Furthermore, the diameter of average surface of the sampled diesel aerosol can be determined using DC and CPC data. This allows qualitative statements on the dynamic behavior of the nucleation mode during an experiment, since the diameter of average surface will shift as the concentration of the nucleation mode changes. Using these findings, real-time monitoring of general traffic exhaust in test bench as well as field studies is possible with the use of these three instruments.

Introduction

In the last decades a large effort has been made to characterize airborne particles near or on highways (Whitby et al., 1975; Harrison, 1996; Weingartner et al., 1997), and to link particle emissions of individual vehicle types to ambient particle concentrations from general traffic. Related to these studies intense investigations are in progress about the health aspects of submicron aerosol particles emitted by traffic (Dockery et al., 1993). After years in which the main focus was put on the mass concentration, the particle number concentration as well as the surface concentration now is an important subject to research with respect to possible health effects (e.g. Seaton et al., 1995; McAughey, 1997).

Traffic submicron particles originate to a substantial extent from diesel engines, which produce a higher level of particulate matter than spark ignition engines. However, with advances in diesel combustion and aftertreatment technology the contribution of diesel vehicles to general traffic particle emissions is decreasing.

Fig. 1 shows a typical diesel particle size distribution. The accumulation mode around 70-120 nm has been found to be the main characteristic for diesel exhaust. It has been found to consist of diesel soot, i.e. carbonaceous material (black carbon and associated organic carbon including polycyclic aromatic hydrocarbons, PAHs). In contrast, the nucleation mode around 5-40 nm is subject to current debate about its composition and possible effect on health, since the particle number concentration of this mode is – once it is formed - usually higher than the accumulation mode particle concentration. Like other studies, this study confirms that the nucleation mode consists of volatile material that evaporates at temperatures far below 300 °C, indicating that these particles do not consist of elemental carbon. Furthermore, recent observations suggest that the nucleation mode particles contain hydrocarbons, other organics and an unknown percentage of sulphuric acid and water, formed by condensation after the combustion process. Streit et al. (2000) found that nucleation mode particles at an urban site (Milan, Italy) were characterized by high volatility and non-hygroscopic behavior, suggesting that these particles consisted mainly of hydrophobic organic material. The formation of the nucleation mode has been shown by Abdul-Khalek et al. (1999) to be extremely dependent on the dilution conditions of the engine exhaust (e.g. residence time in the dilution volume, dilution air temperature, relative humidity and the dilution ratio, all of them being parameters determining the cooling rate and thus the supersaturation of condensable species).

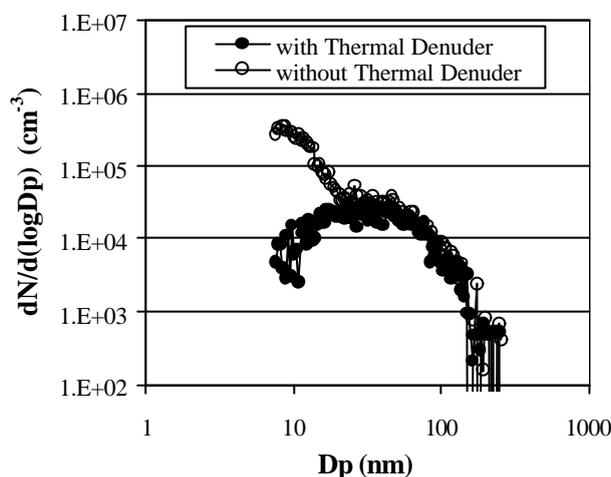


Fig. 1: Two examples for a diesel exhaust particle number size distribution. The volatile nucleation mode is completely removed when the sampled aerosol is run through a thermal denuder at 300 °C.

This extreme sensitivity of nuclei mode formation to emission conditions has turned out to be a critical issue in establishing a standard procedure for measuring nanoparticle emissions from engines. Worldwide there are studies in progress whose purpose it is to represent a base for future particle emission and immission regulations. Vehicle emission studies are generally performed in engine test cells, using chassis dynamometer or engine dynamometer technology. A study in which diesel engine emissions are characterized under real-world conditions by chasing diesel trucks with a mobile laboratory is currently in progress in the U.S. (Kittelson et al., 2000).

Since emission conditions are highly variable under real-world conditions, it is difficult to link the on-highway emissions with the corresponding ambient concentrations in a simple way. Furthermore, the presence of other aerosol types in the diluting atmosphere air is believed to have a great effect on the nucleation and growth processes of the exhaust (Kittelson, 1998; Abdul-Khalek et al., 2000).

All observations mentioned above result in an increasing demand for highly time-resolved on-site measurements and suitable instrumentation for particle number and surface area measurements, in order to guarantee a proper interpretation of results. For the last decades the SMPS has been a standard instrument for measuring highly resolved mass-independent particle number distributions (Wang et al., 1990). In recent years the Diffusion Charger and the Photoelectric Aerosol Sensor have been presented as additional tools for monitoring diesel particulate emissions and ambient concentrations. Both instruments have a time resolution of < 10 seconds.

The Photoelectric Aerosol Sensor (PAS) responds to photoemitting substances on the surface of aerosol particles. Ultraviolet irradiation of the sampled aerosol leads to the emission of photoelectrons from surface material that readily undergoes photoemission (Burtscher, 1992). The remaining positively charged aerosol particles are separated from the electrons and collected on a filter connected to an electrometer. The measured signal is a function of the total available surface area and the photoemission properties of the surface materials. Diesel accumulation mode particles strongly respond to the PAS (Matter et al., 1999), as it will be confirmed below.

The Diffusion Charger (DC), consisting of a diffusion charging section combined with a current sensor, measures the surface area concentration of the aerosol. The measured surface does not correspond to the geometric surface obtained by mobility measurements, but represents the portion of the total aerosol surface that actively is involved in the diffusion charging process. While this surface portion previously has been described as Fuchs Surface (Gäggeler et al., 1989; Fuchs, 1964), recent studies introduced the measured quantity as “active” surface (Siegmann et al., 2000).

PAS/DC Ratio

The ratio PAS/DC has been described as a characteristic property for individual types of combustion aerosols (Matter et al., 1999). A plot of PAS response versus DC surface has been found to result in a linear relationship for a single type of combustion aerosol being monitored. Since both instrument responses are a function of the total aerosol surface area, the slope of PAS versus DC plots can be considered as the capability of the surface to undergo photoelectric charging, which depends on the surface material. Further aspects on the interpretation of such plots are subject of this study and will be discussed below.

The diameter of average surface, $D_{Ave,S}$

If both the total active surface concentration S_A and the total number concentration N (e.g. measured by a Condensation Particle Counter, CPC) of a specified sample volume are known, one can define the diameter of average surface, $D_{Ave,S}$, as

$$D_{Ave,S} = \left(\frac{S_A}{\rho \cdot N} \right)^{0.5}$$

(Kittelson et al., 2000). Thus, $D_{Ave,S}$ represents the diameter of a hypothetical monodisperse aerosol that has the same surface area concentration as the measured polydisperse aerosol. Referring to the experimental fact that diesel particle size distributions in most cases have similar shapes for particles > 60 nm, $D_{Ave,S}$ can therefore be interpreted as an indicator for the presence of an ultrafine

mode during time series experiments, thus, a higher concentration of nucleation mode particles will result in a decreasing $D_{Ave,S}$. In contrast, a change in the total particle number concentration will not affect $D_{Ave,S}$ as long as the shape of the size distribution remains fairly constant.

Fig. 2 shows an experimental verification example of this relationship using a dry ammonium sulfate aerosol and an SMPS as reference instrumentation. The geometric number mean diameter of the aerosol was approx. 30 nm. The results show that $D_{Ave,S}$ (DC) matches $D_{Ave,S}$ (SMPS) within 10 %. According to theory the active surface only corresponds to the geometric surface for particles < 100 nm (Fuchs, 1964; Allen et al., 1982). However, S_A (DC) is supposed not to relevantly differ from S_{geom} (SMPS) for diesel exhaust submicron particles, since typical diesel particle number size distributions do not show a significant contribution of particle diameters higher than 100 nm.

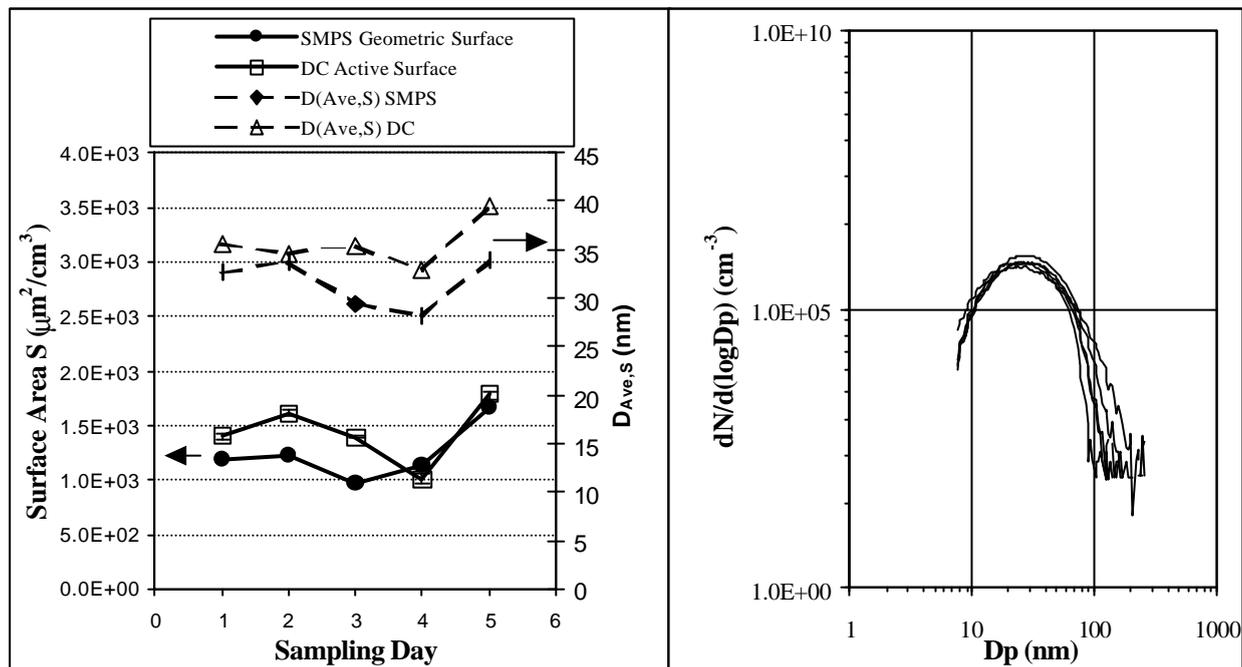


Fig. 2: Comparison of $D_{Ave,S}$ (DC,CPC) and the active surface (DC) with $D_{Ave,S}$ (SMPS) and the geometric surface (SMPS), using a dry ammonium sulfate aerosol. The number geometric mean diameter of the particle number size distribution is approx. 30 nm.

Characterization of diluted diesel exhaust during chassis dynamometer tests

As described by Abdul-Khalek et al. (1999), dilution of raw diesel exhaust is strongly dependent on local conditions. Not only the design of the dilution tunnel has a large influence on the particle characteristics of the diluted exhaust, but also the temperature and humidity of the dilution air, as well as the dilution ratio and the residence time. Figures 3, 4 and 5 show the effect of a temperature change of the dilution air during a chassis dynamometer experiment in which a diesel engine was running at conditions that simulate a 55 mph on-road high load cruise. A detailed description of the involved instrumentation can be found in (Kittelson et al., 2000). The raw exhaust was diluted approx. 600:1 using a two-stage dilution tunnel. It is clearly seen that the particle characteristics change as the dilution temperature increases (Fig. 3).

Initially, the SMPS size distributions (Fig. 3) show a large nucleation mode at approx. 10 nm that changes its concentration with time and finally disappears, leaving only the soot mode. The latter exhibits a constant concentration throughout the experiment. The same behavior is also reflected in the $D_{Ave,S}$ curve, calculated from the DC and CPC data (Fig. 4). Following the PAS and DC signals during the same time frame (Fig. 5) leads to the distinction between two clearly different situations. As long as a nucleation mode is present the histories of the PAS and DC signals show opposite behavior. However, as soon as the ultrafine mode has disappeared, there is a monotonous increase of both signals. The plot PAS signal vs. DC surface area concentration (Fig. 5) reveals two branches of data for the above situations, each of them indicating a different relationship between the two instrument responses. In case of absence of a nucleation mode, a highly positive slope results, indicating a high positive charge collected on the PAS current filter. On the other hand, the presence of a large nucleation mode concentration prevents a large positive PAS signal; therefore a negative slope is obtained for this situation.

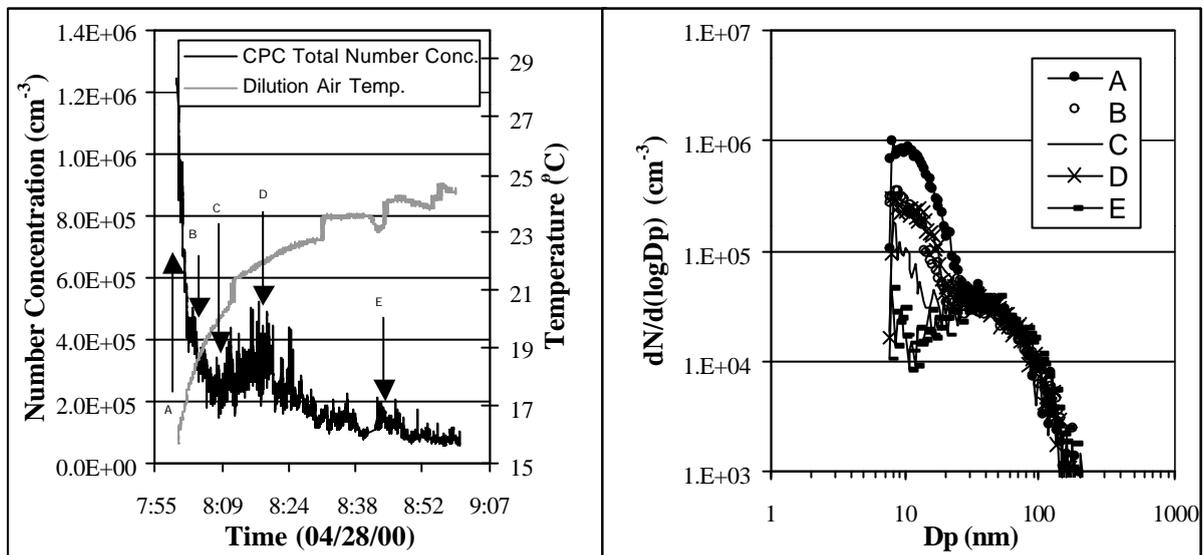


Fig. 3: Total number concentration N and SMPS size distributions during a diesel engine chassis dynamometer experiment. The shown data illustrates the effect of a change in dilution air temperature on the diesel exhaust characteristics. The SMPS size distributions A-E were collected at time points indicated by arrows.

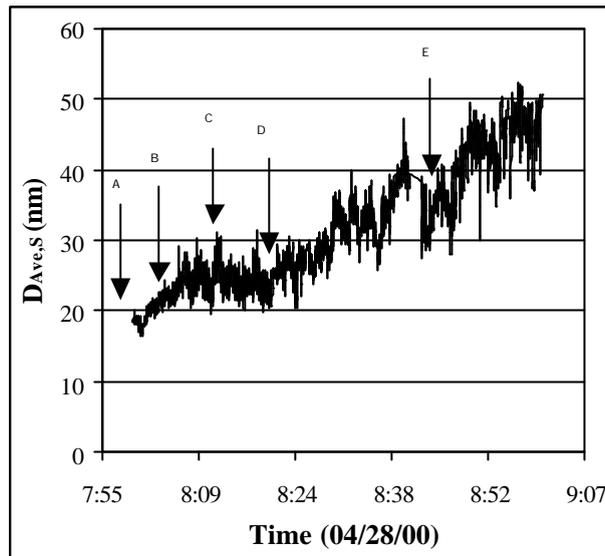


Fig. 4: Diameter of average surface $D_{Ave,S}$ for the chassis dynamometer experiment shown in Fig. 3. The letters A-E in the chart mark points of time at which the SMPS size distributions shown in Fig. 3 were collected.

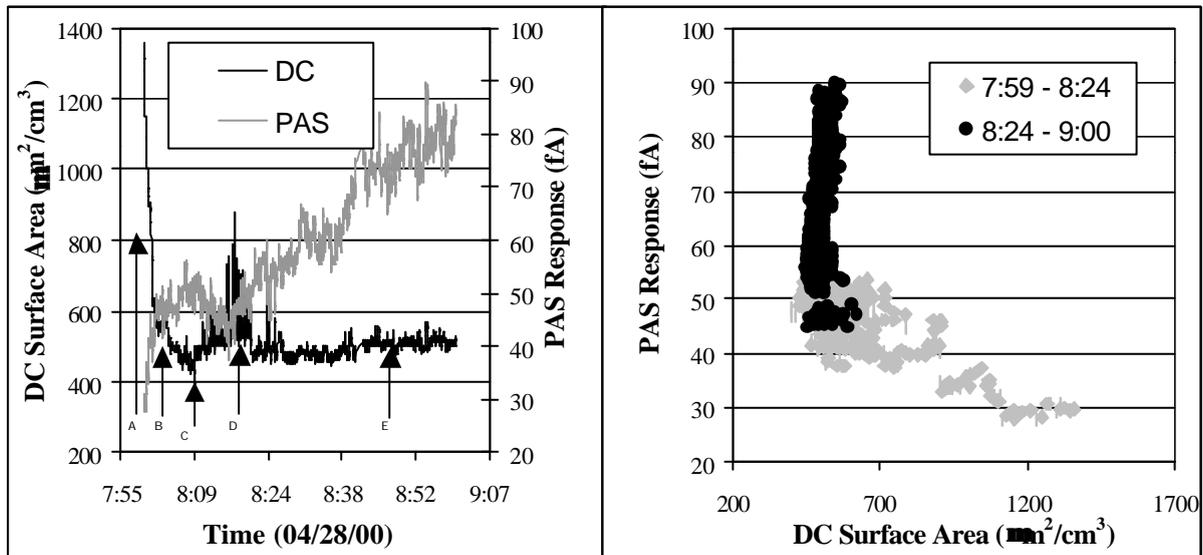


Fig. 5: PAS and DC responses during the time frame of the chassis dynamometer experiment described in the text and shown in Fig. 3. Again, the letters A-E in the left hand chart mark points of time at which the SMPS size distributions shown in Fig. 3 were collected.

Ambient monitoring

The same plot types were created with ambient air data, collected by the Mobile Emission Laboratory (MEL) that was constructed by the University of Minnesota (Kittelson et al., 2000). Figure 6 shows PAS vs. DC plots for two time periods in which the MEL monitored the air at a loading dock with heavy diesel truck traffic. As a further example of ambient monitoring, Fig. 7 shows PAS and DC signals for a 4-hour freeway ride in the Minneapolis city region with continuously changing ambient conditions.

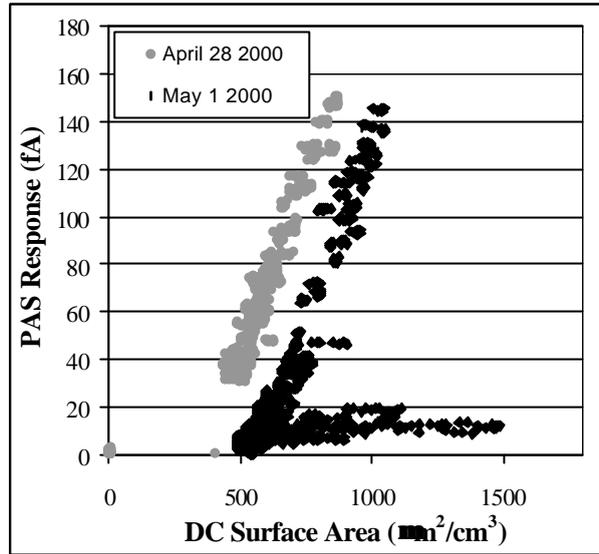


Fig. 6: PAS/DC plot for ambient air containing high concentrations of diesel exhausts. The data were collected on two different days at a busy loading dock. The two branches representing the non-nucleation mode situations have the same slope but show different zero offsets with respect to the PAS response.

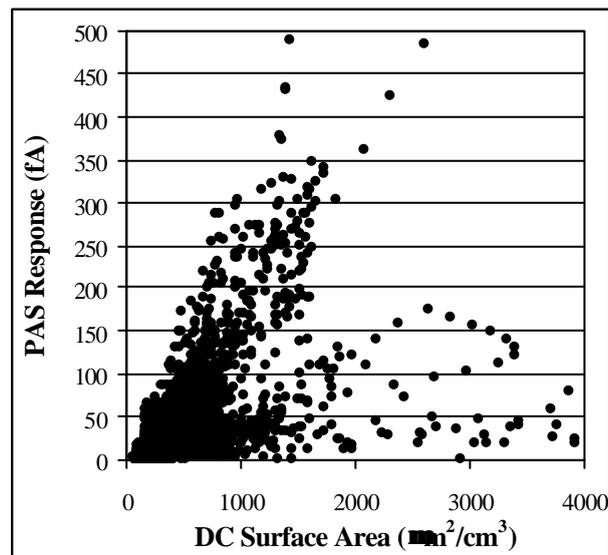


Fig. 7: PAS/DC plot of data collected during a late summer afternoon 4h freeway ride described in the text.

In Figs. 6 and 7, the same type of linear relationship between the PAS and DC signals can be observed as during the chassis dynamometer experiment. Again, two distinct branches are present for surface area concentrations higher than $500\text{-}700\ \mu\text{m}^2/\text{cm}^3$. The branch with a flat slope again reflects situations with a highly concentrated nucleation mode in the corresponding SMPS size distributions.

Figure 8 shows $D_{Ave,S}$, calculated from CPC and DC data, for the 4-hour freeway ride, along with corresponding SMPS size distributions. The curve reflects the concentration and the temporal behavior of the nucleation mode with a high time resolution.

It is important to point out that for traffic monitoring a flat branch in a PAS/DC plot is not only caused by the presence of a diesel nucleation mode, but also by situations in which a large concentration of spark ignition particulate exhaust is present, for which the PAS does not respond as strongly as for diesel soot exhaust. However, these two situations can be separated looking at $D_{Ave,S}$.

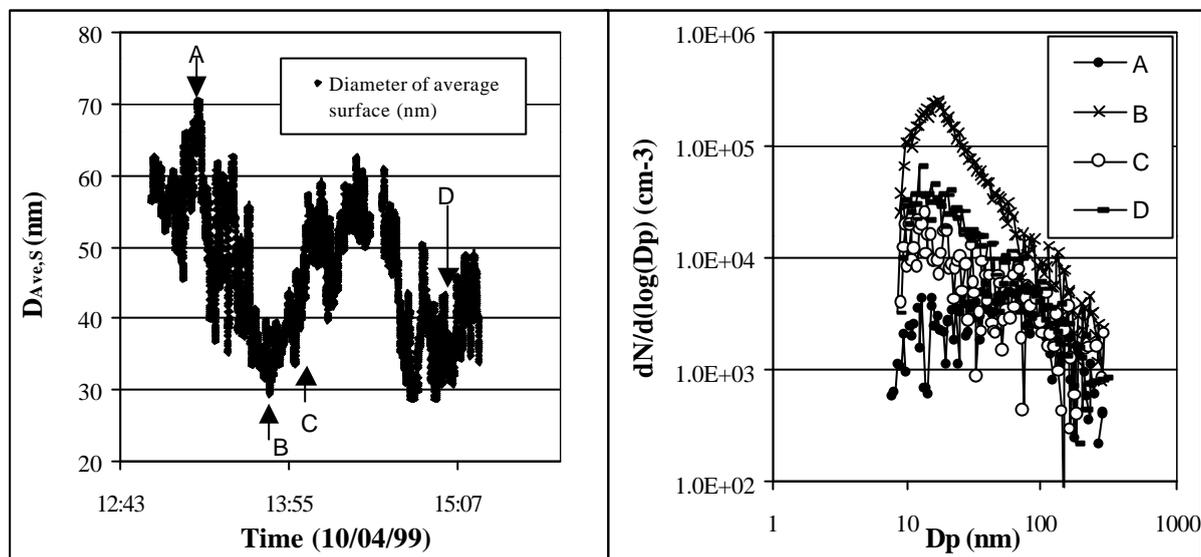


Fig. 8: $D_{Ave,S}$, calculated from CPC and DC data, for a 4-hour freeway ride described in the text and shown in Fig. 7, along with corresponding SMPS size distributions A-D. The presence of a nucleation mode in the size distributions is clearly reflected in $D_{Ave,S}$.

Discussion and Conclusions

PAS vs. DC plots are suitable for separating diesel exhaust situations in which a highly concentrated nucleation mode is present in the sampled air from situations in which only a highly concentrated diesel soot mode is present. The two situations are represented in the plots by two distinctly different branches. It has been shown that this yes/no type answer can be obtained even for traffic air monitoring.

The chassis dynamometer experiment as well as the ambient monitoring confirmed that the formation of a nucleation mode is a process that can be triggered by only small changes in the predominant conditions (dilution air temperature etc.). This is reflected in the fact that there are hardly any data points between the two branches of the PAS/DC plots.

$D_{Ave,S}$ curves represent the relative concentration of ultrafine nucleation mode particles throughout an experiment, assuming a fairly constant size of the diesel soot mode particles. Since the physical principles to determine the DC active surface and the CPC particle number concentration are basically independent from each other, $D_{Ave,S}$ can be considered as a reliable relative parameter. All of the three involved instruments (PAS, DC and CPC) have a time resolution lower than 10 seconds, which allows real-time monitoring of particulate exhaust.

As shown in this report, the presence of a nucleation mode in the sampling volume causes a strong decrease in the PAS signal, despite of the coexisting soot mode, which is known to cause a strong PAS response. With the current design of most PAS types, several processes have an influence on the instrument response. First, the coexistence of neutral, poorly photoemitting particles and particles that readily undergo photoemission in the irradiation volume yields a reduced positive charge collected on the current filter, since the emitted photoelectrons can attach to the remaining neutral particles. Additionally, the absorption of photoelectrons emitted from the UV lamp wall by positive or neutral sample particles can even enforce this signal suppression effect. These two effects can result in a negative total charge on the current filter. Although the wall effect is minimized for the current PAS designs it is not completely avoidable. It has to be emphasized that the PAS always measures the overall charge on the current filter. Strongly photoemitting substances that are present on a particle surface lead to positively charged particles in any case, but the above effects may quench the instrument signal.

However, the question has to be addressed whether the characteristic PAS response during the chassis dynamometer experiments and the ambient monitoring is only caused by the above PAS-internal effects or by a different composition of the soot particles in the presence of a nucleation mode. Further experiments are planned in 2000 to examine further details of this characteristic PAS response to diesel exhaust particulate matter.

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