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Industry comments on proposed particulate measurement techniques

OICA contribution to PMP

Part 1: Synthesis Report

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Summary

Data and information on several techniques for measuring vehicle PM emission are presented in this report.

This review shows that only the gravimetric method fulfils the measurements requirements for a technique to be applied for type approval. Other mass based methods may have the potential to fulfil these requirements.

The investigated new measurement instruments can, as yet, only be used for the qualitative assessment of particulate number and size distribution as a relative comparison. They are still far from achieving the absolute quantitative measurement of these parameters. The measured particle number and size distribution can be manipulated with a careful choice of test conditions. Any new particulate measurement methodology should fulfil the same quality criteria as the current gravimetric method. Based on the above assessment, gravimetric measurement is considered to have the highest potential for future development.

1. Introduction

At the 41st meeting of ECE-GRPE (16. – 19. 01.2001, Geneva) it was agreed to set up an ECE-GRPE ad hoc WG PMP to develop a new particulate assessment and measuring system for application during exhaust emission type approval testing of light-duty vehicles and heavy-duty engines.

The European automotive industry is actively involved in the PMP program and is doing intensive research work in this respect. It has been suggested that a new particulate measurement methodology may be introduced in a future exhaust emission regulation with a set of limits in parallel to the existing particulate measurement legislation based on the principle of gravimetry (determination of the mass of particulate matter (PM)).

The first investigations (about 20 years ago) into a possible health risk of diesel particulates were carried out with toxicological studies with the support of the automotive industry. The results[1] show that animal experiments cannot be applied to human beings. Comparative studies between monkeys and rats prove furthermore that the deposition of particulates in lungs differs considerably. In the lungs of monkeys, that are very similar to those of humans, particulates are mainly deposited in the tissue and cell interspaces without causing inflammations that often precede the formation of tumours. In rat lungs, however, the particulates are mainly deposited in the lung pulmonary alveoli causing changes in the tissue and inflammations. Therefore within the international discussion the animal experiment results are not considered valid for application to humans. Hence they are unsuitable as a basis for risk assessment for humans.

The results of the subsequent epidemiological studies are not clear enough to make a conclusive statement[2]. Aside from a few exceptions the studies are based on measurements of the exposure in relation to the total particulate mass. This requires further clarification before new legislation can be introduced.

The independent HEI[3] states[4] that the results of an extensive study "indicate that epidemiological evidence of PM's effects on morbidity and mortality persist even when the alternative explanations have been largely addressed".
Although HEI places special emphasis on the necessity of

- further research to clarify the impacts of the health effects and
- caution in the use of these results in the political field

the above statement is often used in isolation and an immediate drastic reduction of particulates is demanded as a precaution.

Furthermore, the HEI[5] commented that both the ultrafine (0.010-0.100 µm) and fine (0.010-2.5 µm) particle fractions have shown associations with human mortality; however 'no clear pattern of association indicates relative or temporal differences between ultrafine and fine particles'. This essentially means that there is currently no clear evidence to preferentially address air quality or emission standards for ultrafine particles, as compared to the existing standards for fine PM.

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[1] M. Spallek: Stellenwert der Tierversuche zu Dieselmotoremissionen aus arbeits- und umweltmedizinischer Sicht, ErgoMed 4 (1997), 102-104

[2] M. Spallek: The effects of exhaust emissions on human beings – A never ending story?, VDA Technischer Kongreß, 20./21.09.1999, Frankfurt, S. 201-209

[3] HEI = Health Effects Institute, Cambridge MA, USA (www.healtheffects.org)

[4] Airborne Particulates and Health: HEI Epidemiological Evidence, HEI Perspectives, Cambridge MA, USA, June 2001

[5] HEI Research Report 98

The US- EPA[6] currently does not perceive a need for a new metric for PM emission regulation, other than PM mass, due to the lack of health effects evidence. This statement is based on the acknowledged health effects related to PM mass, which has led to implementation of ambient PM mass standards and emission inventories. However, the US-EPA remains open to considering alternative methods of determining the PM mass emissions[7].

In principle, the automotive industry is of the opinion that the reduction of particulate matter which has already been achieved and which may still be possible in future can be already considered as a health precautionary measure.

Following the outcome of the research activities of BMW, Bosch, DaimlerChrysler, Ford, JAMA, Opel, Renault, Volkswagen and ADA[8] concerning the evaluation of the different instruments is outlined and discussed below:

2. Results of measurement programmes from ADA, BMW, Bosch, Daimler-Chrysler, Ford, JAMA, Opel, Renault, and Volkswagen

2.1 Influences of engine, fuel and measurement and sampling conditions on aerosol measurements

Measuring aerosols in terms of size, number and surface is much more complex than measuring mass, since aerosol measurements determine integrated properties which are based on individual particles distributed in a carrier gas. Number concentration and morphology change continuously due to external influences such as temperature, dilution and gas velocity. Therefore aerosol measurement (and this includes measurement of engine exhaust) is just a momentary photograph at time and location of measurement with an unknown relationship with the real world situation.

?? Nucleation (fuel sulphur) and artefact particle effects

NSD[9] emission measurements results from Ford, BMW, Volkswagen, Opel and ADA show that nucleation particles occur in the <10 nm to 30 nm size range. The nucleation mechanism and chemical composition of these particle droplets is highly complex and not well understood. Nucleation particles occur during cooling and dilution. However, currently, there is no method available to reproduce the atmospheric dilution conditions in the laboratory. The formation of nucleation particles is dependent on the fuel sulphur content (see Figure 1 and 2), engine load and catalyst activity (Figure 3 and 4) and will be reduced by the introduction of future low sulphur fuels.

[6] EPA Report: Health Assessment Document for Diesel Engine Exhaust
[7] CRC workshop San Diego, EPA presentation M. Spears
[8] ADA Abgaszentrum der Automobilindustrie
[9] NSD = Number Size Distribution

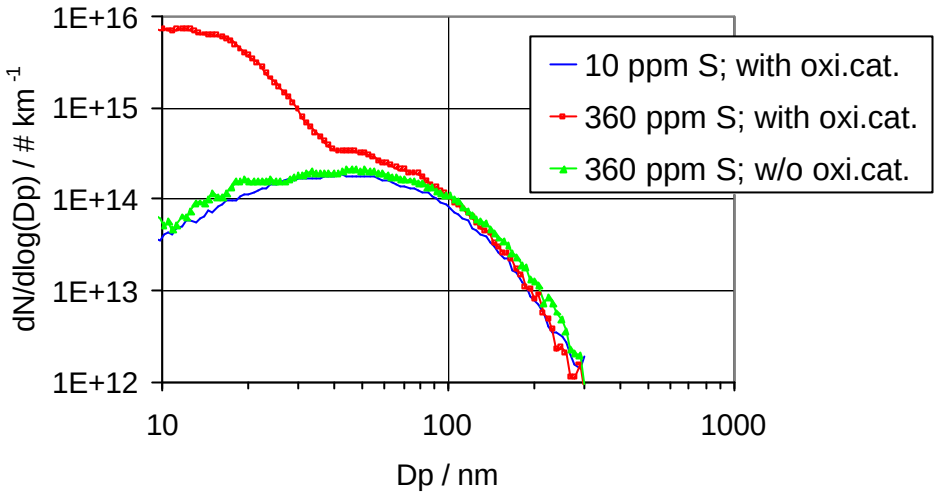


Figure 1: Real-world particle size distributions measured by SMPS[10] at 120 km/h chasing the exhaust plume of a diesel test vehicle operated with 360 ppm S fuel with and without oxidation catalyst with a mobile laboratory (red squares and green triangles). The blue solid line represents a measurement with 10 ppm S fuel with oxidation catalyst, showing the absence of nucleation particles. The distance between test vehicle tailpipe and sampling inlet was 14 m (0.4 s). Ambient temperature was 20 °C, relative humidity 60 %. Nucleation particles occurred only if an oxidation catalyst and high sulphur fuel were applied. *(Vogt and Scheer, 5th Int. Workshop on Nanoparticle Measurements, Zürich, 6.-8.8.2001, Proceedings Bundesamt für Umwelt, Wald und Landschaft, Bern (2001)).* (Source: See Annex 5.5, Ford)

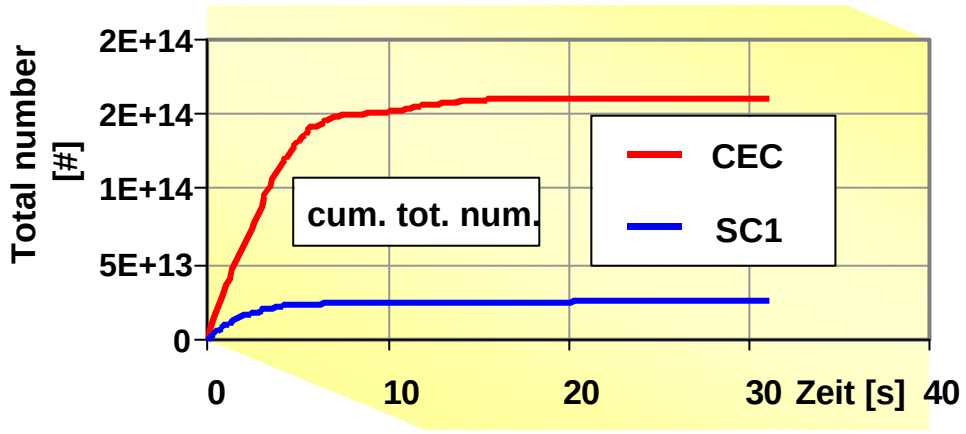


Figure 2: Braking 120 to 0 km/h with down shifting from 5th to 1st gear within 19 sec, OPEL Astra with 2.0 DTI diesel engine. The figure shows the accumulated number of particles (TDMPS[11]) during braking and subsequent idling for a CEC fuel (CEC) and the Sweden Class 1 fuel (SC1) . Despite the fuel cut off under braking conditions, the number of particles increases. This is attributed to residual fuel and deposits and is a much smaller effect with the low sulfur Sweden Class 1 fuel. (Source: Opel)

[10] SMPS = Scanning Mobility Particle Sizer
[11] TDMPS = Transient Differential Mobility Particle Spectrometer

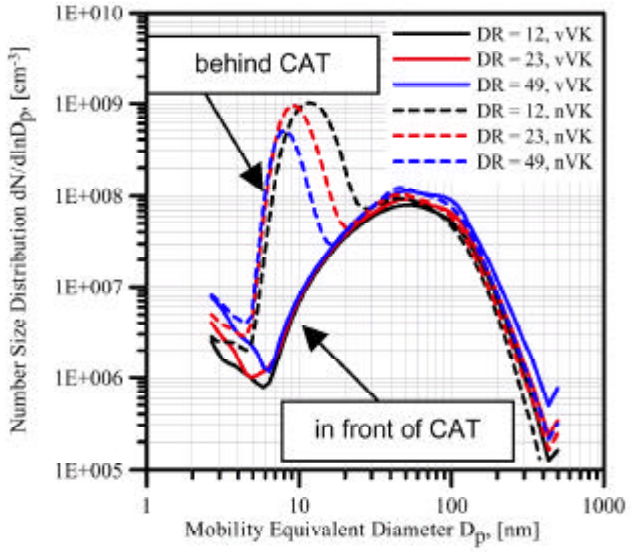


Figure 3: Two sampling points in front of the catalyst (vVK) and after the catalyst (nVK) are shown. In the range above 30 nm, the shapes of the curves of sampling in front and after the catalyst are nearly the same. Below 30 nm, the strong nucleation effect is clearly influenced by dilution ratio (DR) effects. The particle size distributions were measured with a twin SMPS with a Faraday-Cup Electrometer. The tests had been carried out on an engine test bed with a BMW Diesel engine at an operation point corresponding to a vehicle speed of 120 km/h with 210 ppm sulphur fuel content. (Source: See Annex 5.2, BMW)

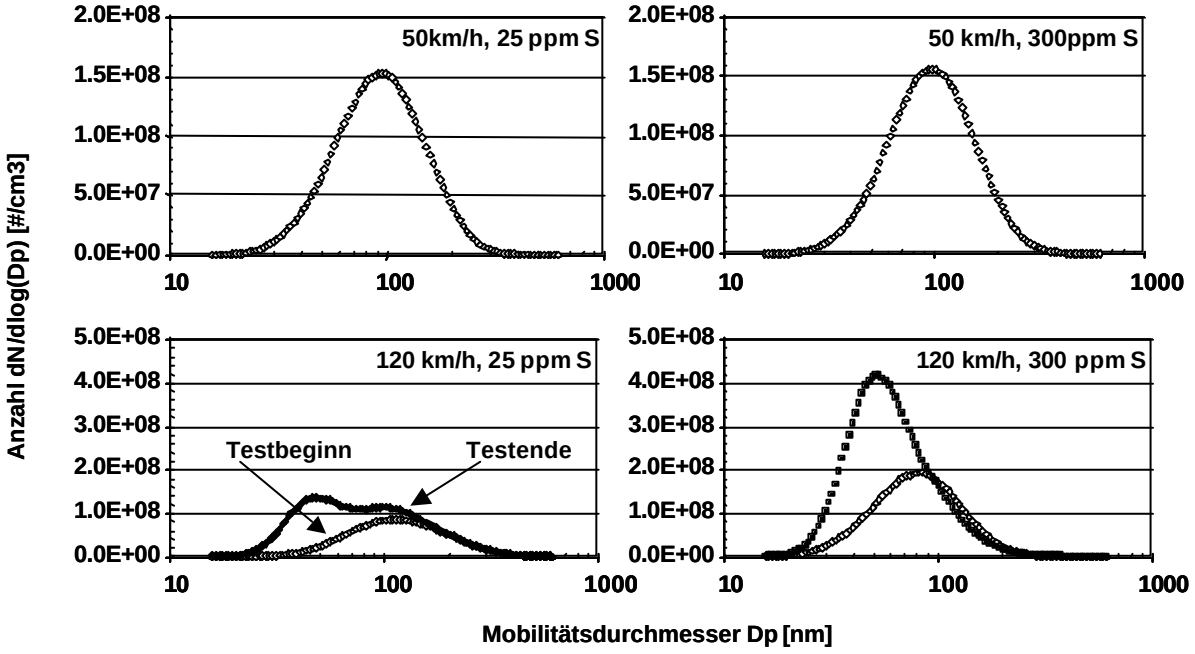


Figure 4: Comparison of SMPS Diesel particulate size distribution at 50km/h (upper diagrams) and 120km/h (lower diagrams) using diesel fuels containing 25 ppm sulphur (left diagrams) and 300ppm sulphur (right diagrams). At 50 km/ h the size distribution is monomodal with a maximum particulate size of approx. 90 nm. No significant influence of the sulphur content of the fuel can be observed. The results at 120 km/h show a clear difference when using fuels with different sulphur contents. With high sulphur content a condensation particulate mode can be observed which finally dominates the size distribution. (Source: See Annex 5.6, VW)

Large artefact effects showing high numbers of nucleation particles have been documented (see Figure 5).. The “false” measurements (result influenced by high number of artificial particles) occur due to pyrolysis of tube connectors, or due to the evaporation and condensation of deposit material from the transfer line.

a.) b.)

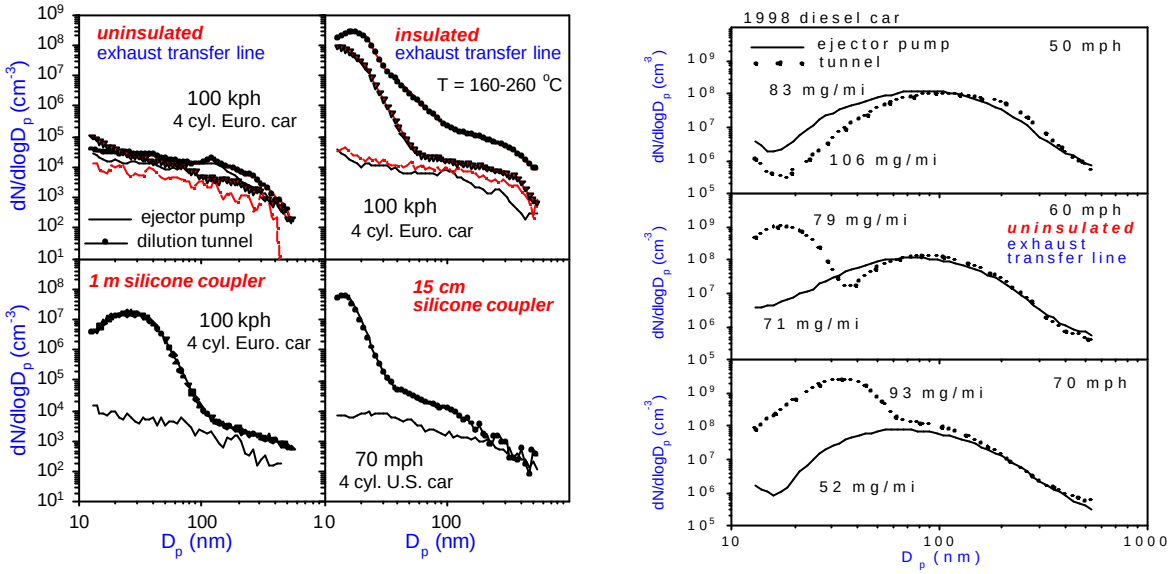


Figure 5: Comparison of particle size distributions (SMPS) for a European gasoline car a.) and a 1998 diesel car b.) taken by ejector pump versus dilution tunnel when using a 1) *not insulated* transfer line, 2) *insulated* transfer line, 3) *not insulated* transfer line plus a 1 meter silicone rubber coupler, and 4) *not insulated* transfer line plus a 15 cm silicone rubber coupler. It is shown that with excessive heat, high numbers of artificial particles occur in the dilution tunnel which are absent when sampled directly from the tailpipe *(Maricq et al., SAE 1999-01-1461)*. All concentrations are converted to tailpipe concentrations. The tunnel background level was in the order of 5000 particles cm-3 and was subtracted. (Source: See Annex 5.5, Ford)

A new PM measurement metric which is sensitive to nucleation particles is potentially susceptible to large measurement artefacts and should therefore not be considered further.

?? Use of thermodenuder TD

The thermodenuder is a device to remove volatile particles and is being considered to overcome measurement errors caused by the occurrence of nucleation particles. In some cases this might be an optimistic assumption because

- the efficiency for removal of volatile particles is not 100 %;
- size dependent losses of non-volatile particles occur.

A thermodenuder has a particle size-dependent transmission efficiency which is also related to the TD carbon bed temperature. This means that it is not at all suitable for use in combination with size-unresolved total particle count (see Figures 6 and 7).

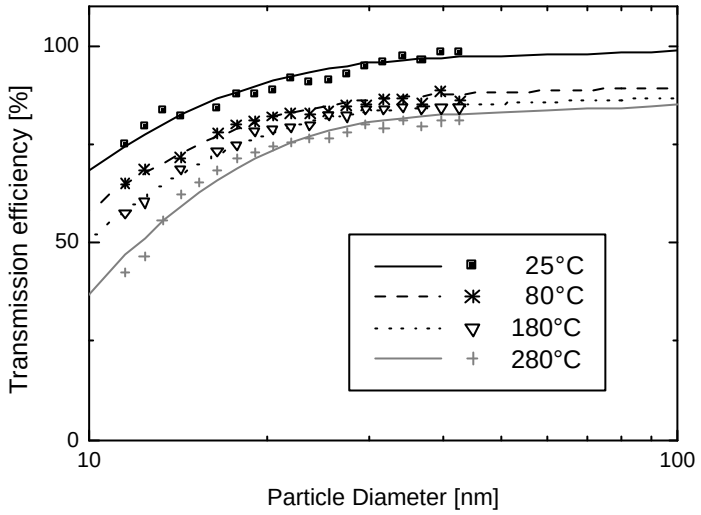


Figure 6: Particle size-dependent transmission efficiency of silver particles within a thermodenuder for different temperatures, SMPS measurements (Wehner et al. J. Aerosol Sci. 33, 1087 (2002).

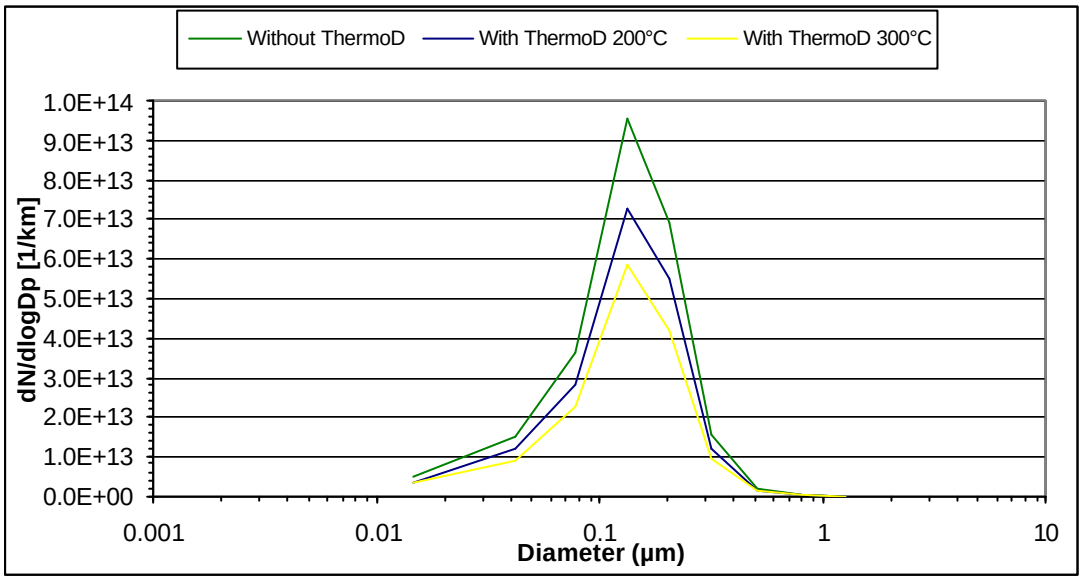


Figure 7: Relative effects of a thermodenuder and different temperature conditions on the size-number distribution (ELPI[12] - greased sintered plates - sample from the CVS - secondary dilution (x 10) with N_2) of Diesel exhaust particles as measured over an hot NEDC test cycle (Euro 3 - Common Rail Turbo-charged Diesel car - Fuel : 270 ppm S). The total particle numbers are drastically affected by the presence of the thermodenuder and the carbon bed temperature conditions ($5 * 10^{13}$ /km without heating ; $4 * 10^{13}$ /km with (200 °C) and $3 * 10^{13}$ /km with (300 °C) respectively) . In addition, the trapping efficiency is strongly size dependent and will be probably influenced by maintenance and ageing. (Source: (Source: See Annex 5.7, Renault)).

The efficiency of a thermodenuder to remove volatile particles and the size-dependent transmission efficiency for solid particles is dependent on various parameters such as flow rate, inlet and carbon bed temperature, chemical composition of the aerosols (see Figure 8), residence time in heating and adsorption section, carbon bed absorption

[12] ELPI = Electrical Low Pressure Impactor

capacity, design etc. In principal it is necessary to validate the performance of a thermodenuder both before and after every test as there is no obvious means of determining when the carbon in the adsorption bed is saturated.

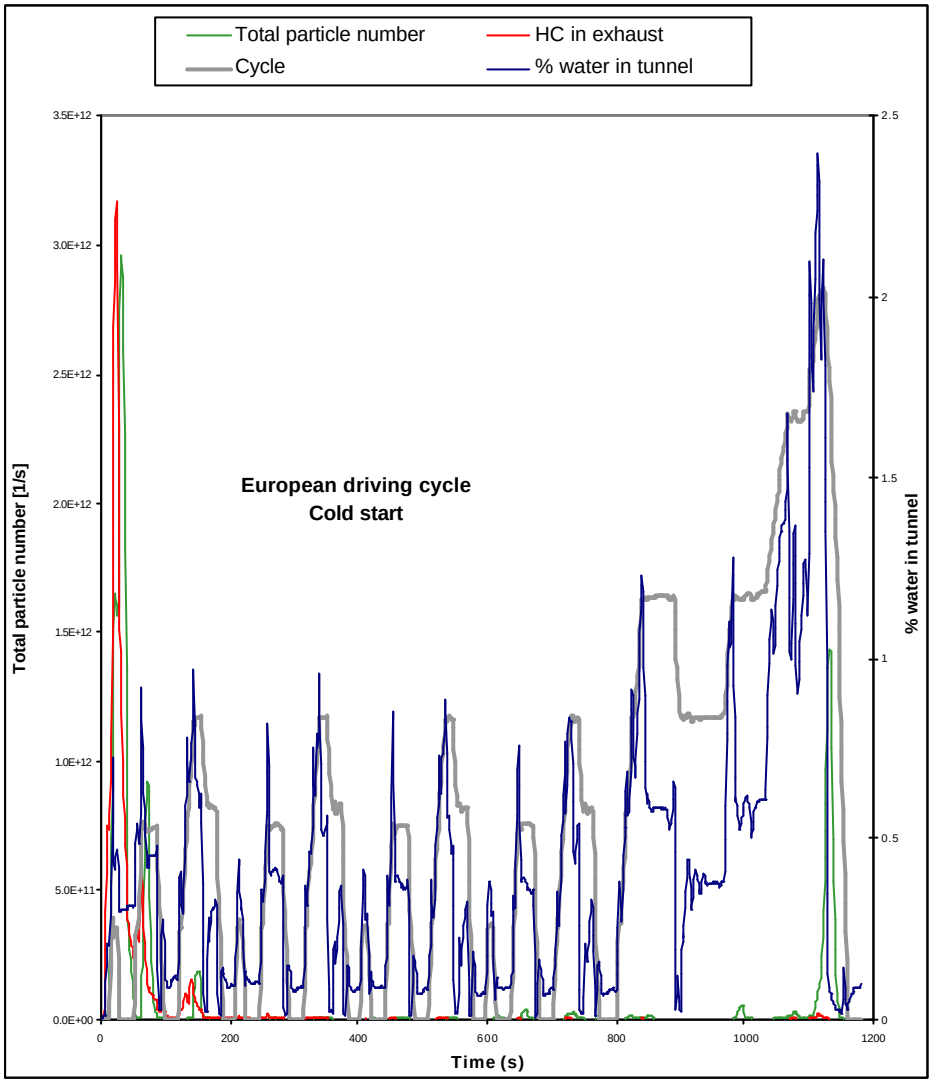


Figure 8: Total particle number ($3.3x10^{11}$ /km ELPI - greased Al plates - sample from the CVS - secondary dilution (X 10) by N2) of a typical Gasoline exhaust as measured (without a thermodenuder) over a cold NEDC test cycle (Euro 3 - MPI Gasoline car ; Fuel : 130 ppm S).
A thermodenuder (250 °C) used under the same test conditions will strongly reduce the total particle number ($1.4x10^{11}$/km) mainly as a result of trapping condensed water aerosols: Under hot NEDC conditions (with extremely low residual HC emissions – i.e. efficient after-treatment), the only significant effect of the thermodenuder is on the water based particle emissions. This occurs towards the end of the NEDC cycle. It demonstrates that the performance of a thermodenuder is directly influenced by the test conditions and will probably reveal an unreliable behaviour over extended periods of time, depending on the maintenance scheme. (Source: See Annex 5.7, Renault)

A combination of thermodenuder with size-unresolved total particle count cannot give valid data, because of size-dependent particle losses, and likely chemical species dependency on denuder efficiency.

Because of the many parameters that must be kept constant and verified by regular calibration, a thermodenuder is in principle not suitable for regulatory measurements.

?? **Sampling location and residence time (coagulation) effects**

The measured number/size distributions may also be dependent on the sampling system, even in the absence of nucleation particles. Depending on sampling location and the residence time, particles may coagulate and shift the size distribution to somewhat larger diameters, whilst the total particle number is significantly reduced (see Figures 9, 10, 11, 12).

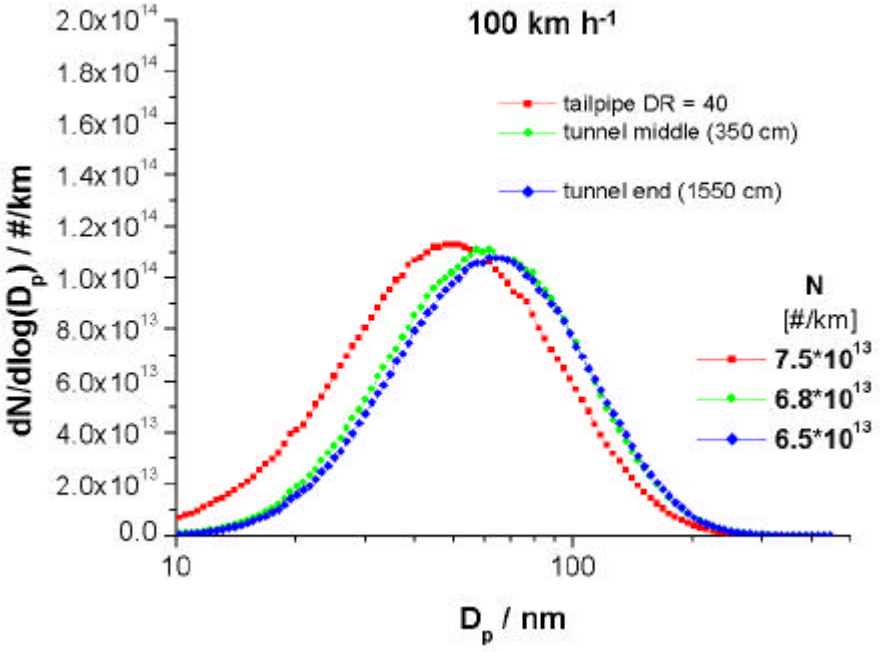


Figure 9: Comparison of particle size distribution (SMPS) measured at three sampling locations with a rotating disk diluter. The diesel vehicle was running at 100 km h^{-1} constant speed. The diluter was set to a dilution ratio of 1:40. At the tunnel the total dilution ratio was 1:440. Under these conditions the measured particle size distribution shifted to larger diameters and the total number decreased with longer residence times. *(Vogt and Scheer, 5th Int. Workshop on Nanoparticle Measurements, Zürich, 6.-8.8.2001, Proceedings Bundesamt für Umwelt, Wald und Landschaft, Bern (2001)).* (Source: See Annex 5.5, Ford)

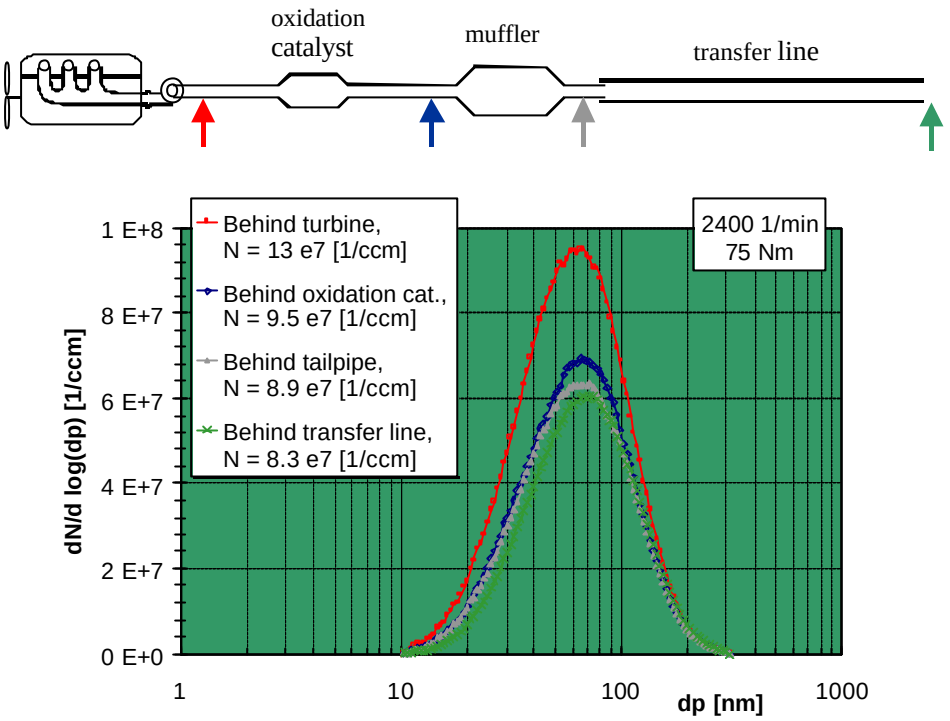


Figure 10: Size distribution and count median diameter, measured at various sampling locations with a DMPS[13] in the heated path (350 °C) and a one stage ejector dilution system. The decrease in number concentration and the slight shift in particle size is caused by agglomeration, diffusion and thermophoresis. The engine was a 3 l, 6 cylinder, common-rail direct injection diesel engine from a passenger car, operated with low sulphur fuel. (Source: See Annex 5.3, Bosch)

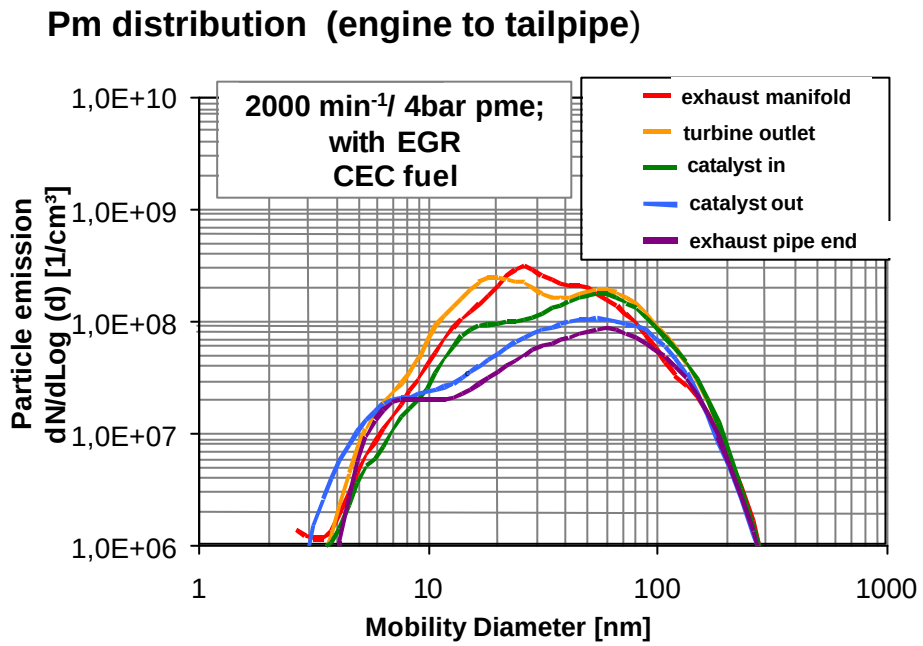


Figure 11: Size distribution and count median diameter measured along the exhaust pipe system of the Opel X20 DTdiesel engine. The size distribution is affected by the coagulation process which occurs along the exhaust system. In the catalyst formation of nucleation particles through sulphur oxidation occurs. Measurement was done with a 10 channel Transient Differential Mobility Particle Spectrometer (TDMPS) in collaboration with the University of Wien. (Source: Opel)

There is a different aerosol residence time for the undiluted gas which is dependent on the length of the transfer lines. Interaction of the aerosol with the surface of the lines and agglomeration increases with longer lines (see Figure 12).

[13] DMPS = Differential Mobility Particle Sizer

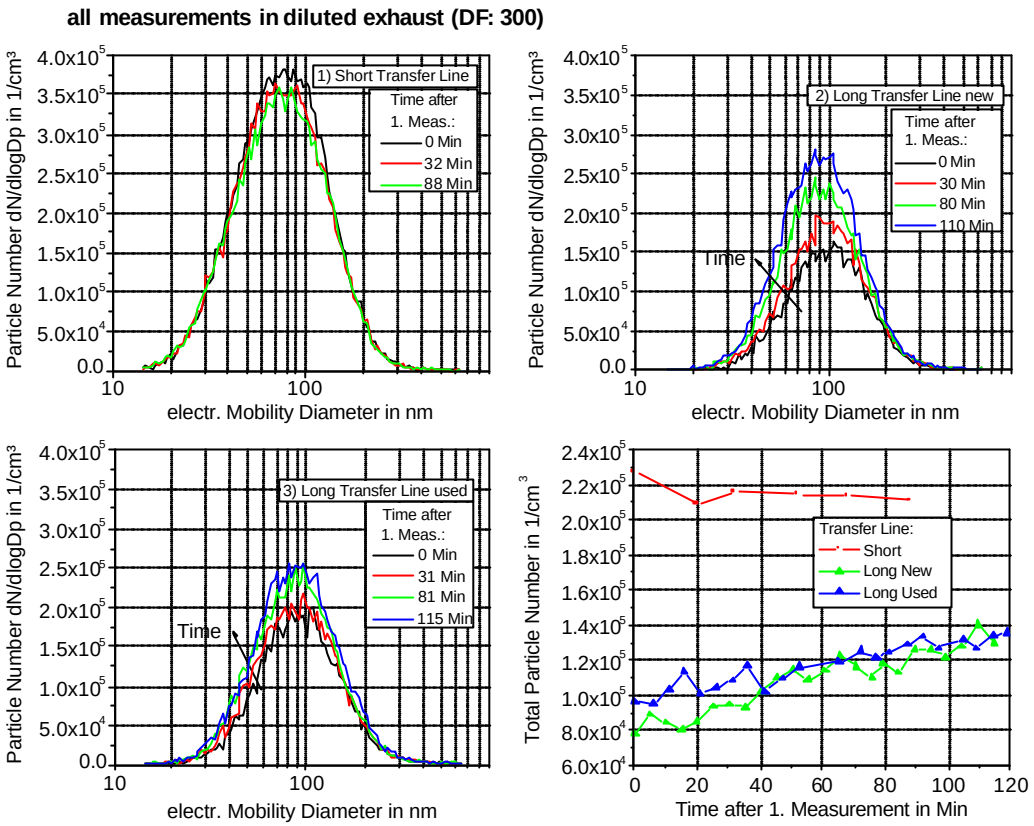


Figure 12: Number size distribution measured with SMPS combined with dilution system NanoMet rotating disc. Use of two transfer lines (Material: stainless steel) with different lengths (Short: 0.3 m , long: 1.7 m). The long line was tested in two different conditions: new (clean) and after a few days of being used for measurement (contaminated with diesel exhaust). The heated transfer line (120 °C) transports the undiluted gas from sampling position to the diluter. The engine operating point is held constant during all measurements. With the short transfer line, the NSD and particle number concentration remain nearly constant over measuring time. In comparison, the long line (1.7m) shows NSD changes and number concentration increasing with time, although the concentrations measured with the short line are not reached even with an extended measurement time. Changes of NSD over time with a new line are higher than with a used line. (Source: See Annex 5.1, ADA)

A measurement metric based on 'solid' particle number is problematic because of the influence of aerosol dynamics on the measured value.

?? Particle morphology influences on size measurements

TEM (Transmission Electron Microscopy) measurements (see Figure 13) suggest that morphology changes of particles induced by changes of operating condition and fuel quality can lead to results which are not reproducible. The method of classifying particles, i.e. the aerodynamic diameter (i.e. ELPI) and the electrical mobility diameter (i.e. SMPS) have a large influence on the measured particulate number and size distribution (see Figure 14).

Various measurement technologies are based on different physical quantities. During measurements the idealised physical behaviour of the particles (e.g. constant density, spherical shape, ...) cannot be assumed. Therefore, the results depend on time, location, operation point and fuel quality.

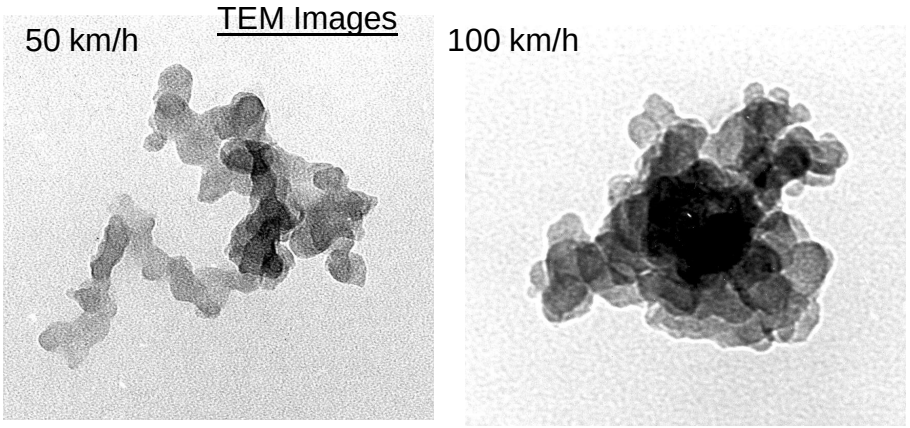


Figure 13: TEM images of Diesel particles samples at 50 and 100 km/h load. (Source: See Annex 5.6; VW)

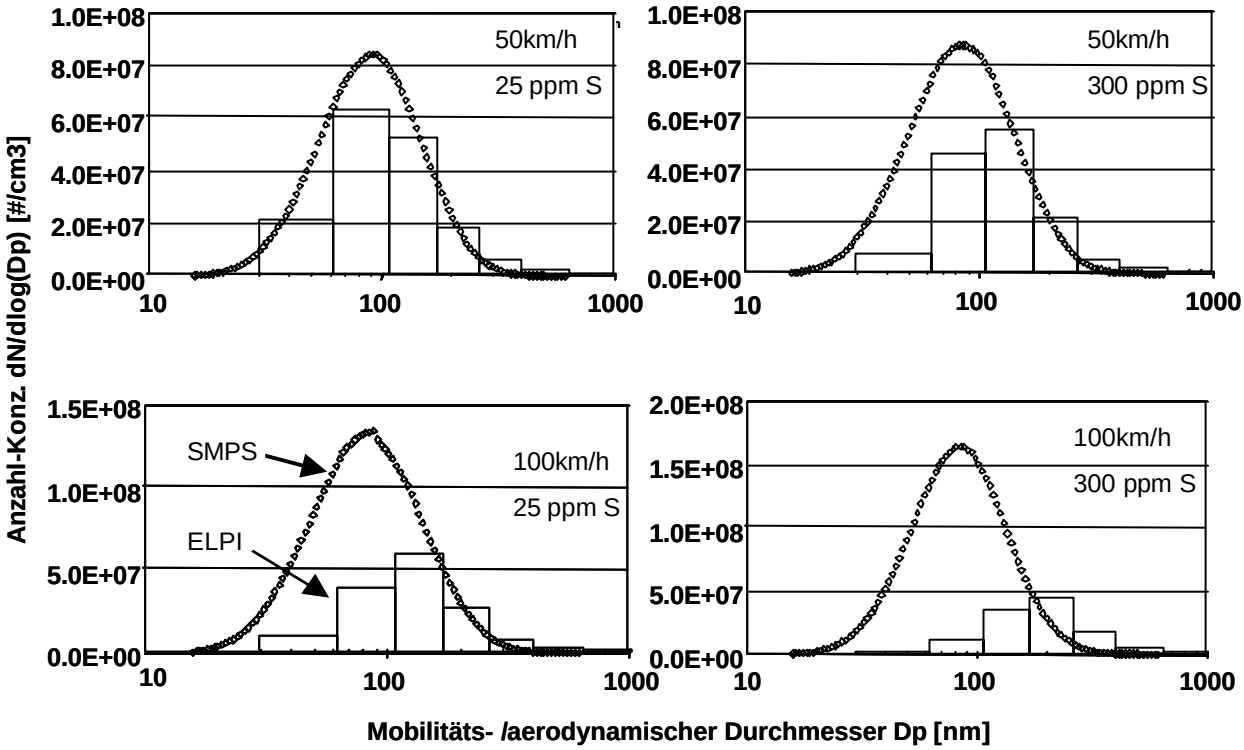


Figure 14: Comparison of parallel SMPS and ELPI measurements under different loads and fuel sulphur content. With increasing load and sulphur content the ELPI shows a decrease of the particulate number and a shift of the distribution maximum towards bigger particulate diameters. Whereas in the SMPS the distribution maximum remains constant and only the number increases. Load and fuel sulphur induced morphology changes are thought to be the reasons for this effect. (Source: See Annex 5.6, VW)

Engine load and fuel dependent particle morphology changes can lead to unpredictable aerosol measurement effects. Examples include aerodynamic and mobility aerosol behaviour. Metrics influenced by this type of effect are neither reliable nor repeatable.

?? Dependence of particle size distribution on injection pressure

The influence of the injection pressure on the particle size distribution is being discussed. The number size distribution in the exhaust of a high pressure, direct injection diesel engine has been measured over a wide range of injection pressures

(see Figure 16) When the original injection pressure of 550 bar is varied over a range of 250...1600 bar and the engine torque, the soot and the NOx level are kept stable, no effect of injection pressure variation on particle size distribution can be found.

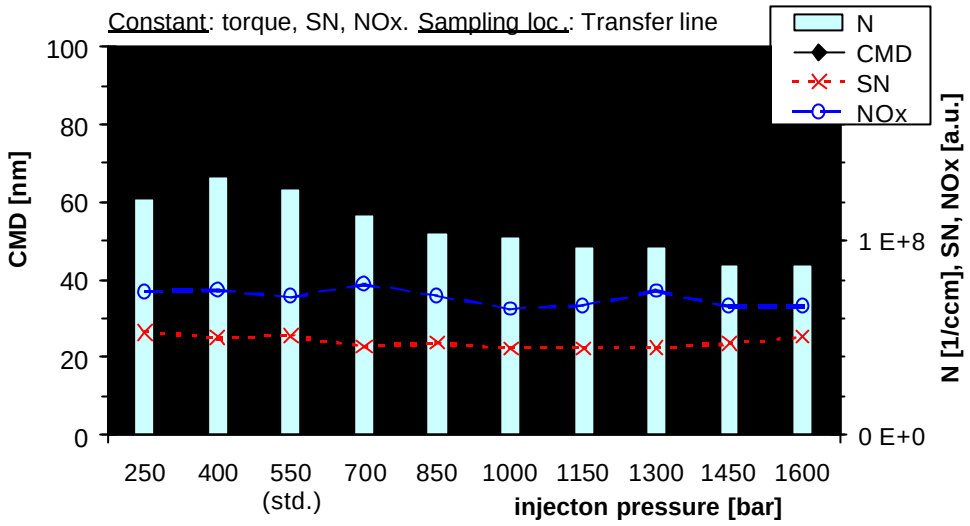


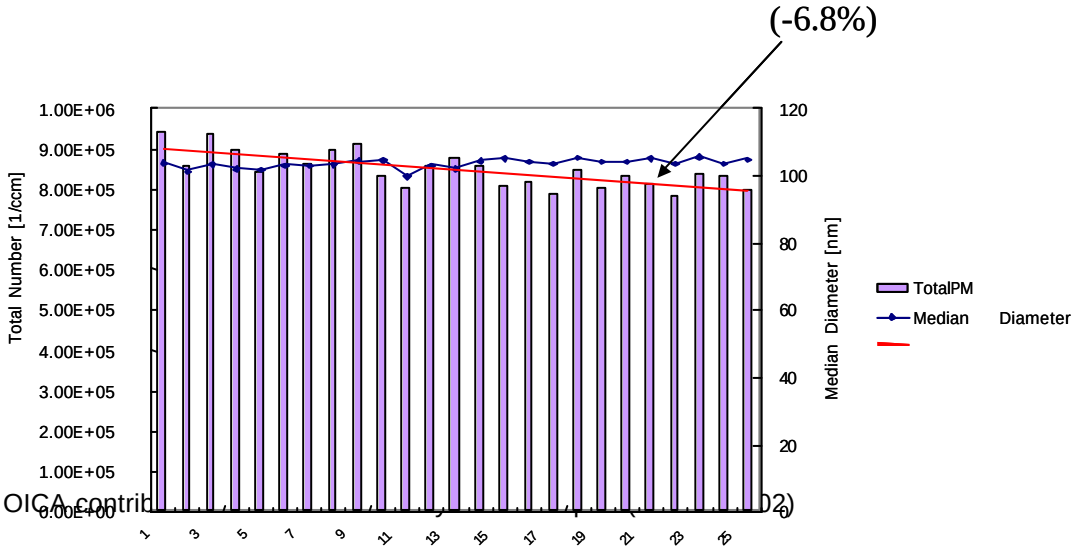
Figure 16: Particle size (CMD) and number concentration (N) versus injection pressure; n = 2000 1/min, M = 82 Nm (--> v = 100 km/h). Torque, NOx and the smoke number were set to their original value, after changing the rail pressure (standard values at this engine operation point: rail pressure = 550 bar, smoke number (SN) = 1.0, NOx = 140 ppm). Sampling location was behind a transfer line. The number size distribution has been measured with a SMPS and a one stage ejector dilution unit by Bosch. The measurements were carried out on a stationary test bench with a 3 l, 6 cyl., common rail direct injection engine from a passenger car. (Source: See Annex 5.3, Bosch)

With a test procedure of practical relevance, no correlation between particle size and injection pressure of a modern, direct injection diesel engine was identified. As particles are formed in the gas phase, their size is not related to the droplet size in the diesel spray or to the injection pressure. Size resolved particle measurement gives no additional information and can therefore be replaced by mass measurements.

2.2 Evaluation of instrumentation systems

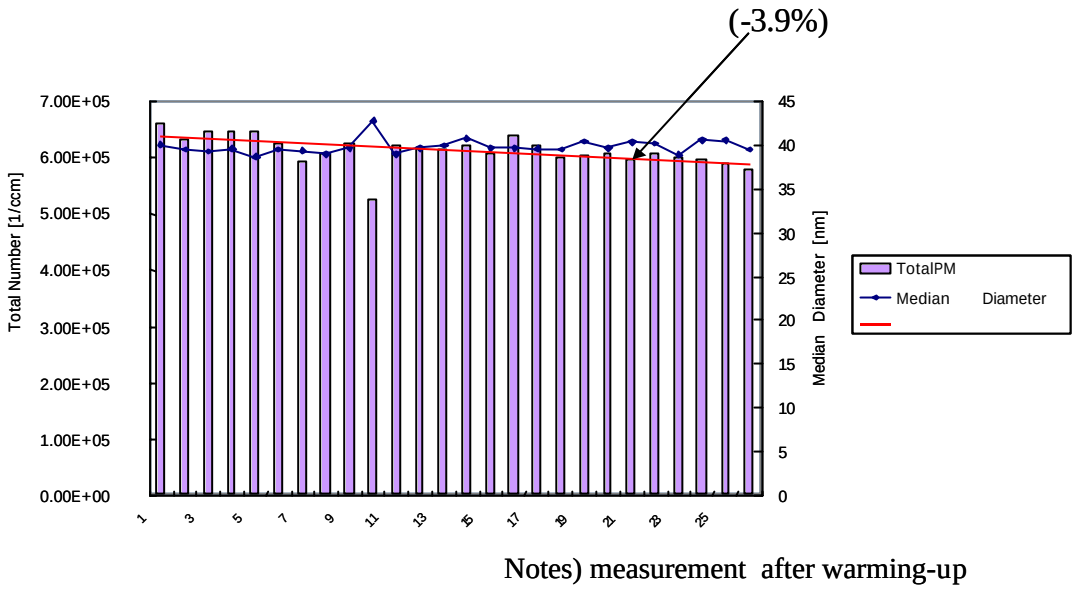
2.2 .1 Combustion aerosol standard (CAST)

Currently, the CAST is the only instrument offered as a calibration aid. Particles of a polydisperse distribution are formed in a quenched propane flame. The maximum of the



distribution can vary between 30 and 180 nm (count median diameter CMD) as stated by the manufacturer.

Figure 17a: Repeatability of continuous SMPS-scans (1 to 3 minutes each) with a CAST and a particle distribution with a maximum at 100nm (Source: see annex 5.8, JAMA)



Notes) measurement after warming-up

Figure 17b: Repeatability of continuous SMPS-scans (1 to 3 minutes each) with a CAST and a particle distribution with a maximum at 30nm (Source: see annex 5.8, JAMA)

The particles generated by CAST show a stable average diameter (CMD), but a trend towards decreasing number concentration with time. It appears to be unsuitable as a calibration aid.

2.2.2 Particle surface metric

?? Diffusion charging sensor (LQ1-DC, Matter Engineering)

Metric: Active surface [$\mu m^2/cm^3$]

The LQ1-DC measurement method uses the probability of deposition of ions on particles for measuring the active particle surface area. Particles are electrically charged by diffusion (unipolar corona charging). The discharge current of the particles is determined by a downstream measurement filter (electrometer). This is a measure for the deposition coefficients of the ions from which the Fuchs surface area or active surface area can be calculated. The measurement does not take place on a single particle basis, only the total active surface area within a defined aerosol volume is given.

The results of surface measurements with LQ1-DC in the nano particle range, can not be explained and are not plausible (see Figure 18).

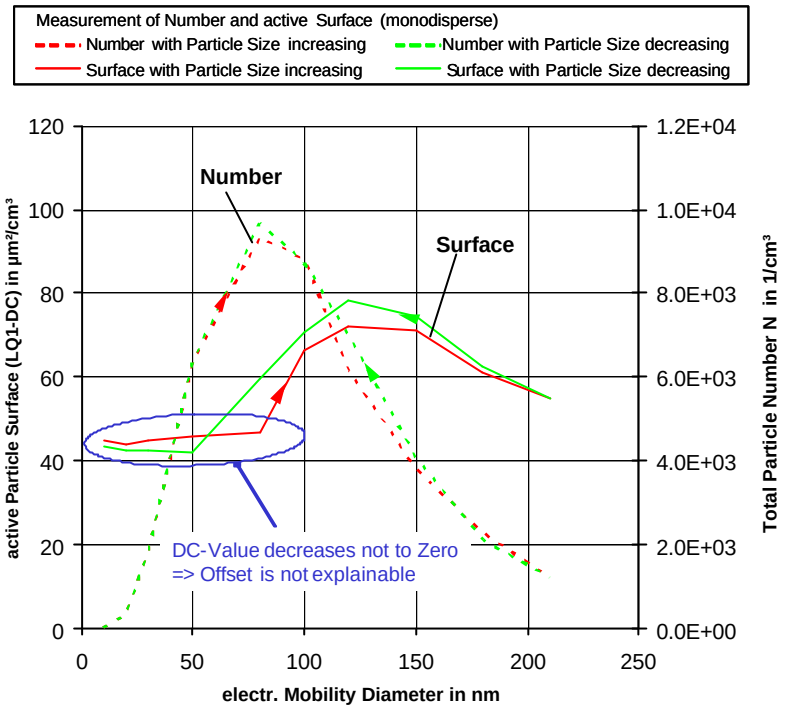


Figure 18: A combination of number (CPC) and surface measurement (LQ1-DC) of monodisperse diesel engine particles, which are sorted by DMA, is shown. The resulting NSD has a maximum at 80 nm as expected. Surface measurement shows a maximum at 120 nm electrical mobility diameter. Below 70 nm there is an offset value, which is not explicable. (Source: See Annex 5.1, ADA).

Measurement of diesel exhaust may lead to contamination of the corona needle (see Figure 19). The principle of charging particles by corona is also used on electrostatic air cleaners. It is known that particle deposits at the corona needle can disturb the discharge. There are hints that this ageing effect can occur also at the LQ1-DC when measuring diesel engine exhaust, although the cause of this has not been established. Changes in particle charging influence the surface measurement directly.

Contamination of Corona Needle (Electrostatic Air Cleaner after 180 h in Use)

(Air contains Cyclomethicone, which is often used in deodorant sprays)

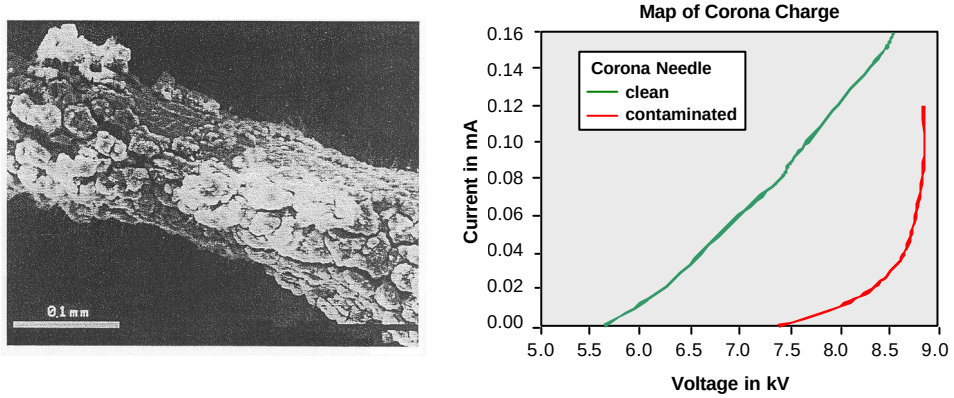


Figure 19: Contamination of Corona Needle (Electrostatic Air Cleaner). (Source: See Annex 5.1, ADA).

Measurements with the LQ1-DC in the particle range less than 70 nm are not plausible. The observed ageing effects make the general suitability of a corona charger questionable. Humidity and variation of the inner electrical insulation caused by deposited particles give a poor stability of the measurement signal. Additionally, no absolute particle surface calibration standard is available for system verification.

?? **Photoelectric Aerosol Sensor (PAS 2000; EcoChem)**

Metric: Photo electric charging [fA]

The PAS 2000 measurement method makes use of the sensitivity of particles to photoelectric charging. The wavelength of the UV radiator (222 nm) used for the charging is adjusted to suit the ionization of polycyclic aromatic hydrocarbons (PAH) deposited on the particles.

The discharge current of the particles is determined by a downstream measurement filter (electrometer). This can be correlated with the PAH deposited on the particles. With an appropriate calibration, predictions of mass concentration of PAH in µg/m^3 can be made. In some cases this instrument is used for the measurement of Elemental Carbon (EC)[14]. For diesel exhaust measurements, the measured photoelectric signal can not be correlated to the gravimetric mass (see Figure 20).

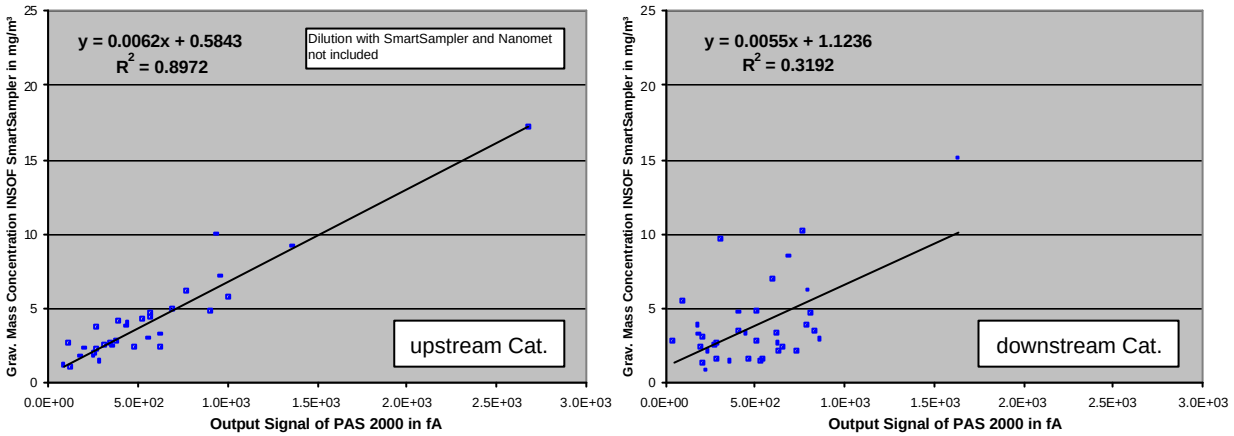


Figure 20: Correlation between gravimetric particulate mass (INSOF) and Output Signals of PAS 2000, separated upstream and downstream of oxidation catalyst. (Source: See Annex 5.1, ADA).

It is observed that the PAS 2000, in principal, is not capable of performing particle surface or mass measurements in exhaust gas from internal combustion engines with reliable and quantitative results. Additionally, no absolute calibration standard is available for system verification.

2.2.3 Particle number metric

?? **Electrical Low Pressure Impactor ELPI**

Metric: Aerodynamic size distribution of diffusion charged particles [1/cm^3, 12 size bins]

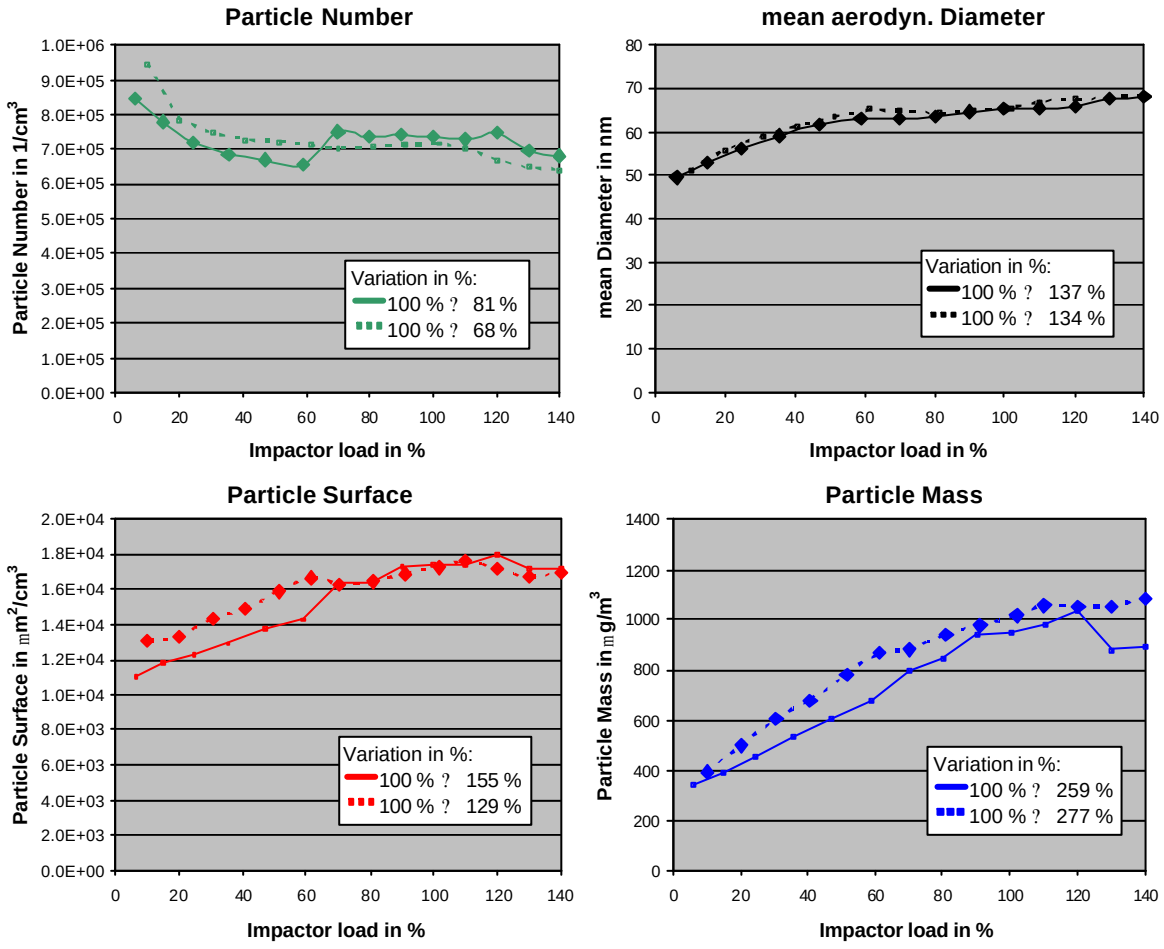
The ELPI method is based on the impactor principle in which the particles are sorted, according to their aerodynamic diameter, into 12 size-classes and are separated on the impactor plates. The counting of the previously electrically charged particles takes place at each stage by means of an electrometer. From the electric charge, assuming an idealized multi-charging based on spherical particles, a complex calculation is

[14] Przybilla; Berkhahn; Burtscher; Dahmann; Matter; Rietschel
"Monitoring diesel particulates in working areas with the photoelectric aerosol sensor"
Gefahrstoffe - Reinhaltung der Luft Nr. 6, June 2002

necessary to convert to particle number. The particles remain on the impactor plates after their detection.

The total number of collected particles is displayed by the device as "Total estimated particle mass load in %" as the sum of all discharge currents. Depending on the impactor load value, the device must be cleaned frequently, i.e. be dismantled to ensure proper functioning.

A long-term test is carried out at a constant engine operating point with continuous measurement of the NSD over a period of 2 - 3 test days. The impactor load value rises from 0 % (cleaned device) to 140 %. The measured NSDs are a function of the value of impactor load and change in the course of the test. The values derived from NSD (number, aerodynamic diameter, surface, mass) depend on the impactor load of the instrument (see Figure 21). In addition the measurements reveal that the changes in the NSD are not reproducible. A correction of ELPI measurements, dependent on the current impactor load, to a defined (e.g. cleaned) reference state of the device is therefore not possible. The steepest gradients occur in the first phase of each set of measurements at around 0 ... 30 % impactor load. This means that cleaning of the device before each individual measurement does not provide a valid solution.



Impactor load value as displayed by ELPI

Figure 21: Particle number, aerodynamic diameter, surface and mass calculated from ELPI measurement with rising impactor load (1st (continuous line) and 2nd measurement (dotted line)). Some of the curves show steps in the course due to breaks (measurement stopped over night) during the measurement period of 3 days. The value of particle concentration at the next morning changed considerably compared

to the value of the day before. The total number of particles measured tend to drop with increasing impactor load whilst the mean measured particle diameter increases. At 140 % impactor load, the total number amounts to 81 % and the mean diameter 137 % of the value at the initial, cleaned state. For the values calculated from these two measured variables for total surface area and total mass (spherical form with uniform density assumed) result in even greater changes: the surface area increases to 155 % of the initial value for 140 % impactor load, the mass increases even more to 259 % of the initial value. The primary cause of this is the change in NSD in the upper ELPI stages where the larger particles are separated off, since these particles make an above-average contribution to the total surface area and total mass. After the device was cleaned, the test was repeated to check the reproducibility of the change in impactor load as a function of time. The changes are reproducible. (Source: See Annex 5.1, ADA)

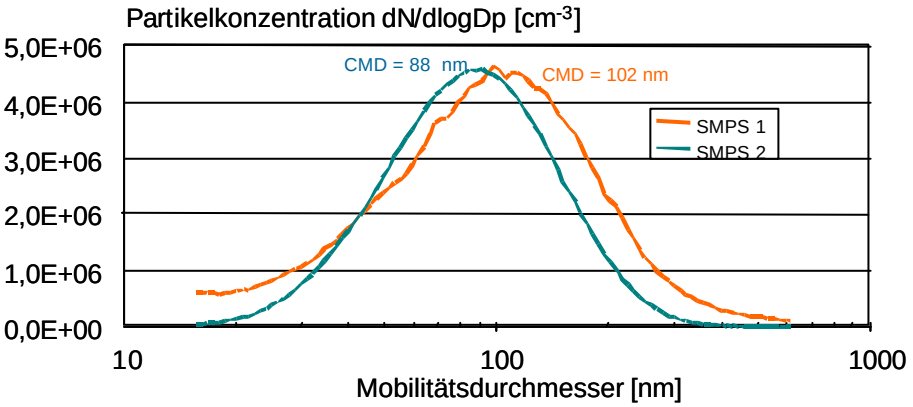
It has not yet been possible to assess the long-term behavior of the corona principle used by ELPI for particle charging. With a Matter-Engineering LQ1-DC instrument, which uses a similar measurement method based on this charging principle, quartz deposits on the corona needle can substantially alter the charging characteristic (see Section 2.2.2).

The reproducibility and comparability of ELPI measurements is limited unless a demanding maintenance/operation protocol is strictly observed. The ELPI is not suitable for performing regulatory measurements. Additionally, no absolute particle number calibration standard is available for system verification.

?? Scanning Mobility Particle Sizer SMPS

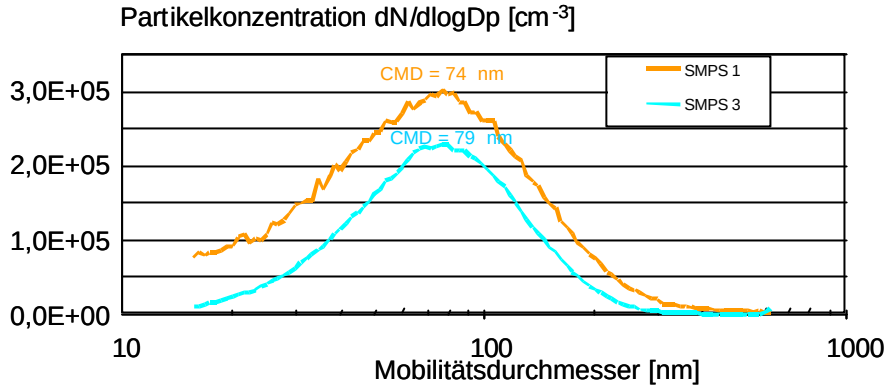
Metric: Mobility size distribution of particles in the load equilibrium classified by their mobility behaviour in a electric field. Particles counted by an optical single particle counter. [1/cm^3, 64 size bins].

A comparison of three SMPS instruments shows significant differences in the results even though two were used just after calibration by the manufacturer (see Figure 22a/22b). The results show that the basic requirements for the calibration ability and reproducibility are not fulfilled for this type of instrument. Another drawback is that the instrument is not capable of dynamic measurements.



	Anzahl-K. [#/cm3]			Peak-Höhe [#/cm3]		
	SMPS 1	SMPS 2	Verh. 1 : 2	SMPS 1	SMPS 2	Verh. 1 : 2
Scan 1	3,30E+06	2,77E+06	1,19	4,92E+06	4,87E+06	1,01
Scan 2	3,13E+06	2,59E+06	1,21	4,48E+06	4,69E+06	0,96
Scan 3	3,06E+06	2,44E+06	1,25	4,60E+06	4,23E+06	1,09
Mittel	**3,16E+06**	**2,60E+06**	**1,22**	**4,67E+06**	**4,60E+06**	**1,02**

Figure 22a: Comparison of SMPS measurement instruments 1 and 2, SMPS1 (Model 3071/3025) and an SMPS2 (Model 3080/3010). SMPS2 was used just after calibration by the manufacturer. SMPS1 showed a median number diameter that was 14 nm larger (15% difference) and a higher total number of approx. 22%. (Source: See Annex 5.6, VW).



	Anzahl-K. [#/cm3]			Peak-Höhe [#/cm3]		
	SMPS 1	SMPS 3	Verh. 1 : 3	SMPS 1	SMPS 3	Verh. 1 : 3
Scan 1	2,099E+05	1,394E+05	1,51	3,108E+05	2,405E+05	1,29
Scan 2	2,166E+05	1,326E+05	1,63	3,083E+05	2,317E+05	1,33
Scan 3	2,181E+05	1,293E+05	1,69	3,157E+05	2,236E+05	1,41
Scan 4	2,165E+05	1,288E+05	1,68	3,060E+05	2,239E+05	1,37
Mittel	**2,153E+05**	**1,325E+05**	**1,62**	**3,102E+05**	**2,299E+05**	**1,35**

Figure 22b: Comparison of SMPS measurement instruments 1 and 3. , SMPS1 (Model 3071/3025) and SMPS3 (Model 3080/3010) showed that the total particulate number was considerably higher as compared to SMPS1 (62 %) and that the median number diameter even deviated in the opposing direction (-5 nm) compared to SMPS3. (Source: See Annex 5.6, VW):

The SMPS does not fulfil basic requirements for quantitative or reproducible measurements. It is not capable of dynamic measurements. Additionally, no absolute particle number calibration standard is available for system verification.

?? Condensation Particle Counter CPC

Metric: Particles enlarged by alcohol condensation counted by an optical single particle counter. [1 to 10^4 particles/cm^3].

Referring to section 2.1 subsection `Nucleation and artefact particle effects`; the CPC is potentially susceptible to large measurement artefacts. However, parallel PM and particle number measurements show (see Figure 23) that, in principle, particle number correlates with mass measurements when the above mentioned effects are avoided (nucleation, artificial particles). However, the gradient of the relationship can not be reproduced because of the dependency of the particle number and morphology on the measurement conditions.

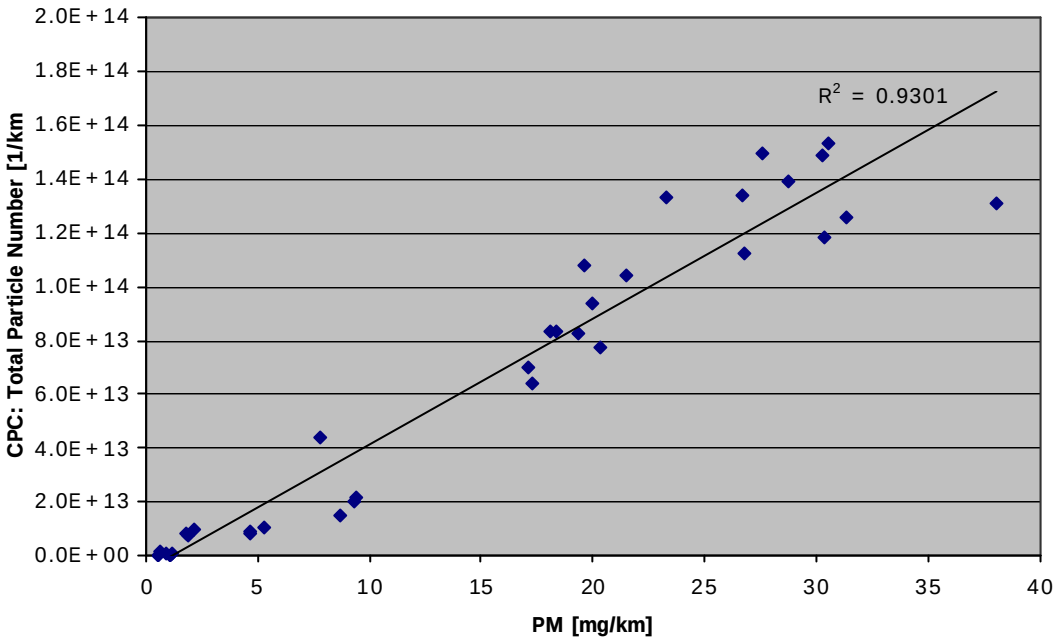


Figure 23: Correlation between CPC and PM measurements for a gasoline direct injection vehicle and a diesel vehicle in the NEDC transient cycle and at constant speeds of 50 km/h, 100 km/h and 120 km/h. The tests were conducted at a roller dyno test stand. For the CPC measurements, the sample was treated by using secondary dilution of 100 to 800 times with a rotating disc diluter after the CVS dilution tunnel. (Source: VW)

Compared with parallel PM measurements the CPC shows higher relative standard deviations at the same emission level as can be seen in Figure 24.

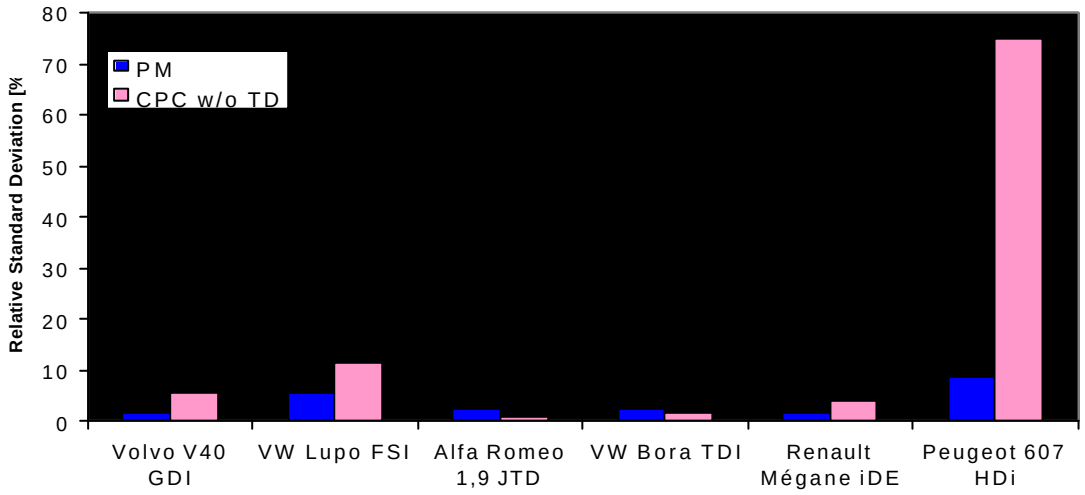


Figure 24: Comparison of relative standard deviation of parallel PM and CPC measurements in the NEDC driving cycle on a roller dyno. The CPC measurements were carried out by sampling out of the CVS tunnel and additional dilution by a factor of 10 with a ejector diluter.
At low particulate emission conditions, the CPC measurements are less reproducible than the PM measurements. (Source: ACEA Programme on the Emissions of Fine Particles from Passenger Cars [2], www.acea.be)

The CPC is very sensitive to nucleation effects. Due to the lack of size resolved information, these effects are not identifiable. The operation range is limited (variable high dilution needed) and the repeatability is low compared to state of the art PM mass methodology. Additionally, no absolute particle number calibration standard is available for system verification.

2.2.4 Particle mass metric

?? **Photo acoustic soot sensor – PASS**

?? **Laser induced Incandescence – LI²SA**

Metric of PASS: Photo acoustic response of soot particles stimulated by light absorption.

Metric of LI²SA: Incandescence of laser pulse-heated soot.

Time-resolved measurements of elemental carbon are feasible with the photo acoustic sensor as well as with the laser induced incandescence system. Neither technique is susceptible to nucleation particles. No cross interference of other exhaust gas components is exhibited.

Both systems reveal a very good correlation with PM mass. Figures 25, 26 and 27 show the correlation characteristics of the PASS and LI²SA measurements with the standard gravimetric method or thermogravimetric results (non volatile particulate mass on filter) respectively. As LI²SA, PASS and Coulometry are soot-specific measurement tools, they account for typically about 80 % of total gravimetric mass. Results from opacimetry and thermogravimetry are slightly higher and reach values around 90 %.

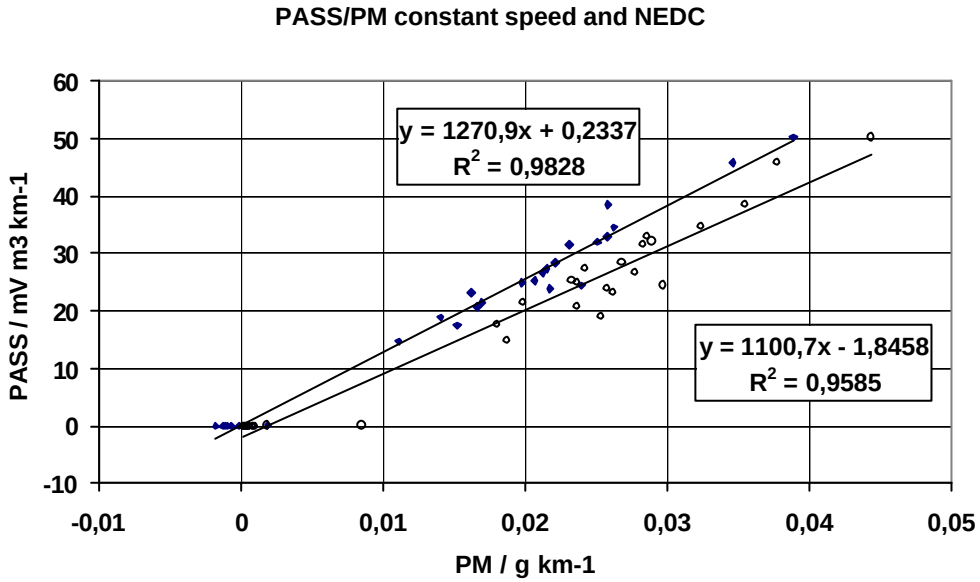


Figure 25: Correlation of integrated PASS signal and particulate mass (open circles) measured during constant speed tests and NEDC2000 for 1 diesel passenger car and 1 diesel passenger car equipped with a particle trap. The correlation is further improved (filled rhombus), if volatile organics and soluble inorganic material are subtracted from the measured PM mass. (Source See Annex 5.5, Ford)

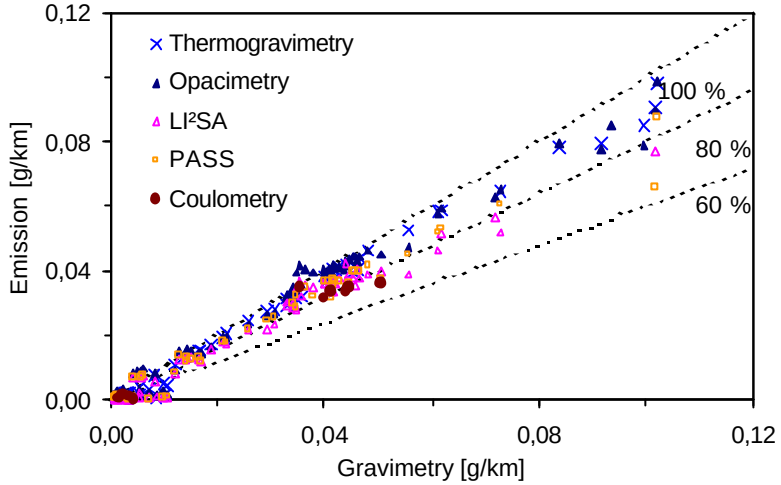


Figure 26: NEDC-Phase average concentrations of different mass-based measurement methods of different diesel and gasoline vehicles plotted over results from gravimetry. Opacimetry: Opacity across the CVS tunnel. Coulometry: Particle load of filters analysed by coulometry for total carbon mass. (Source: See Annex 5.4, DaimlerChrysler)

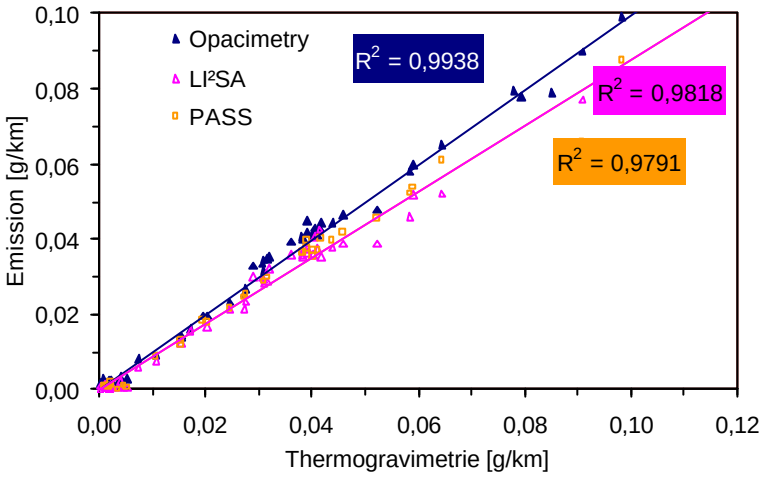


Figure 27: Correlation of mass calculated from opacity, LI²SA and PASS with thermogravimetric data of different diesel and gasoline vehicles in the NEDC (Source: See Annex 5.4, DaimlerChrysler)

At very low emission levels PASS and LI²SA show a reasonable correlation (see. Figure 28). These results confirm that PASS and LI²SA are sensitive enough also for the measurement of future emission levels.

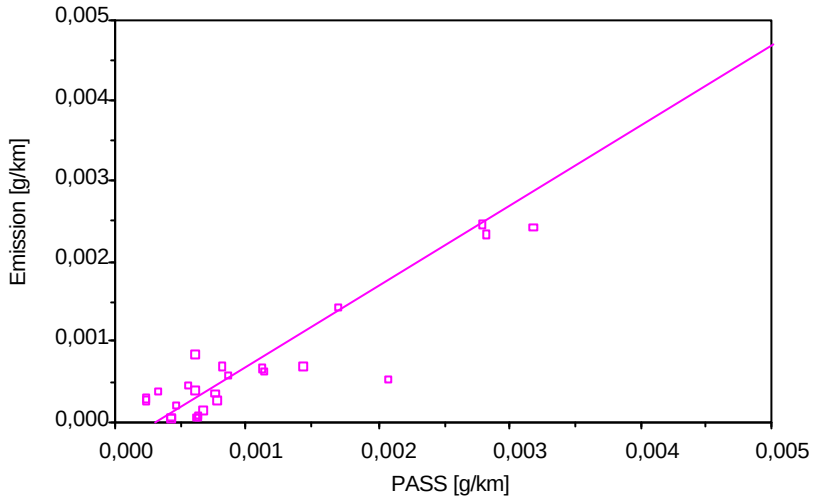


Figure 28: Correlation of LI²SA with PASS at low emission levels (Source: See Annex 5.4, DaimlerChrysler)

The time resolution of PASS and LI²SA (see Figure 29) is satisfactory – which makes these systems suitable for real time measurement purposes. The PASS offers a sampling rate in the order of 3 Hz, the LI²SA system featured a sampling rate of 0.5 Hz, (systems with a sampling rate in the order of 20 Hz are available), for the examined measurement set up used (sample extraction from CVS tunnel, with a delay time depending on length of sample line).

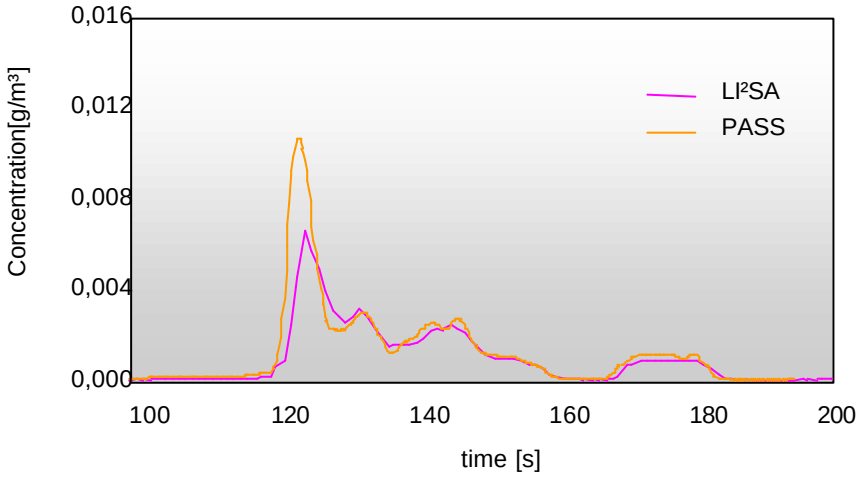


Figure 29: Comparison of time resolution (100 s section of an NEDC). (Source: See Annex 5.4, DaimlerChrysler)

The measurement techniques, PASS and LI²SA, for the determination of the mass emission of elemental carbon are characterised by the following:

- Significant correlation to gravimetrically determined solid particle emissions (regression coefficient = 0,98).
- Cross interference to other exhaust components (e.g. volatile nanoparticles) does not occur.
- With a time resolution of ? 5 Hz it is suitable for real time measurements.

Measurement of elemental carbon by PASS or LI²SA provides a sensitive and time-resolved measurement technique, which could in principle be absolutely calibrated by coulometry.

Additionally the LI²SA measurement technique offers the possibility to determine the primary particle diameter of the soot particles. As Figure 30 shows, this diameter is independent of particle concentration (and thus engine load) and combustion principle. For all vehicles investigated, the primary particle size was in the range of 25 – 35 nm.

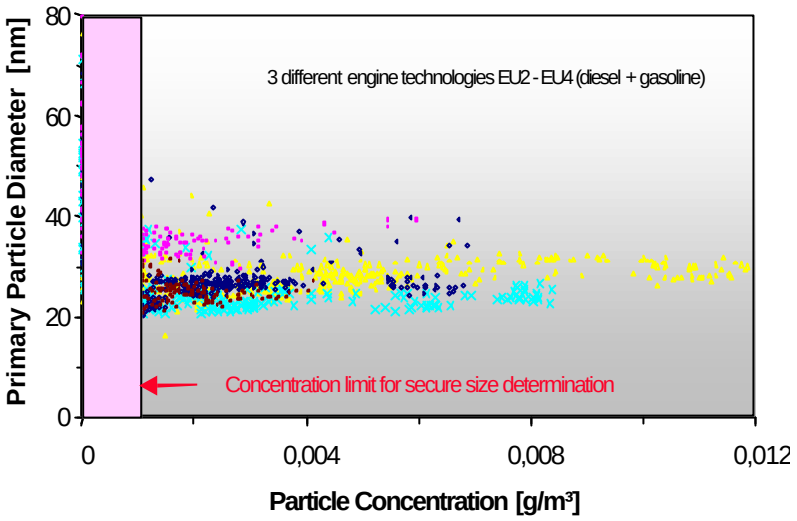


Figure 30: Primary particle size plotted over particle concentration for four different vehicles. The primary particle size is independent of particle concentration and combustion principle. (Source: See Annex 5.4, DC)

The measurement of primary particle diameter by LI²SA does not offer notable size differences, therefore the usefulness of this parameter is questionable.

?? Dekati Mass Monitor MasMo

The operation principle of the newly developed MasMo is based on particle charging, particle mobility measurement, the assumption of a unimodal symmetrical size distribution, particle size classification with inertial impaction (6 stages: 0-1.2 µm), and electrical detection of charged particles for real time measurement of particle mass.

The missing link to calculate the particle mass from size resolved aerosol measurements is the particle density. Dekati solved the problem by a combination of a ELPI and a simple SMPS. Comparing the aerodynamic diameter with particle mobility information should make it possible to calculate an average particle density.

VW tested a prototype version under different conditions. The data analysis reveals that for Diesel vehicle measurements the MasMo results correlate well with the gravimetric results. Gasoline and gasoline direct injection prototype vehicles results correlate well but show a significant discrepancy in the slope (see Figure 31). The reasons for this discrepancy is probably due to the limited ability to measure the correct particle density.

In addition a significant scattering in the MasMo result was observed which reveals that the MasMo does not achieve the reproducibility of the PM mass measurements.

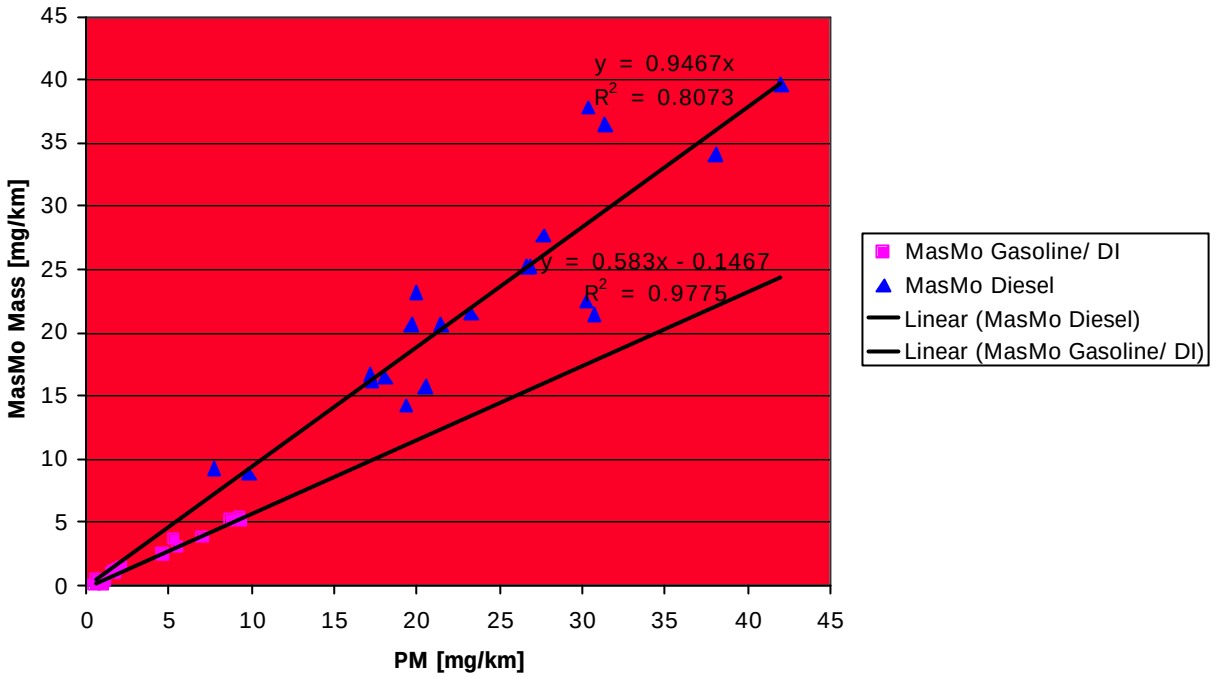


Figure 31: Correlation between MasMo and PM for Diesel, gasoline and gasoline direct injection vehicles in the NEDC transient cycle and at constant speeds of 50 km/h, 100 km/h and 120 km/h. The tests were conducted on a roller dyno test stand. For the MasMo measurements the sample was treated by using secondary dilution of 10 with a Dekati ejector diluter after the CVS dilution tunnel. (Source: VW)

The general applicability of the MasMo for regulatory engine exhaust measurements is questionable. In its current development status, it has low reproducibility compared to state of the art PM methodology. In addition, no absolute particle density calibration standard is available for system verification.

2.2.5 Instrumentation correlation assessment

A study was carried out to assess the correlation between several instruments of the same type simultaneously, using CAST and diesel exhaust as the particle source. This study included testing different types of instruments (DMA+CPC, ELPI, DC).

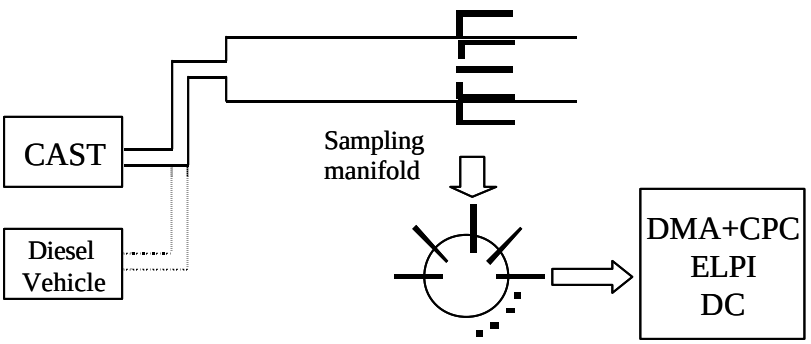


Figure 32: Correlation study test set-up (source: JAMA, annex 5.8)

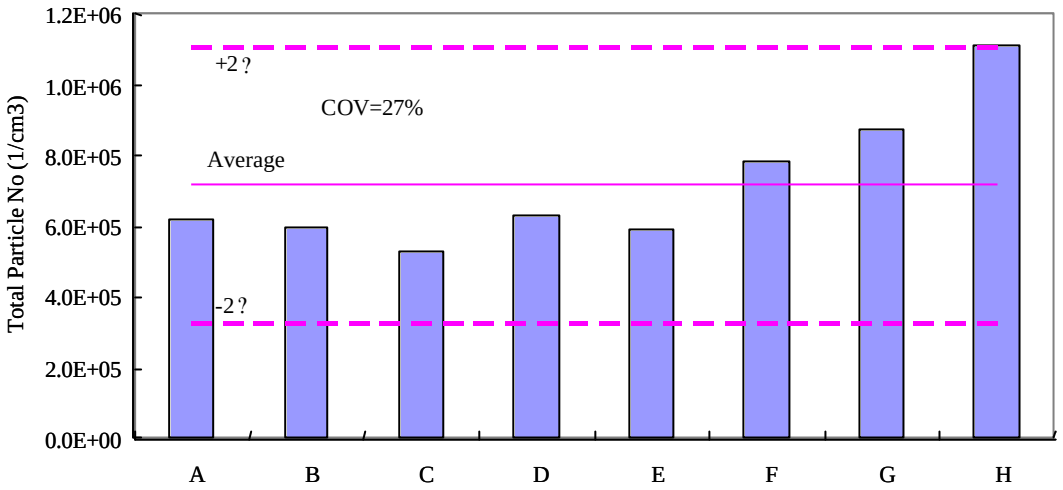


Figure 33a: Simultaneous measurements of total number of particles from CAST (CMD = 100 nm) using eight ELPIs. COV = Coefficient of variation (source: JAMA, annex 5.8)

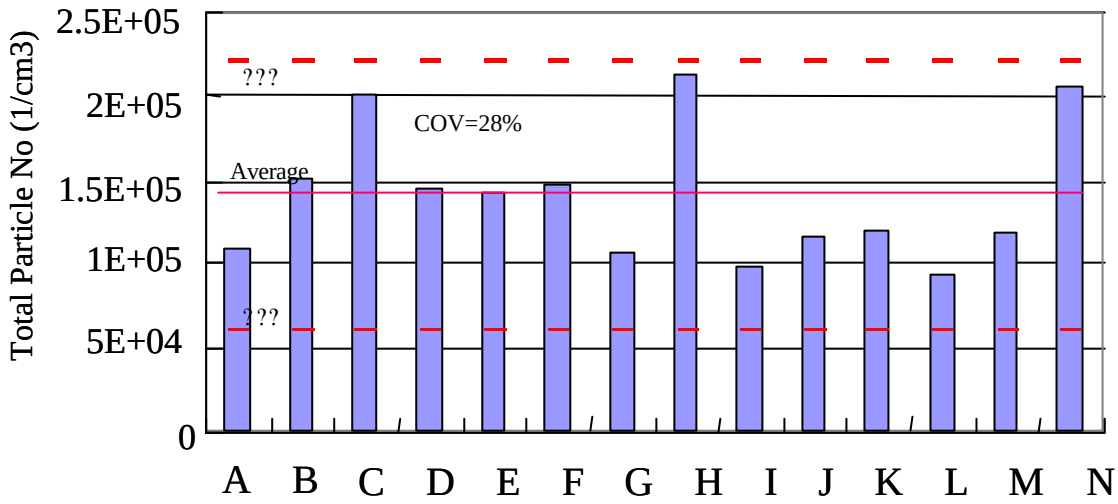


Figure 33b: Simultaneous measurements of total number of particles from CAST (CMD = 100 nm) using 14 DMA+CPCs. COV = Coefficient of variation (source: JAMA, annex 5.8)

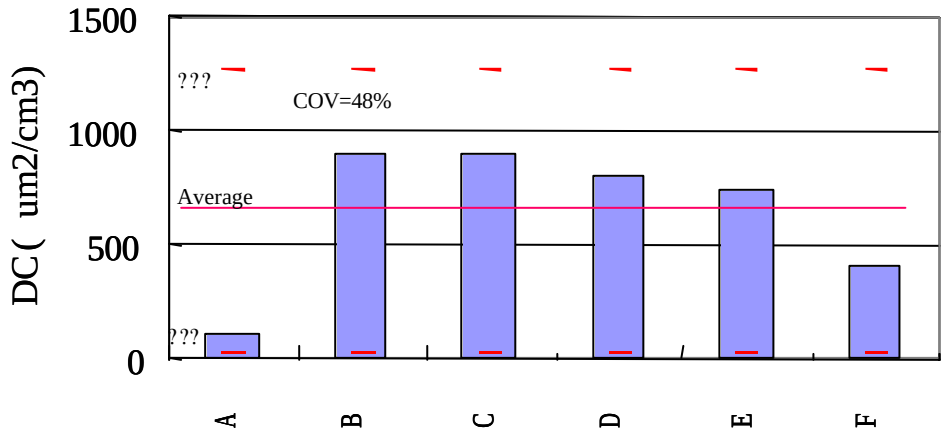


Figure 33c: Simultaneous measurements of total number of particles from CAST (CMD = 100 nm) using 6 DCs. COV = Coefficient of variation (source: JAMA, annex 5.8)

	CAST(1) MP3(100nm)	CAST(2) MP6(30nm)	Diesel Exhaust
ELPI Total Particle Number	27%	40%	23%
DMA+CPC Total Particle Number	28%	19%	27%
DC Total Surface Area	48%	48%	54%

Figure 34: Summary of correlation tests (COV) with different kinds of equipment for particle measurements (DMA+CPC, ELPI, DC) using CAST and diesel exhaust (source: JAMA, annex 5.8).

The variation between several instruments of the same type is very high even when they are simultaneously measuring the same particle source. Since a robust calibration method does not exist, these instruments are clearly not suitable for certification.

2.3 Evaluation of the gravimetric method

2.3.1 Light duty

The particulate gravimetric measurement method is described in EU regulation 70/220/EC. For the measurement of the particulate mass, a sample of the diluted exhaust gas (partial flow) is extracted from the dilution tunnel and drawn through a filter system.

The particulate mass is calculated knowing the mass of particulate on the filter, the partial flow volume and the total flow volume. The higher boiling point hydrocarbons and sulphur compounds are also deposited on the filter. As a result of the reduction in hydrocarbon emissions and the use of fuels with a low sulphur content, the proportion of those components which can influence the particulate measurement is reduced.

The detection limit of the current standard gravimetric procedure for light duty vehicles was examined by DaimlerChrysler, BMW and Volkswagen.

In order to determine the limit of detection of the entire process (weighing, filter handling, loading, weighing) NEDC-blank tests (tests without vehicle) were performed by DaimlerChrysler (see Figure 35). As a result, the LOD (3 * ?) is estimated to be 0.025 mg. This is equivalent to approximately 1 mg/km in an NEDC which is 4 % of the Euro-IV emission limit. By further optimization steps of the gravimetric method (e.g. optimized flow, micro balance with increased accuracy) it will be possible to decrease the LOD to approximately 0.01 mg filter loading.

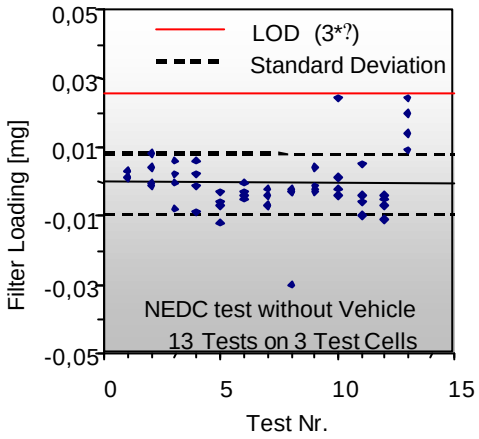


Figure 35: Determination of LOD of gravimetric method by blank tests. The difference in weighing before and after test is shown for NEDC tests without a vehicle. The zero scatter (standard deviation ?) is +/- 0,008 mg. Therefore, the LOD (3 * ?) is estimated to be 0,025 mg filter loading (source: see annex 5.4, DaimlerChrysler).

To estimate the lower limit of the gravimetric mass measurement, BMW also carried out NEDC blank-tests. The results are shown in Figure 36.

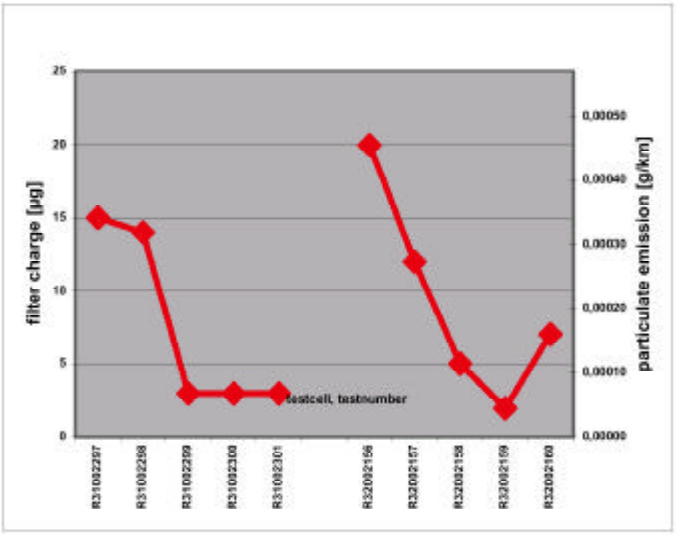


Figure 36: Results of blank-tests on two chassis dynos. Instead of sampling the vehicle exhaust, the air of the test-cell was sampled during a NEDC test. (Source: See Annex 5.2, BMW)

Five NEDC blank tests were made in succession on each of two chassis dynos. The results show that the mass emission appears to decrease with increasing test number. It was assumed that particles are removed from the surface of the sampling system and in time this “particle-source” decreases.

The mean value of all 10 tests is 0.0002 g/km with a standard deviation of 0.00015 g/km. One contribution to this relatively high standard deviation is from the decreasing “particle-source”. Compared with the Euro-IV limit of 0.025 g/km this standard deviation of 0.00015 g/km is less than 1% of that limit value. Tests with very low emission vehicles had smaller standard deviations of about 0.0001 g/km.

Volkswagen investigated the detection limit of the particle measurement procedure by conducting NEDC blank tests and additionally NEDC test with vehicles with a particulate emission level less than 0,010 g/km. As DaimlerChrysler and BMW did, the determination of the “detection limit” of the complete measurement sequence was carried out without using a vehicle, but sucking ambient air into the CVS system. As shown in Figure 37, the “background emissions” value was below 0.001 g/km. The

corresponding mean filter loading during the determination of the background value was 0,02 mg. This is considerably lower than the filter loading of at least 1 mg recommended in the European regulation.

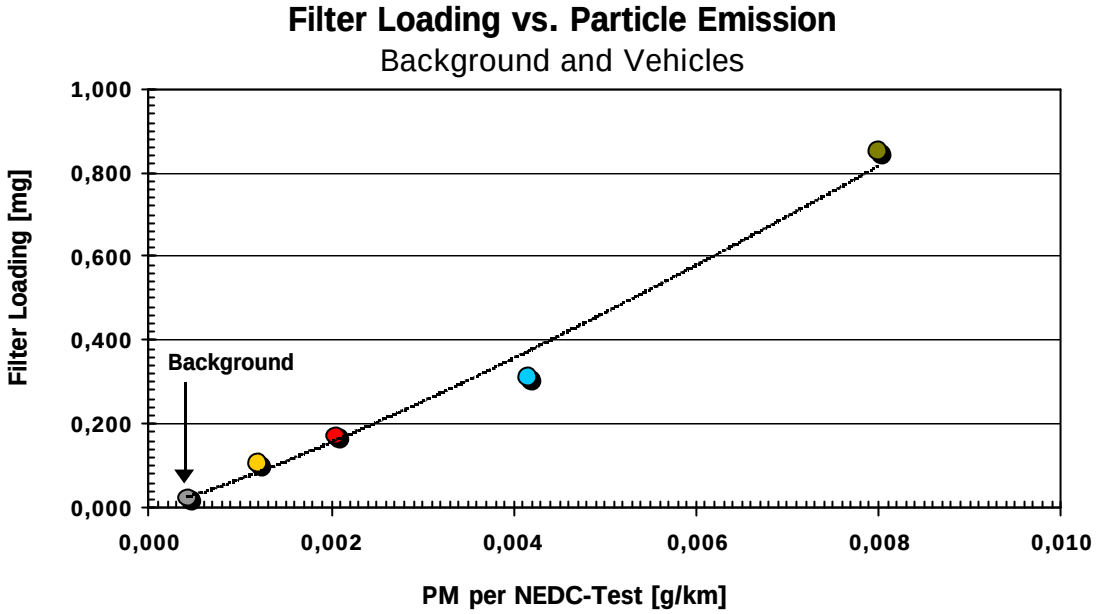


Figure 37: Lower practical limit of the gravimetric measurement procedure. For the determination of the "detection limit" of the complete measurement sequence, NEDC blank tests were performed sucking ambient air into the CVS system. The "tunnel background" value was below 0.001 g/km. The other measurement points show the mean filter loading of the vehicle in the new European Driving Cycle (NEDC). Each measurement point represents a mean value of 3 – 25 measurements. (Source: Annex 5.6, VW)

The measurement sequence with the four vehicles demonstrates a slight scattering of the measurement values (see Figure 38). Their absolute standard deviation can be compared with the standard deviation of the background emissions although the measurement chain has been extended by the parameters chassis dyno, vehicle and driver. The results show clearly that the accuracy of the particulate measurement technique is much better than can be assumed on the basis of the current regulations.

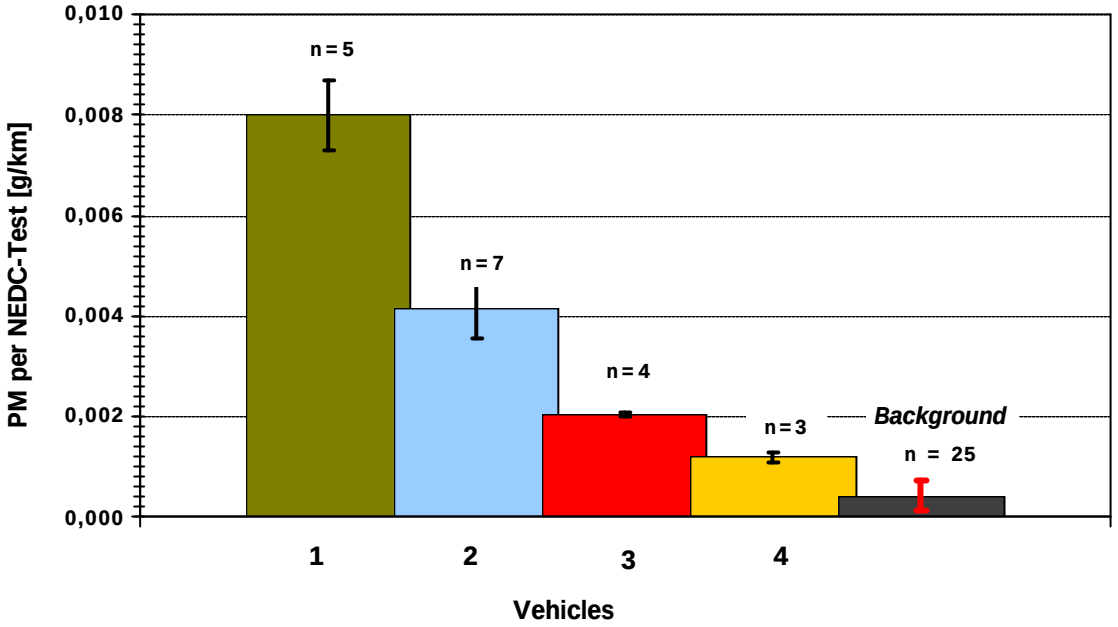


Figure 38: It describes the average particulate emissions in g/km and the standard deviation of four vehicles and the tunnel background measurement. The emissions of 0,0004 g/km (= 0,02 mg filter loading) could be measured with a standard deviation of 0,0003 g/km. This gives a relative standard deviation of approx. 75%. Based on the Euro IV limit of 0,025 g/km, this corresponds with a deviation of the measurement results of less than 2 % for the sampling system including the determination of the volumes and weighting of the filters. The relative standard deviation of the vehicles is between 5 % and 9 %. (Source: See Annex 5.6, VW)

In summary, it can be seen that the gravimetric particulate measurement is a calibratable particulate measurement technique. The boundaries of the particulate measurement process have not yet been reached and further optimisation is possible. Examples include, but are not limited to: determination of stricter tolerances, reduction of the minimum filter loading, sampling only on one filter and conditioning of the dilution air (synthetic…

The standard gravimetric procedure reveals the potential for particulate emission measurements also beyond Euro 4 regarding accuracy and the limit of detection. Optimization possibilities exist for further improvements.

2.3.2 Heavy duty

For heavy-duty engines, the gravimetric method is described in Directive 1999/96/EC and in the US Federal Register Part 86, Subpart N. The measurement principle is identical to the light duty procedure with some minor differences in the details. Those are mainly the widespread use of 70 mm diameter filters and the double dilution system, in which the PM sample from the primary dilution tunnel is diluted once again. The Euro 4 limit values are 0.02 g/kWh and 0.03 g/kWh on the ESC and ETC test cycle, respectively.

PM measurement variability is influenced by two major factors

- PM calculation by the tolerances of the relevant measuring instruments
- PM composition by the sampling conditions and the dilution process

??**PM calculation**

The final PM result of g/kWh is calculated from the differential weighing before and after test, the CVS (or exhaust) flow, the sample flow, and the engine power. The Directive specifies the tolerances of the respective measuring instruments. Figure 39 summarizes the allowable tolerances in comparison to results from round robin testing. It should be noted that the weighing tolerance refers to the tolerance of reference filter weighing rather then to the capability of the balance. The error of a 1 µg balance would be as low as 0.8 % at a 0.25 mg filter loading.

ESC		
Measured Value	Error	Remarks
Particle weight (mg)	? 3.9 %	Based on 2.5 mg particulate weight
Diluted exhaust flow (kg/h)	? 4.0 %	Max. error allowed
Sample flow (kg)	? 2.0 %	
Engine power (kW)	? 2.0 %	Max. allowed error is ? 3.6 %
PM (g/h)	? 5.9 %	average total error (RMS method)
PM (g/kWh)	? 6.3 %	
PM (g/kWh)	4.7 % - 15.8 %	COV range on ACEA round robin
ETC		
Measured Value	Error	Remarks
Particle weight (mg)	? 4.2 %	Based on separate weighing
CVS flow (kg)	? 2.0 %	Max. error allowed
Sample flow (kg)	? 4.9 %	Based on double dilution
Engine cycle work (kWh)	? 2.0 %	
PM (g/Test)	? 6.8 %	average total error (RMS method)
PM (g/kWh)	? 7.0 %	
PM (g/kWh)	3.8 % - 12.0 %	COV range on ACEA round robin

Figure 39: Comparison of theoretical vs. observed measurement variability (Source: ISO TC 22/SC5 engine tests)

The calculated average total error should in principal be representative of the test repeatability of a given lab, expressed as the coefficient of variation (COV = STD/AVE). This has been confirmed by the ACEA round robin, although some labs had significantly worse repeatabilities. Therefore, it can be concluded that test repeatability can be improved if the measurement tolerances of the legislation are tightened.

USEPA in their MY 2007 rules and ISO 16183 haven already taken steps to reduce the tolerances. The potential improvement of measurement variability is shown in Figure 40. Compared to the Directive 1999/96, the EPA procedure is expected to halve the variability. Figure 40 also shows the good agreement between theoretical measurement error and test repeatability (COV) at around 5 %, as found on the ISO correlation study for a typical Euro 3 engine, and thus confirms the results of the ACEA round robin indicated in Figure 39.

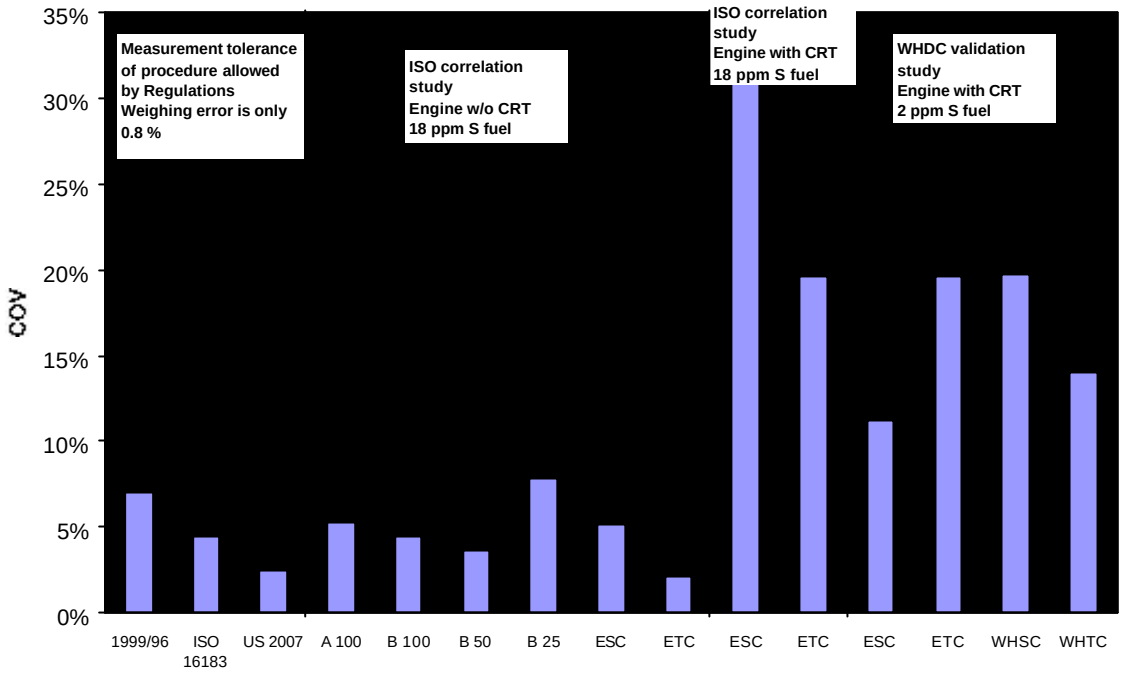


Figure 40: Relative PM measurement variability for heavy-duty engines (Source: ISO TC 22/SC5 engine tests)

Test repeatability significantly increases to values between 20% and 30% when the engine is equipped with a particulate trap and operated on a fuel with 18 ppm sulfur content. However, the major reason for this deterioration is not related to the measurement equipment or the low PM values of a trap-equipped engine, but to changes in the PM composition, as outlined in more detail, below. An improvement of the repeatability has been achieved when further reducing the sulfur level to approximately zero.

?? **PM composition**

PM mainly consists of elemental carbon (EC, soot), the volatile organic fraction (VOF) adsorbed onto the soot, and sulfate. Whereas EC is not affected by the dilution process and only slightly affected by the sampling conditions, both VOF and sulfate are very sensitive to dilution and sampling.

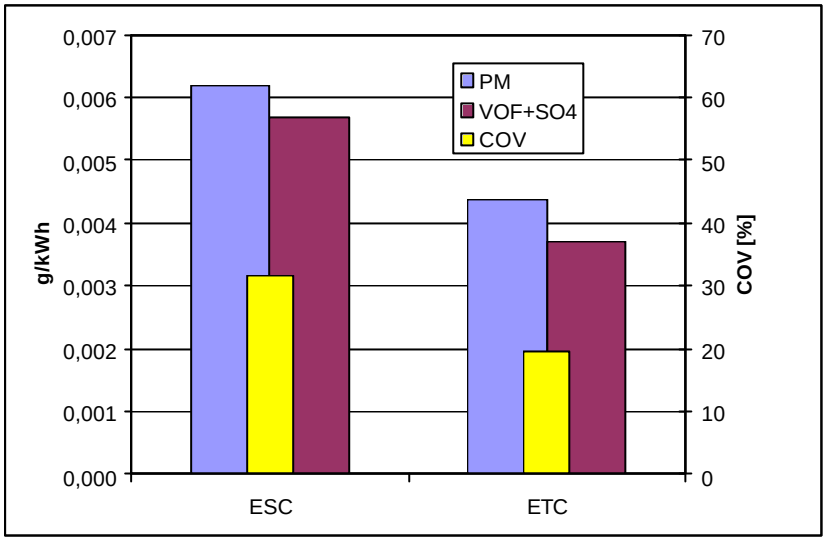


Figure 41: Influence of PM composition on measurement variability for an engine with particulate trap (Source: ISO TC 22/SC5 engine tests).

Figure 41 shows the influence of the PM composition on the measurement variability shown in Figure 40 for the trap-equipped engine running with 18 ppm sulfur fuel. It demonstrates that the measurement variability (COV) deteriorates significantly, if sulfate and VOF levels are high and the predominant portion of total PM. Although on both ESC and ETC test cycles the VOF/Sulfate fraction of the total PM is about the same (92% vs. 85%), the COV is more affected by the absolute level, which is 54% higher for the ESC.

As a conclusion, the measurement variability caused by PM composition is related to the PM definition rather than to the gravimetric procedure and will likely occur with any other PM measurement method, as demonstrated in this report. Sulfate formation is a problem specific to exhaust aftertreatment systems with oxidation catalysts. In such a case, high PM variability can only be avoided if sulfur free fuel is used.

??Potential of the gravimetric PM measurement

The potential of the gravimetric method is shown in Figure 42, as derived from the ISO correlation and the WHDC validation studies. Overall, the measured standard deviation (STD) varied between 0.001 and 0.002 g/kWh. With the improvements introduced by US 2007 rules and ISO 16183, the STD can be cut down to 0.001 g/kWh even at very low PM levels, whereby the weighing procedure itself is better by one order of magnitude (0.0001 g/kWh). Such low number is hardly achievable by any other instrument available, today.

For most test laboratories, a STD of 10 % is acceptable at Euro 4 and US 2007 PM levels, although the target value is preferred to be 5 %. Under those assumptions, PM measurement with 10 % accuracy is possible down to a PM level of 0.01 g/kWh. Further improvements towards the 5 % target value are feasible, if the engine is operated with virtually sulfur-free fuel (less than 5 ppm).

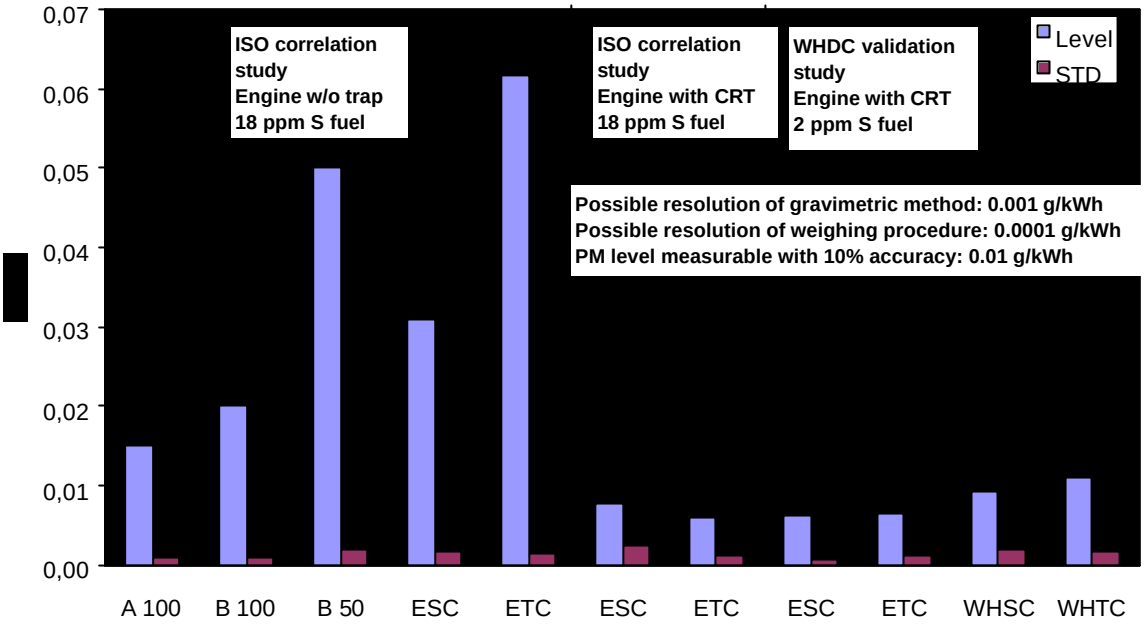


Fig. 42: Potential of gravimetric PM measurement method for heavy-duty engines (Source: ISO TC 22/SC5 engine tests)

PM measurement is possible down to a level of 0.01 g/kWh with a 10 % measurement error, which is acceptable to most test labs. Further improvements are feasible, if sulfur free fuel can be used. Taking into account this potential of the current type approval method, it should be retained for the future.

3 Discussion

The potential of a measurement instrument for certification testing can be evaluated by comparing it with the following requirements.

TABLE 1
Minimum requirements for the instrument incl. sampling system for measurement of particulate mass, number and surface area

	Mass	Number	Surface
Measurement Capability	10% of regulatory limit value	10% of CVS dilution air background	Unknown
Calibration checkable on site	yes		
Repeatability	10* % of regulatory limit value		
Reproducibility	20* % of regulatory limit value*		
Time resolution	Integral individual phases of the test cycle		

*Value considers light duty and heavy duty requirements

Mass measurement instrumentation evaluation

nstrument	Practical	Repeatability	Reproduci-	Time	Calibration

	limit		bility	resolution	checkable on site
Pass	Yes, but only EC	Yes	Yes	Yes	Yes, indirectly
LI²SA	Yes, but only EC	Yes	Yes	Yes	Yes, indirectly
MasMo	Yes	limited	limited	Yes	No
Gravimetry	Yes	Yes	Yes	Yes	Yes

Number measurement instrumentation evaluation

nstrument	Practical limit	Repeatability	Reproduci-bility	Time resolution	Calibration checkable on site
CPC	Yes	Yes	No	Yes	No
ELPI	Yes	Yes	No	Yes	No
SMPS	Yes	No	No	No	No

Surface measurement instrumentation evaluation

nstrument	Practical limit	Repeatability	Reproduci-bility	Time resolution	Calibration checkable on site
OC	unclear	No	No	Yes	No
Pas 2000	unclear	No	No	Yes	No

The analysis shows that only the gravimetric method completely fulfils the measurement requirements. The other mass-based methods may have the potential to fulfil the Table 1 requirements.

4 Conclusions

Influences of engine, fuel and measurement and sampling conditions on aerosol measurements

?? ***A new PM measurement metric which is sensitive to nucleation particles is potentially susceptible to large measurement artefacts and should therefore NOT be considered further.***

?? ***A combination of thermodenuder with size-unresolved total particle count cannot give valid data, because of size-dependent particle losses, and likely chemical species dependency on denuder efficiency.***

?? ***Because of the many parameters that must be kept constant and verified by regular calibration, in principal a thermodenuder is not suitable for regulatory measurements.***

?? ***A measurement metric based on 'solid' particle number is problematic because of the influence of aerosol dynamics on the measured value.***

?? ***Engine load and fuel dependent particle morphology changes can lead to unpredictable aerosol measurement effects. Examples include aerodynamic and mobility aerosol behaviour. Metrics influenced by this type of effect are neither reliable nor repeatable.***

- ***With a test procedure of practical relevance, no correlation between particle size and injection pressure of a modern, direct injection diesel engine was identified. As particles are formed in the gas phase, their size is not related to the droplet size in the diesel spray or to the injection pressure. Size resolved particle measurement gives no additional information and can therefore be replaced by mass measurements.***

Instrumentation related investigation results

- ***The particles generated by CAST show a stable average diameter (CMD), but a trend towards decreasing number concentration with time. It appears to be unsuitable as a calibration aid.***

- ***Measurements with the LQ1-DC in the particle range less than 70 nm are not plausible. The observed ageing effects make the general suitability of a corona charger questionable. Humidity and variation of the inner electrical insulation caused by deposited particles give a poor stability of the measurement signal. Additionally, no absolute particle surface calibration standard is available for system verification.***

- ***It is observed that the PAS 2000, in principal, is not capable of performing particle surface or mass measurements in exhaust gas from internal combustion engines with reliable and quantitative results. Additionally, no absolute calibration standard is available for system verification.***

- ***The reproducibility and comparability of ELPI measurements is limited unless a demanding maintenance/operation protocol is strictly observed. The ELPI is not suitable for performing regulatory measurements. Additionally, no absolute particle number calibration standard is available for system verification.***

- ***The SMPS does not fulfil basic requirements for quantitative or reproducible measurements. It is not capable of dynamic measurements. Additionally, no absolute particle number calibration standard is available for system verification*.**

- ***The CPC is very sensitive to nucleation effects. Due to the lack of size resolved information, these effects are not identifiable. The operation range is limited (variable high dilution needed) and the repeatability is low compared to state of the art PM mass methodology. Additionally, no absolute particle number calibration standard is available for system verification.***

- ***Measurement of elemental carbon by PASS or LII provides a sensitive and time-resolved measurement technique, which could in principle be absolutely calibrated by coulometry.***

- ***The measurement of primary particle diameter by LI²SA does not offer notable size differences, therefore the usefulness of this parameter is questionable.***

- ***The general applicability of the MasMo for regulatory engine exhaust measurements is questionable. In its current development status, it has low reproducibility compared to state of the art PM methodology. In addition, no absolute particle density calibration standard is available for system verification.***

- ***The variation between several instruments (DMA+CPC, ELPI, DC) of the same type is very high even when they are simultaneously measuring the same particle source. Since a robust calibration method does not exist, these instruments are clearly not suitable for certification.***

- ***For light duty vehicles the standard gravimetric procedure reveals the potential for particulate emission measurements also beyond Euro 4 regarding accuracy and the limit of detection. Optimization possibilities exist for further improvements.***

- ***For heavy duty engines the PM measurement is possible down to a level of 0.01 g/kWh with a tolerable 10 % measurement error. Further improvements are feasible, if sulfur free fuel can be used. Taking into account this potential of the current type approval method, it should be retained for the future.***

The new measurement instruments can, as yet, only be used for the qualitative assessment of particulate number and size distribution as a relative comparison. They are still far from achieving the absolute quantitative measurement of these parameters. The measured particle number and size distribution can be manipulated with a careful choice of test conditions. Any new particulate measurement methodology should fulfil the same quality criteria as the current gravimetric method. Based on the above assessment, gravimetric measurement is considered to have the highest potential for future development. Other mass-based methods may have the potential to fulfil these requirements.

Industry comments on proposed particulate measurement techniques

OICA contribution to PMP

Part 2: Technical Annex

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OICA contribution to PMP - Part 2

5 Technical Annex

5.1 Abgaszentrum der Automobilindustrie (ADA)

5.2 BMW

5.3 BOSCH

5.4 DaimlerChrysler

5.5 Ford

5.6 Volkswagen

5.7 Renault

5.8 JAMA

ABGASZENTRUM DER AUTOMOBILINDUSTRIE

Assessment of Particle Measurement Methods

Contents

1 Project Description

Within the context of the continuing uncertainties about possible health-related parameters of particle emissions from engine combustion [1], discussion continues about the extension to the definition of the limits. In addition, new particle measurement methods, which ought to be able make statements on certain particle sizes possible, are increasingly forcing their way onto the market. Apart from determining the mass by a gravimetric measurement method, additional information is to be so obtained on particle size or surface area.

For the corresponding measured variables, there are measurement methods on the market or in development that can be used as laboratory instruments and for immission measurement.

It is the task of the ADA project to assess these methods in terms of their implementation and suitability in determining the measured variables in the exhaust gas of internal combustion engines. Still to be cleared up are the relevant measurement boundary conditions that can influence the measurement result. For the overall assessment, the correlations between the individual measurement methods and the gravimetric method are to be reviewed. The aim is the derivation of a standard procedure that is then suitable for the determination of particle emissions in the exhaust gas of internal combustion engines, both on engine test bench and chassis dynamometer test bench. To guarantee a secure and reproducible measurement operation, a suitable calibration procedure is an absolute precondition for test stand operation.

All investigations carried out up to now within the project refer to a current automobile diesel engine with common rail injection (EU III exhaust gas standard) that is run on a stationary engine test bench.

The particle measurement methods used in the project are listed in Table 1.1.

As hardly any of these measurement methods can be used in undiluted engine exhaust gas, systems for the dilution of raw exhaust gas are necessary.

The dilution systems used in the project are listed in Table 1.2.

These dilution systems cannot be combined with all particle measurement methods as the volumetric flow necessary in each particular case is device-specific. A comparison of dilution systems using one selected particle measurement method is therefore only possible within certain restrictions.

2 The Complexity of Aerosol Measurement

2.1 Basic Considerations

As fundamental difference between gravimetric particle mass determination and measurement of the parameters: particle number, particle size or surface area; individual particles are measured using the latter of these two methods.

These particles in engine exhaust gas are in principle undefined in terms of their phase – liquid or solid particles can occur; particles with mixed properties (e.g. a solid core surrounded by a liquid phase) are also possible.

These particles are spatially distributed within the gas surrounding them – an aerosol is the result. Having to measure in diluted exhaust gas can give rise to problems with disturbances. Components of the dilution air can increase the total number of particles and make the demarcation between them and the particles produced by the combustion more difficult. Processes of change caused by external influences are taking place all the time in the aerosol. Coagulation, agglomeration and condensation take place as a function of temperature, air humidity and particle concentration. The number and the morphology of the particles are especially influenced by these factors. Systems for exhaust gas dilution must be in a position to stabilize these processes – in the ideal case, to avoid them completely. At the very least, precise knowledge must be available concerning changes in the aerosol along the path from the sampling point in the exhaust gas to the measuring instrument. These changes must be quantifiable in order to guarantee the comparison of measurements from different test stands.

A comparison is only possible when the boundary conditions that prevailed during the measurement are precisely stated and adhered to. A standardization of these conditions is an urgent necessity.

Even when the aspects listed here are guaranteed, an aerosol measurement can only represent a momentary snapshot.

2.2 Influence of the Sampling Line

The transport of the measurement gas from the sampling point (e.g. in the exhaust gas equipment) to the dilution system requires a sampling line.

Stainless steel sampling lines of various lengths are used one after the other on the stationary engine test stand. The particle measurement is carried out with SMPS at a constant engine operating point and with lines heated to 120°C.

The given length of the line (0.3 or 1.7 meters) is the distance between the sampling point close to the engine (exhaust probe ahead of the catalytic converter) and the inlet to the dilution system NanoMet Md19-2E. This then constitutes the transport path of the undiluted exhaust gas.

In addition, the state of the 1.7-meter line is varied in that a new line is compared with a line that has been used for measurement over several days of test operation:

With a constant measurement gas sampling rate (SMPS 0.3 liter/min), different residence times of the undiluted measurement gas result from the various lengths of the line (for 0.3 meter: 1.7 sec. and for 1.7 meters: 9.6 secs.). Processes of change within the aerosol (see Sect. 2.1) and interactions with the wall of the line (e.g. deposition of particles due to thermophoresis) can have a correspondingly greater effect for longer sample lines.

The measurement results for number size distribution (NSD) with SMPS are shown in Fig. 2.1. The parameters of the NSD measured with the short sample line (0.3 meter) are well reproducible over the measurement period of 88 minutes. Mean particle diameter (arithmetic mean) and total number of particles remain approximately constant.

With the new, long sample line (1.7 meters), the parameters of the NSD change with increasing measurement period. The mean particle diameter shows a slightly falling tendency, whilst the total number of particles rises. Even after 110 minutes, the values have still not leveled out. The total number of particles measured using the short line is not reached by far.

With a long, used sampling line (1.7 meters) that has been used for measurements over a period of days, there is a similar trend over the measurement period.

The changes in NSD with time are, however, somewhat "softened" compared with the new line. Also here, even after 115 minutes testing, the total number of particles measured using the short line is not reached; the mean particle diameter is, however, relatively constant.

These differences can be explained by the storage and release effects in interaction with the wall of the line. Deposition or agglomeration of particles causes correspondingly more particles to "disappear" in the long line.

This test has shown the need for a sampling line to be as short as possible for the undiluted aerosol. In addition, a new or cleaned line has to be first conditioned in the exhaust gas.

These results have consequences for the transfer lines used in vehicle measurements with which the undiluted tail pipe emission is led to the CVS system. The heated lines have a length of 3 to 6 meters in common. Because of the changing exhaust gas volumetric flows during the drive cycle, the residence time of the exhaust gas in the line also varies. In addition, the cleaning or replacement of the lines must be taken into account when measuring.

2.3 Influence of the Boundary Conditions

An enhanced nanoparticle concentration can arise under certain conditions, depending on the type of sampling and dilution process used.

It still has to be clarified how the magnitude of the nanoparticle mode in the NSD (here during the SMPS measurement) can be influenced by the type of boundary condition.

To understand these processes, a NSD measurement of the ambient air is carried out on the engine test bench using SMPS. The measurement set-up is shown in Fig. 2.2. A part of the exhaust gas flow from the engine can freely exit from the open sampling point. There is no dilution system, the exhaust gas is spontaneously diluted and simultaneously cooled during the outflow into the surrounding air. The resulting dilution factor of around 10,000 can be estimated from the number of particles in the agglomeration mode.

Nanoparticles can be created by condensation when the pressure falls below the saturation value for volatile components in the exhaust gas.

The NSD measurement of the exhaust gas-enriched ambient air using SMPS takes place at about 1.4 meters from the open sampling point.

Fuel (sulfur content), engine operating point (exhaust gas temperature) and oxidation catalytic converter activity are varied during the test series in order to influence the effect.

The fuels used are standard commercial diesel from the filling station and Greenergy (see specifications in Table 2.1).

Firstly, using standard commercial diesel fuel and positioning the sampling after the catalytic converter, the engine torque is raised from 40 Nm to 140 Nm at 2000 rpm (see Fig. 2.3). The water content of the exhaust gas and the catalyst temperature (from 220°C to 360°C) rise correspondingly.

At 40 Nm, the NSD measurement shows no nanoparticles in the ambient air. At 80 Nm, a small nanoparticle mode forms with a mean particle diameter of < 10 nm.

With further increases in load, a steeper rise in the number of nanoparticles results with an increase in the mean particle diameter from approximately 10 nm to 20 nm.
To estimate the character of the nanoparticle, measurements are carried out with a DMA setting of 15 nm for electrical mobility diameter. For this, a sample filter is placed between DMA and CPC to yield monodisperse (= one size class) particles. Subsequently the particles are analyzed in a transmission electron microscope (TEM). The copper grid filter used is covered with a carbon film which is also suitable for separating off particles in this size range. A CPC comparison measurement, with and without filter, gives correspondingly large differences in the number of particles.

The optical analysis of the TEM samples from the fresh air supplied to engine test bench and of the sample from the air mixture containing elements of exhaust gas shows no differences (see Fig. 2.4).

In both cases, the number of the particles separated onto the filter is very small. The very large difference in the number of particles as measured by SMPS (see Fig. 2.5) is not found here.

The comparison of SMPS and TEM results leads to the supposition that in the case of the SMPS-measured nanoparticles it must be a matter of liquid components, e.g. condensates (water, hydrocarbons) or sulfates. The SMPS measurement method cannot differentiate between solid and liquid particles whilst the TEM can only depict solid particles (TEM measurements are made in high vacuum).

A repetition of these tests (sampling point downstream of the catalytic converter, increasing engine load) with Greenergy show (see Fig. 2.6) no nanoparticle formation at low engine loads (up to 100 Nm). Only above this level is there a small nanoparticle mode at a mean particle diameter of < 10 nm. The number of particles measured with standard commercial diesel fuel is not reached by far.

To determine the effect of catalyst activity, measurements with the sampling point placed ahead of and behind the catalytic converter are compared. This is carried out separately in turn for each fuel. Firstly, the engine operating point is selected: 2000 rpm, 120 Nm (catalytic converter temperature relatively high at 340°C, above light off).

The comparison (Fig. 2.7) shows that the formation of nanoparticles with standard commercial diesel fuel only takes place downstream of the catalytic converter, the NSD ahead of the converter is more or less identical for the two fuels. With the selection of an engine operating point at very low load (Fig. 2.8): 1430 rpm, 35 Nm, catalytic converter temperature 165°C, below light-off), the NSDs are essentially the same, regardless of the fuel used or the position of the sampling point.

As an overall result, the following conclusions can be drawn:

- The formation of nanoparticles only takes place after having left the exhaust gas equipment. Decisive here is the temperature gradient with time ($\Delta T/\Delta t$) during cooling.
- This process is furthered by a high engine load (high exhaust gas temperature),

  high catalytic converter activity and high sulfur content of the fuel.
- The nanoparticles formed under these conditions are not of a solid nature.

2.4 Requirements for a Suitable Method for Type Approval

An aerosol measurement, i.e. an assessment of individual particles, is a complex process in which the measurement result depends on many boundary conditions.

Even when the actual measurement process can be successfully stabilized, the problems of the necessity to take a sample and to dilute always remain.

Possible changes in the NSD via the sampling point and dilution system during the aerosol measurement must be quantifiable under all circumstances; especially a suitable measuring process for vehicle type approval with the necessity for reproducible absolute measured values.

If this does not succeed then, as a consequence, you have to measure without a sampling and dilution system. Only a direct measurement in undiluted exhaust gas can then lead to a conclusion.

This results in a set of requirements for a method that is specially suited to type approval:

- No dilution necessary
- No sampling necessary => direct measurement in the exhaust gas
- Calibration possible on the test stand

3 Assessment of Individual Measurement Methods

3.1 DEKATI Electrical Low Pressure Impactor ELPI Method

The ELPI method is based on the impactor principle in which the particles are sorted, according to their aerodynamic diameter, into 12 size-classes and are separated on the impactor plates. The impactor stages are so arranged that the largest particles are separated off in the uppermost stages and the smallest in the lowest stages. The gas flow is therefore accelerated from stage to stage because of the narrowing gap.

The counting of the previously electrically charged particles takes place at each stage by means of an electrometer. The particles remain on the impactor plates after their detection.

The total number of collected particles is displayed by the device as "Total estimated particle mass load in %" as the sum of all discharge currents. Depending on this impactor load value, the device must be cleaned regularly, i.e. be dismantled. It has to clarified whether this impactor load (inherent from the operating principle) alters the deposition characteristics of the particles on the impactor plates.

For this, a long-term test is carried out at a constant engine operating point with continuous measurement of the NSD using ELPI over a period of 2 - 3 test days. The impactor load value of the ELPI rises from 0 % (cleaned device) to 140 %.

The measured NSDs are a function of the degree of impactor load and change in the course of the test (see Fig. 3.1). The total number of particles measured has tends to drop with increasing impactor load whilst the mean measured particle diameter increases. At 140 % impactor load, the total number amounts to 81 % and the mean diameter 137 % of the value at the initial, cleaned state. For the values calculated from these two measured variables for total surface area and total mass (spherical form with uniform density assumed) result in even greater changes: the surface area increases to 155 % of the initial value for 140 % impactor load, the mass increases even more to 259 % of the initial value.

Decisive for this is especially the change in NSD in the upper ELPI stages where the larger particles are separated off as these particles make an above-average contribution to the total surface area and total mass.

The curves show some steps due to the breaks during the measurement period of 2 - 3 test days. The engine and measurement was stopped over each night for about 14 hours. The measured value of particle number changed compared to the value of the day before.

These changes in the measured NSD can be explained by increasing impactor load of ELPI:

- The reduction in the measured number of particles at higher impactor load can be caused by an obstruction of the charge transfer from the charged particles to the impactor plate which is already covered with particles. The particles cannot therefore deliver electrical count pulses and are not detected.

- The gas flow is accelerated when the space between jet plate and collection plate within an impactor stage becomes smaller, caused by the deposition of the particles. Smaller particles are therefore separated off on this impactor plate. When the device is clean, these particles would not be separated until the next lower impactor stage. The particle size distribution shifts towards the larger diameters, i.e. the mean particle diameter increases.

After the device is cleaned, the test is repeated to check the reproducibility of the change in impactor load as a function of time.

The result is (see Fig. 3.2): the changes in the NSD are not exactly reproducible. A tendency towards similar time curves for the total values of number of particles, surface area and mass is shown. The percentage changes are of a similar order, cannot be reproduced absolutely, however.

An assured, computational correction of ELPI measurements, dependent on the current impactor load, to a defined (e.g. cleaned) reference state of the device is therefore not possible. The steepest gradients occur in the first phase of each case of the measurement at around 0 ... 30 % impactor load. This means that a cleaning of the device before each individual measurement is no solution so long as a defined follow-on measurement time is necessary.

It has not as yet been possible to assess the long-term behavior of the corona principle used by ELPI for particle charging in diluted diesel exhaust gas. With a similarly functioning measurement method based on this charging principle, Matter-Engineering LQ1-DC, quartz deposits on the corona needle can substantially alter the charging characteristic (see Sect. 3.2). Which elements in the diesel exhaust gas or the dilution air cause these deposits is not as yet known.

If this aging effect also affects the corona charging of the ELPI, the result is a change in the count measurement over the run time of the device (drift). An adjustment for correction purposes is not foreseen for the current device.

For the above reasons, the reproducibility and comparability (determination of absolute measured values) of the ELPI measurement are limited.

3.2 Matter-Engineering Diffusion-Charging Sensor LQ1-DC Measurement Method

The LQ1-DC measurement method uses the probability of deposition of ions on particles for measuring the active particle surface area.

Firstly, particles are electrically charged by diffusion (unipolar corona charging). The discharge current of the particles is determined by a downstream measurement filter (electrometer). This is a measure for the deposition coefficients of the ions from which the so-called Fuchs surface area or active surface area can be calculated. The measurement does not take place on a single particle basis, only the total active surface area within a defined aerosol volume is given.

In combination with number and size measurement methods, an attempt is made to determine a size-specific active surface area of the particles. For this, particles are selected with the DMA which have a defined electrical mobility class. With the CPC, the number of particles in the particular mobility class is determined; with the LQ1-DC, the active surface area in this mobility class is determined. By varying the setting of the DMA, various mobility classes are selected one after the other and the number and surface area are determined for each mobility class alternately. In this, the computational corrections, necessary because of the size-dependent charging efficiency of the DMA, are deactivated. Only those particles leaving the DMA are measured.

The particle size distribution put together from the particle number measurements (see Fig. 3.3) shows the well-known curve with the maximum number occurring at around 80 nm electrical mobility diameter. Below approx. 10 nm there are no more particles, above 200 nm the number is quite small.

The size-dependent curve of the active surface area reaches its maximum value at approx. 120 nm electrical mobility diameter. Below around 50 – 70 nm, the active surface area shows a finite value of about 45 $\mu m^2/cm^3$. Although the number continues to fall with reduction in particle size, the surface area remains constant.

The measurement of the numbers by the CPC is reliable, also in this size range [2].

With that, the surface area value given by the LQ1-DC is not plausible.

The method determines a finite surface area of the smallest particles which, according to the CPC measurement, do not exist. The surface area measurement using LQ1-DC therefore leads to an overestimation of the nanoparticles (electrical mobility diameter < 50 nm).

According to Kittelson [3], the detection limit in methods with diffusion charging (DC) lies with particles under 80 nm electrical mobility diameter.

No plausible measured values are to be expected below this particle size.

After a longer time in operation with the LQ1-DC when used to measure surface area in dilute diesel engine exhaust gas, a much slower response time of the device was observed when connected to the gas sample. In addition, it was no longer possible to carry out measurements of the ambient air at low aerosol concentrations with the device. With the corona charging switched off, the measured value should always be zero as no ionization of the particles takes

place. The zero value can be adjusted on the device by a potentiometer. This adjustment must be made very often if the LQ1-DC has been in operation for a longer period of time (several times per day when measurements are being made). A stable zero setting was therefore no longer achievable.

An inspection of the LQ1-DC by the manufacturer Matter-Engineering found a "massive loss in sensitivity". The cause was found to be a white quartz layer that had built up on the platinum wire of the corona charger during measuring operation.

This reduces the corona current and the aerosol can no longer be charged as in the initial state. Which elements ("chemical influences") in the diesel exhaust gas cause these deposits is not as yet known.

Similar quartz deposits have also been observed [4] in electrostatic air cleaners that function by corona charging. Longer operating times of the cleaner in ambient air polluted with cyclomethicone (a siloxane, e.g. present in deodorant sprays) led to a contamination of the corona wire (Fig. 3.4).

The corona-voltage necessary for the charging of the ambient air has to be increased considerably. At the same time, a severe change in the charging characteristic takes place – the voltage/current curve is no longer linear. A loss of the evenly distributed discharges for a clean wire caused by deposits occurs; only few discharge centers are formed. The volume of influence of the corona on the gas decreases sharply.

The diffusion charging of the aerosol using a corona is the basis of the LQ1-DC measuring principle. If the aging effect of the corona found in the air cleaner can be transferred to the measurement method of the LQ1-DC, it means that:

The charging of the particles is no longer reproducible; only a small fraction of the aerosol will be charged. In this situation, no reproducible measurement is possible.

A retro-fitted corona current control from the manufacturer ought to bring an improvement.

A comparison of the surface area measurements with the original device (Fig. 3.5) and with a modified variant (Fig. 3.6) shows severe oscillations in the measurement signals for the variant with corona current control.

A renewed inspection by the manufacturer showed the cause to be an inadequate electrical insulation between the measuring filter and the surrounding enclosure.

The measuring filter captures the charged particles. The electrical resistance between it and the enclosure should be approximately 10^{12} Ohm as only very small discharge currents of a few fA are measured. With particle deposits on the insulating surfaces (carbon is an electrical conductor), the insulation effect can be reduced and corresponding discharge currents can flow over the surfaces with deposits. This leads to instability and drift of the measurement signal.

Similar effects occur when moisture is present in the device.

This results in an assessment of the suitability of the LQ1-DC measurement method for particle measurements in diluted diesel engine exhaust gas:

- Low stability of the measurement signal => continual zero adjustment necessary,
  possible causes: moisture in the device, change in the insulation resistance
- The basic suitability of corona charging is questionable because of the unknown "chemical influences" in the measurement gas with the formation of deposits on the corona wire
- The basic suitability for the surface area measurement of particles < 50 nm (nanoparticles) is questionable

As in testing practice the exhaust gas is neither dry nor carbon-free, the method is not very suitable for long-term measurements in dilute diesel exhaust gas. In addition, the nanoparticles are much overestimated in the current model of the LQ1-DC.

3.3 EcoChem Photoelectric Aerosol Sensor PAS 2000 Measurement Method

The EcoChem Photoelectric Aerosol Sensor PAS 2000 measurement method makes use of the sensitivity of particles to photoelectric charging. The wavelength of the UV radiator (222 nm) used for the charging is adjusted to suit the ionization of the polycyclic aromatic hydrocarbons (PAH) deposited on the particles.

The discharge current of the particles is determined by a downstream measurement filter (electrometer). This is then a measure for the PAH deposited on the particles. With an appropriate calibration, predictions of mass concentration of PAH in $\mu g/m^3$ can be made.

There are hints, that this method can be used to determine the mass concentration of elemental carbon (EC) [5]. This presupposes an unambiguous correlation of the PAS 2000 signal with the mass of the EC, which would only be satisfied by a constant PAH deposition mechanism and a constant PAH deposition quota.

To check this correlation, measurements were made with PAS 2000 and AVL SmartSampler in dilute exhaust gas ahead of and after the catalyst (see Sect. 4.1). The particle mass was able to be determined from the deposits on the sample filters of the SmartSampler as total mass concentration and as mass concentration of the insoluble fractions (insoluble organic fraction INSOF). The INSOF fraction for the diesel engine consists essentially of elemental carbon. Hence a good correlation with the PAS 2000 signal should be obtained if this method can really determine EC.

However, the measurements especially after the catalyst are not plausible as there is almost no PAS 2000 measurement signal present here – although no severe change in particulate mass (especially INSOF) has taken place in the catalyst. On the other hand, it can be assumed that the PAH fractions are oxidized in the catalyst, especially at engine operating points with higher exhaust gas temperature.

This therefore excludes a correlation of the PAS 2000 measurement signal with the mass of the EC for measurements in dilute diesel engine exhaust gas.

The assessment of the suitability of this measurement method is therefore:

- An uncertainty exists about the real measurement variable
  (EC mass concentration is not plausible)
- Measurements after the catalyst indicate no correlation with other measurement methods (e.g. also not with gravimetrically determined particulate mass)
- The photoelectric charging as an optical process functions only at low particle number concentration or high dilution

The method is especially unsuitable for measurements downstream of the catalyst as practically no signal exists there. The method cannot therefore be used for the assessment of the particle emission for a vehicle in an emission test cycle (tailpipe measurement or from the CVS dilution system).

4 Correlation Measurements

4.1 Measurement Programme and Overview of Results

With the measurement methods to be assessed here, various physical properties of the particles are determined in each case. The morphology and the chemical properties of the particles should play a subordinate role or no role at all here.

Of interest is now the question of how far the measurements of various particle properties can be compared with each other. Independent of the type of measurement method used, a correlation between principally identical measurement variables can be expected. The particle number determined by ELPI should, for example, correlate with the number of the SMPS measurement or even, in the ideal case, be identical to it. The same is then true for the measurement or calculation of the comparable surface areas or masses.

If correlations independent off the boundary conditions of the measurement do clearly exist between the various particle measurement variables, this can also be used for calibration or as a chain of traceability to a standard aerosol.

To check the correlations between the measurement methods considered here (SMPS, LQ1-DC, PAS 2000, ELPI, AVL 415S Smokemeter, AVL 472 SmartSampler), a comparison measurement is carried out on the stationary engine test bench. The tests are carried out on a currently available automobile diesel engine with common rail injection (EU III exhaust gas standard) and oxidation catalyst. All measurement methods are connected to a selection valve developed by ADA that feeds a part flow of the engine exhaust gas selectively to each measurement method or dilution system. The measurement set-up is shown in Fig. 4.1.

By switching over the valve, a series of measurements from all the methods with identical exhaust gas is generated. The engine operating point is held stable over the entire measurement period. Twenty-eight operating points are selected from the overall engine map as shown in Fig. 4.2. This series of tests is carried out in sequence with sampling ahead of and behind the oxidation catalyst.

To interpret the results, the assumed linear correlations of seven direct and five derived measured variables are examined and, with the respective coefficient of determination R^2 stated in each case, are shown in Table 4.1. The results are shown in Table 4.2.

The derived variables are calculated from the direct measured variables with certain assumptions. From the aerodynamic diameter of a particle determined by ELPI, a geometric "surface aerodynamics" can be calculated with the simple assumption of a spherical form and a "mass aerodynamics" can be calculated with the assumption of a size-independent, uniform particle density. In combination with the measurement variable particle number, values can in this way be specified for the "aerodynamics" total surface area and total mass. This calculation makes at first no claim to determine quantitatively comparable values for surface area and mass and is not intended to replace a direct measurement.

Interesting, however, is the observation of the correlations between measured and values calculated from the NSD based on simple assumptions.

In addition, because of the grouping of the operating points, the measurement conditions are examined that can influence a correlation. In this, it is differentiated between all measurements, those only ahead of and only after the catalyst as well as the engine operating points under exhaust gas test conditions in the NEDC (these only downstream of the catalyst).

The results of the correlation check of the methods considered here (ELPI, LQ1-DC, PAS 2000, AVL 472 SmartSampler) are compiled in Table 4.2. The particular coefficients of determination R^2 are given with a color-coding depending on the quality of the linear correlation. The cell in the table shows the different measurement conditions.

The highest correlations (R^2 = 0.74 ... 0.97) are obtained between the comparison of the surface calculated from ELPI data and that of the active surface measured with LQ1-DC. There are also, in part, high correlations between the ELPI surface area or mass with the gravimetrically determined mass concentrations of the SmartSampler. The distinction of the mass concentration between total and mass of the insoluble components (INSOF) has no great influence on these correlations.

Nor shown here are the correlations between the mean particle diameter determined from the NSD of ELPI and the measured variables for surface area or mass. All the correlations determined in this series of measurements in combination with the mean diameter have indices of determination with $R^2 < 0.50$ and are therefore not worthy of consideration here.

In the following, several selected correlations will be studied more closely.

4.2 Correlation ELPI Surface Area – LQ1-DC Active Surface Area

Depending on the measurement conditions, medium to high correlations (R^2 = 0.74 ... 0.97, see Fig. 4.3) between the comparison of the surface area calculated from the ELPI's NSD and that of the active surface area measured with LQ1-DC are obtained . The distinction between before and after the catalyst is the difference between the gradients of the linear trend curves. With this separate consideration, higher indices of determination are achieved in each case. Under the conditions of the emission test cycle NEDC, a very high correlation of R^2 = 0.97 is obtained with very low deviations from the trend curve.

If these results can be transferred to vehicle measurements, then a suitable correlation under exhaust gas test conditions can be assumed.

4.3 Correlation LQ1-DC Active Surface – PAS 2000 Measured Value

According to information from the manufacturer, a constant as "chemical fingerprint" for the clear identification of combustion particles [7] should be obtainable from the ratio of the measured values for active surface area (LQ1-DC) and deposited PAH (PAS 2000).

The correlation check (see Fig 4.4) can, however, only confirm the validity of this statement for measurements ahead of the catalyst ($R^2 = 0.93$). The correlation after the catalyst is, at $R^2 = 0.71$, lower and differs greatly from that ahead of the catalyst in the gradient of the trend curve. Under the conditions of the exhaust gas test, virtually no correlation is visible at $R^2 = 0.46$.

So, from this unsuitable correlation no useful statements can be expected for vehicle measurements under emission test cycle conditions like NEDC.

4.4 Correlation of ELPI Mass – SmartSamplerMass

The calculated mass concentration "Aerodynamic" is determined from the NSD calculated with ELPI on the assumption of particle with spherical form and size-independent, uniform density of 1.2 g/cm^3. The comparison of the values obtained by this method with those of the gravimetrically determined total mass of the SmartSampler measurement shows medium to high correlations ($R^2 = 0.70$ ... 0.93; see Fig. 4.5). The coefficient of determination is higher ($R^2 = 0.93$) for the for the measurements downstream of the catalyst. This is also true for the conditions of the emission test cycle with $R^2 = 0.89$. The correlation ahead of the catalyst can be improved to $R^2 = 0.88$ if only the insoluble parts of the particulate matter (INSOF) are considered, while the correlation after the catalyst is not affected (see Fig. 4.6).

As a size-independent density for particles sorted on a size basis from diesel engines cannot be assumed [8], a further improvement in the correlation of the mass values compared here is to be expected from knowledge of this size-dependent density function. However, it still has to be checked here to what extent this density function is engine-specific.

4.5 Assessment of the Correlation Measurements

A combination of number and diameter in the form of the NSD with the calculated values obtained for surface area or mass yields to a usable correlation with the corresponding measurement values. Even with the hypothetical assumption of the spherically-shaped particle and uniform, size-independent density, good correlations are obtained from the NSD for active surface area or gravimetrically determined mass. A further improvement in the correlation quality is to be expected when more realistic assumptions for particle geometry and density are made. For this, however, the state of knowledge in this area still has to be set up or improved. Vehicle measurements on chassis dynamometer show a good correlation between the route-related values for total particle number (in number/km) and particulate mass (in grams/km) [6].

Based on the measurements introduced here, the result is that suitable correlations are those that can be obtained via the measured or calculated values for surface area or mass.

These correlations are then also valid downstream of the catalyst under emission test conditions.

5 Summary and Recommmendations

The relevant parameters are still uncertain in terms of possible health effects due to particulate emission from internal combustion engines. There is an ongoing discussion at the moment about new parameters to be measured in the future such as particle diameter, particle number or particle surface area in addition to particulate mass. The task of this ADA project is to assess the measurement technology for these new parameters in measuring particulate emissions from internal combustion engines.

Measurement of Aerosols is much more complex than determining mass as spatially distributed single particles within a carrier gas are being measured. The number concentration and morphology of the particles are changing continuously under external influences. For this reason, an aerosol measurement is always only a snapshot at a certain measuring point. Large changes in the number concentration of the particles can occur because of agglomeration and interactions of the aerosol with the exhaust gas sampling lines. The residence time of the aerosol in the lines and the condition of the line itself are the major factors affecting the measurement result. The exhaust gas sampling lines should therefore be as short as possible and preconditioned in exhaust gas.

The formation of nanoparticles can increase - even at high dilution ratios - due to the rapid cooling of engine exhaust gas. This process is enhanced by high engine load (corresponding to high exhaust gas temperature), high activity of the catalyst and high fuel sulfur content. The nanoparticles formed under these conditions are not of a solid nature.

Should an aerosol measurement be employed for vehicle type approval, the possible resulting changes in particle size distribution from the boundary conditions of the measurement must be quantifiable as absolute limiting values have to be observed. Without this quantification, no reproducible absolute measurement values can be expected. The only promising solution here is a direct measurement in undiluted engine exhaust gas without the necessity of exhaust gas sampling lines and dilution systems. Without a calibration process that works in practice, there can be no reliable and secure measurement of particulate emission.

Particle size distribution measured using the ELPI method and the variables which can be derived therefrom (number, aerodynamic diameter, surface area, mass) are dependent on the value of impactor total load (governed by the process) in the measuring device. This effect is inherent in the measuring principle.

Reproducibility and comparability of ELPI measurements are therefore limited.

The basic suitability of a corona charger in order to charge particles electrically has to be called into question if this principle is applied to exhaust gas from internal combustion engines.

The measurements with LQ1-DC are not plausible in the nanoparticle range – which is why nanoparticles are overestimated. Here also, the basic suitability of a corona charger for electrical charging of the particles in combustion engine exhaust gas has to be called into question due to aging effects observed. Moisture and a change in the internal electrical insulation resistance due to particle deposition lead to poor stability in the measurement signal. Long-term stability in the measurement of combustion engine exhaust gas is therefore not possible.

In the PAS 2000 measurement method, there is an uncertainty concerning the actual measurement variable. Because of the poor correlation of the measurement output signal with the gravimetric particulate mass determination, especially for measurements downstream of the catalyst, elemental carbon (EC) is practically eliminated as a measurement variable. The method cannot therefore be used for the assessment of the particulate emission for a vehicle during a driving cycle.

There are correlations between methods which determine the number size distribution (NSD) and methods where surface or mass is measured. A combination of number and diameter in the form of the NSD with the values calculated from it for surface area or mass yield to a usable correlation with the corresponding measurement values. Vehicle measurements on chassis dynamometer show a good correlation between the route-related values for total particle number (in number/km) and particulate mass (in grams/km) [6].

None of the measurement methods investigated here (ELPI, LQ1-DC, PAS 2000) is suitable for reliable and quantitative determination of particulate emission in exhaust gas from internal combustion engines.

Especially the long-term stability of the particle measurement methods has to be called into question.

According to the current technical state of the measurement methods, none of the particle measurement instruments investigated here (ELPI, LQ1-DC, PAS 2000) can be recommended for the measurement of number or surface area concentration in the exhaust gas of internal combustion engines.

The reasons for this are in part of a fundamental nature and in part for reasons associated with a specific instrument.

6 Literature

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7 Illustrations

Measurement Method	Measurement Principle	Measurement Variables	Dilution System Required
SMPS Scanning Mobility Particle Sizer	Deflection of electrically charged particles combined with optical counting	• Number size distribution • Electrical mobility diameter • Total particle number	Yes
ELPI Electrical Low Pressure Impactor	Impactor principle with electrical counting	• Number size distribution • Aerodynamic diameter • Total particle number	Yes
LQ1-DC Diffusion Charger	Diffusion charging with electrical detection	• Active particle surface area (not on a single particle basis)	Yes
PAS 2000 Photoelectric Aerosol Sensor	Photoelectric charging (UV light) with electrical detection	• Polycyclic aromatic hydrocarbons (PAH) deposited on particles	Yes
AVL 415 S Smokemeter	Light reflection from a filter paper	• Filter smoke number FSN	No
AVL SPC 472 SmartSampler	Part flow dilution with filter layer deposit and subsequent gravimetric mass determination	• Particulate mass on filter	Integrated in instrument

Table 1.1 Particle measurement methods used in the project

System	Principle	Heating	Dilution Factor
AVL SPC 472 SmartSampler	Mini dilution tunnel, part flow (constant volume flow)	50 °C (Tunnel)	5 - 50
Matter Engineering NanoMet MD 19-2 E	Addition of exhaust gas using rotating chamber disk	120 °C, 150 °C	20 - 3000
TSI / Dekati Ejector dilution stage (2-stage)	Ejector dilution	2nd Stage max. 450 °C	approx. 100

Table 1.2 Dilution systems used in the project

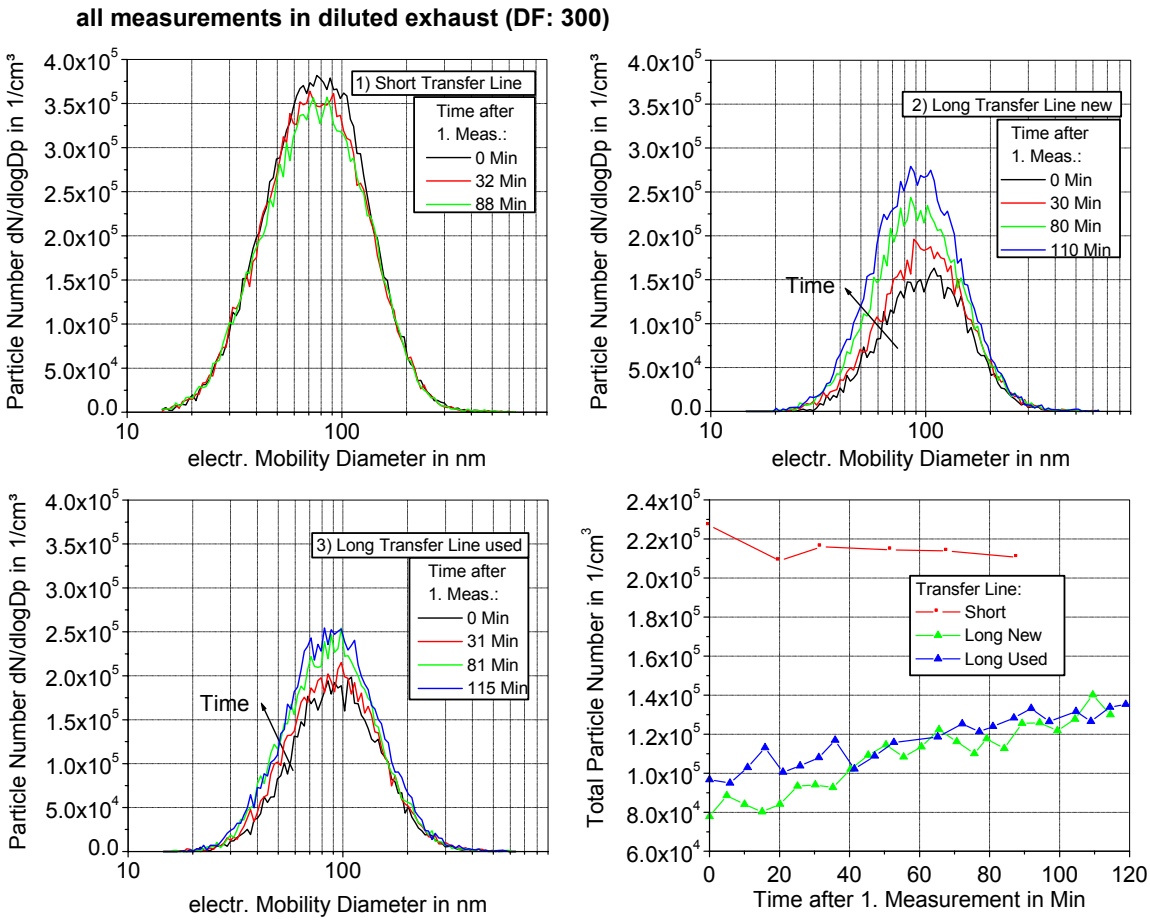


Fig. 2.1 Influence of the transfer line

Measurement of ambient air on engine test bench (open sampling point)

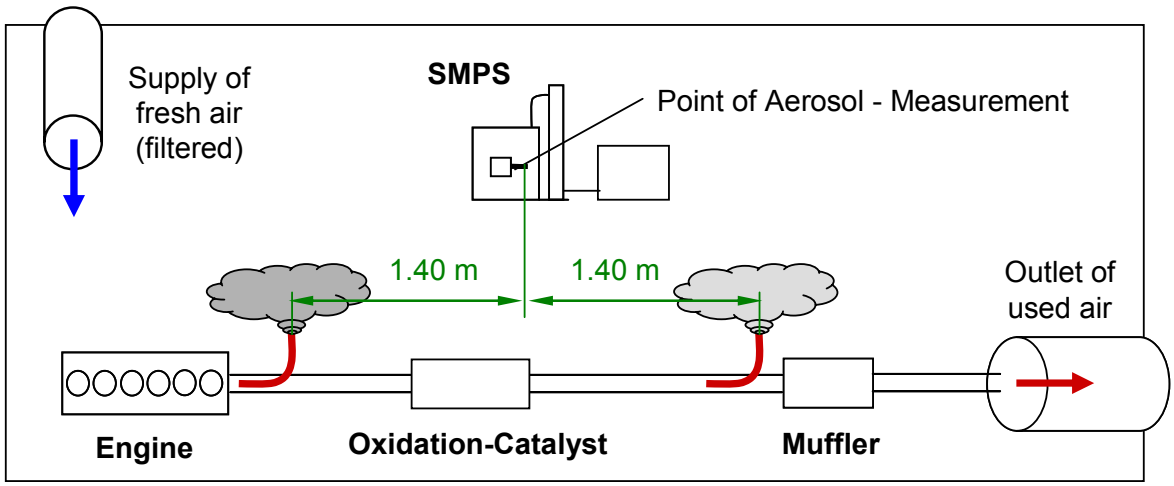


Fig. 2.2 Measurement set-up for ambient air measurement on engine test bench

	Standard diesel (commercially available)	Greenergy
Cetane number acc. to ISO 5165:1998	53.2	53.6
Density in kg/liter	0.8345	0.8259
Sulfur content in mg/kg	190	< 10
Mono-aromatics in Vol %	23.7	12.3
Polycyclic aromatics in Vol %	4.4	1.5

Table 2.1 Fuel specification of standard commercial diesel and Greenergy

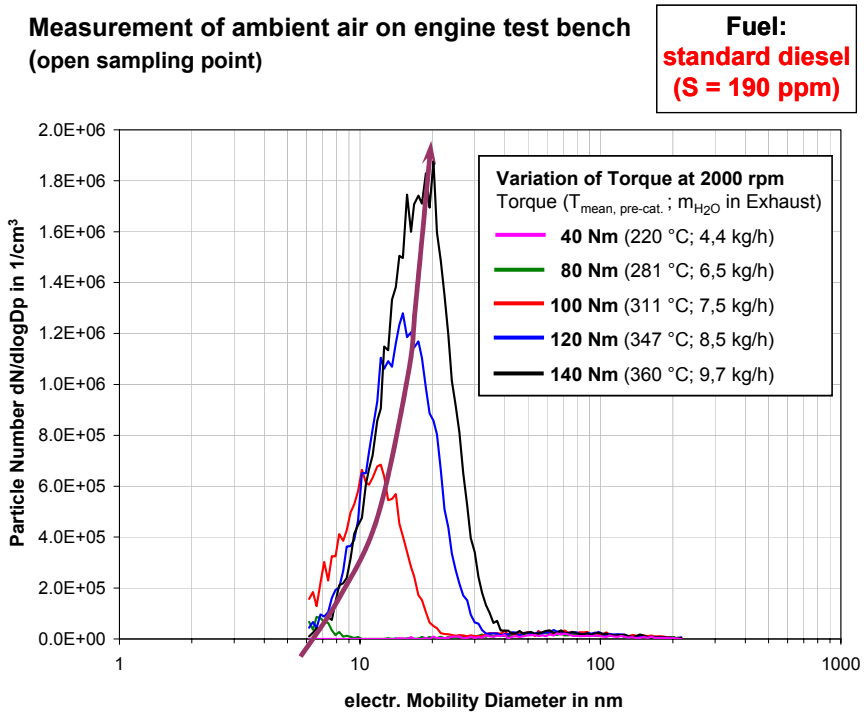


Fig. 2.3 Variation of engine torque at 2000 rpm
(Fuel: standard commercial diesel, sulfur content: 190 ppm)

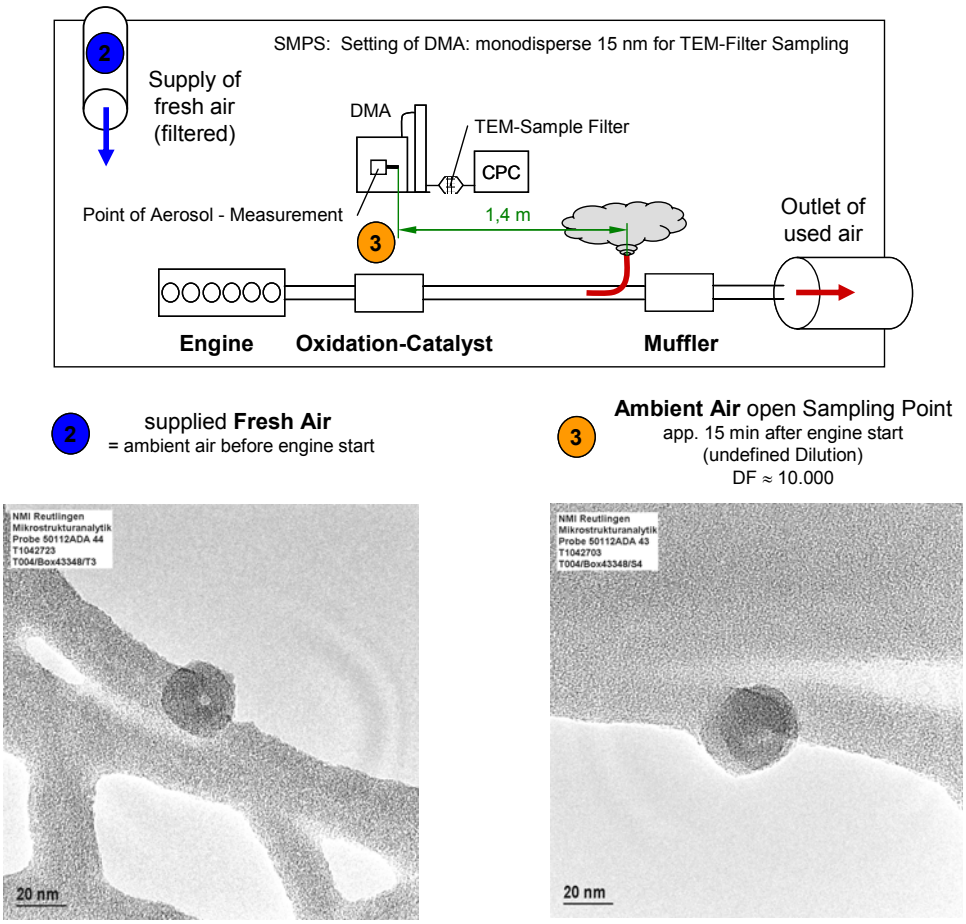


Fig. 2.4 Sampling and TEM analysis of monodisperse nanoparticles, open sampling point (Setting of DMA to electrical Mobility Diameter of 15 nm)

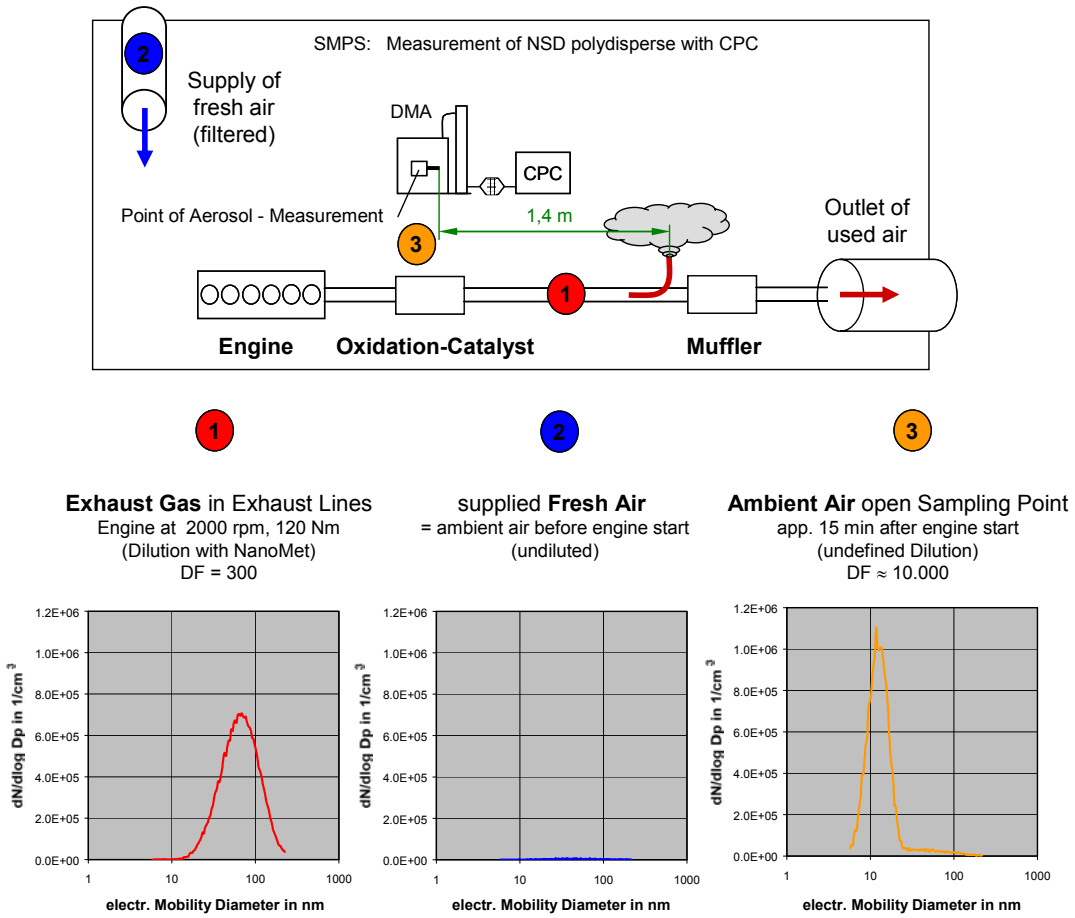


Fig. 2.5 SMPS measurement (polydisperse) of exhaust gas, fresh air and ambient air (open sampling)

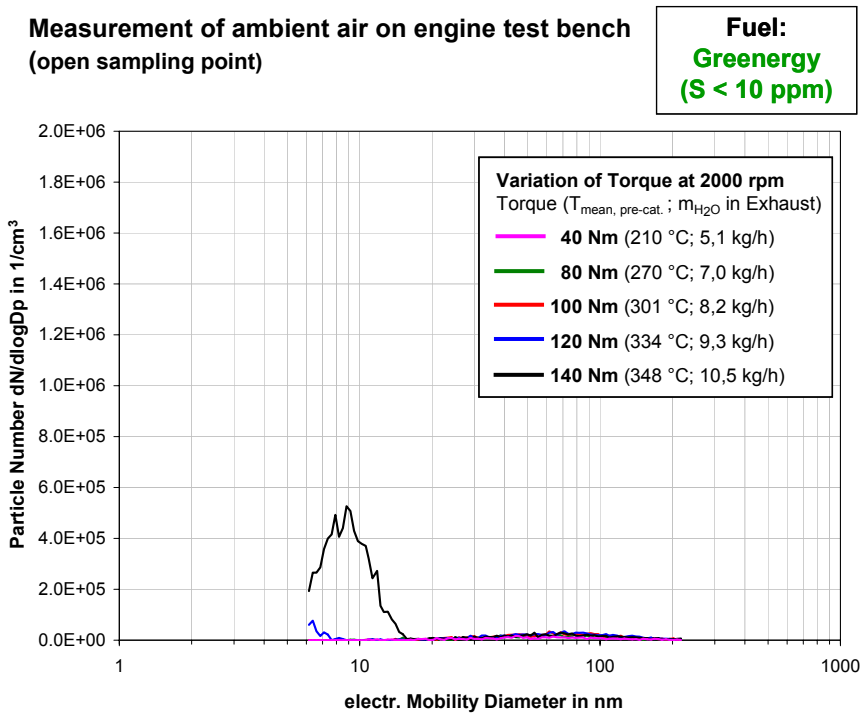


Fig. 2.6 Variation of engine torque at 2000 rpm (Fuel: Greenergy, sulfur content: < 10 ppm)

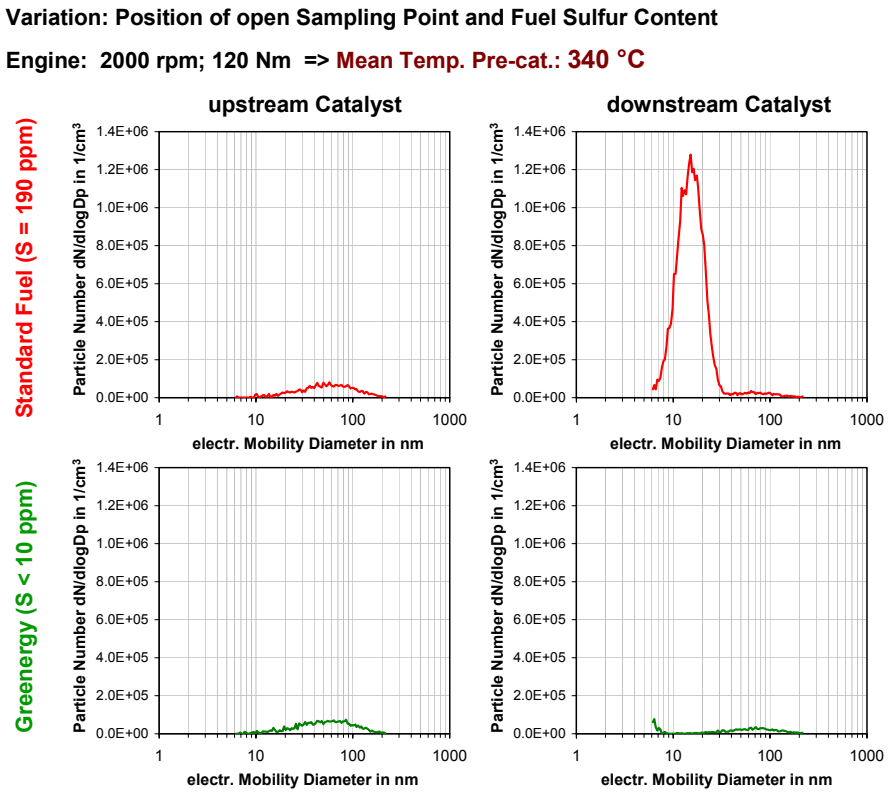


Fig 2.7 Fuel and catalyst influence on nanoparticle formation (engine operating point: 2000 rpm , 120 Nm)

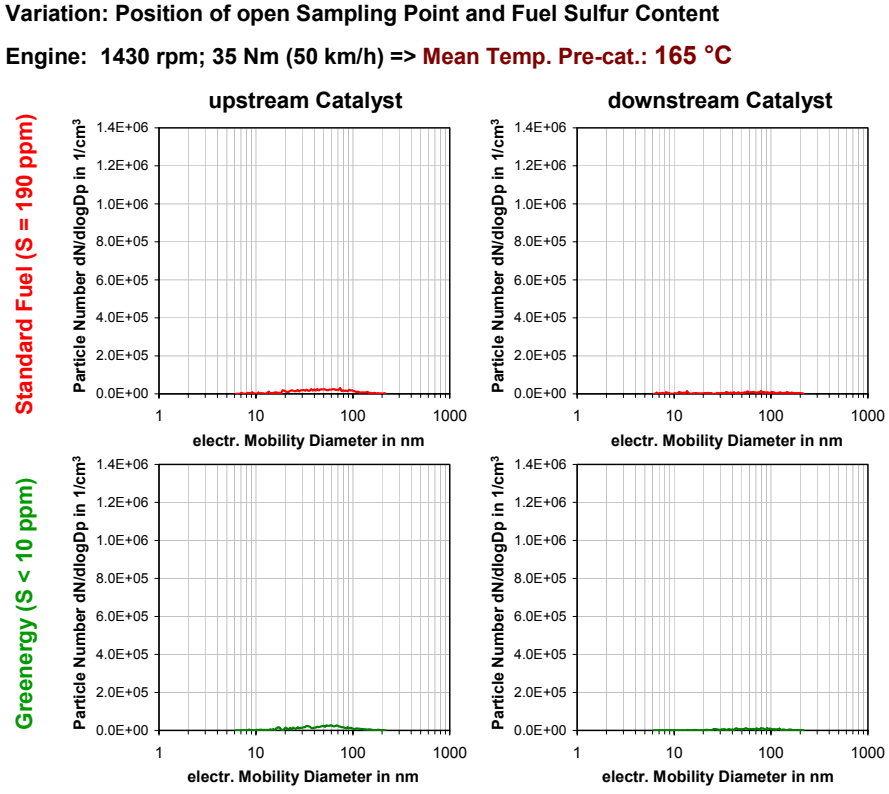
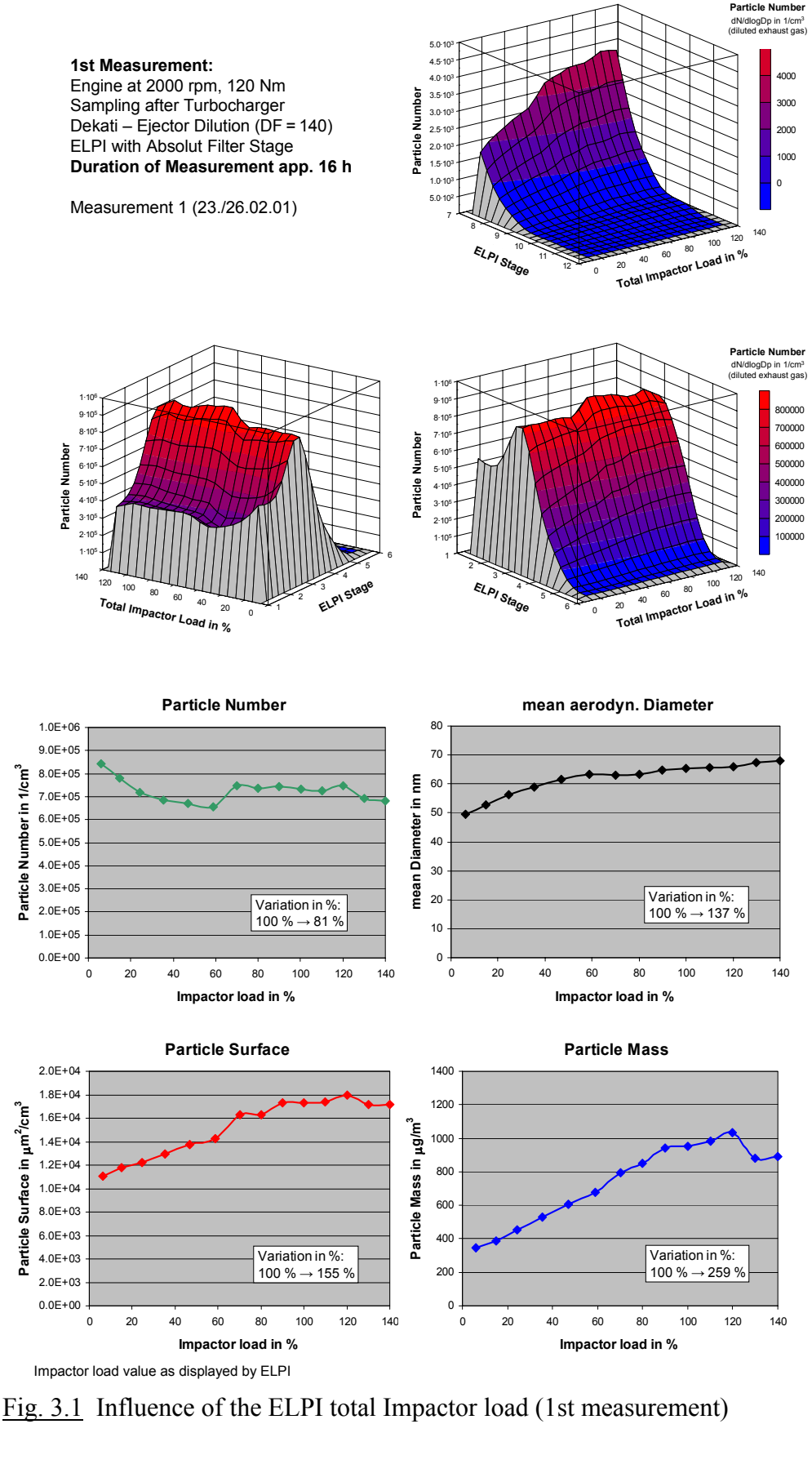


Fig 2.8 Fuel and catalyst influence on nanoparticle formation (engine operating point: 1430 rpm , 35 Nm)

Influence of ELPI – Total Impactor Load

1st Measurement:
Engine at 2000 rpm, 120 Nm
Sampling after Turbocharger
Dekati – Ejector Dilution (DF = 140)
ELPI with Absolut Filter Stage
Duration of Measurement app. 16 h

Measurement 1 (23./26.02.01)



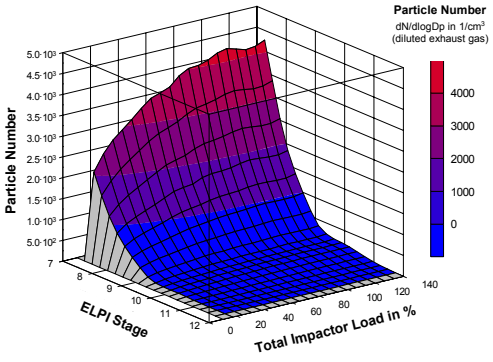
Impactor load value as displayed by ELPI

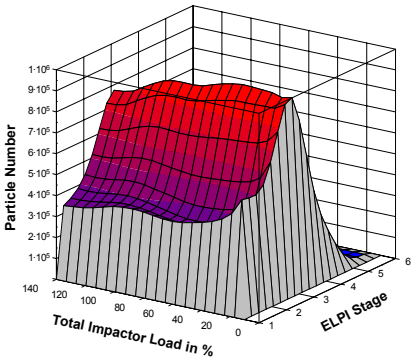
Fig. 3.1 Influence of the ELPI total Impactor load (1st measurement)

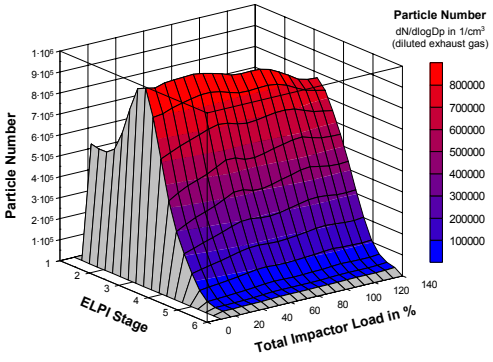
Influence of ELPI – Total Impactor Load

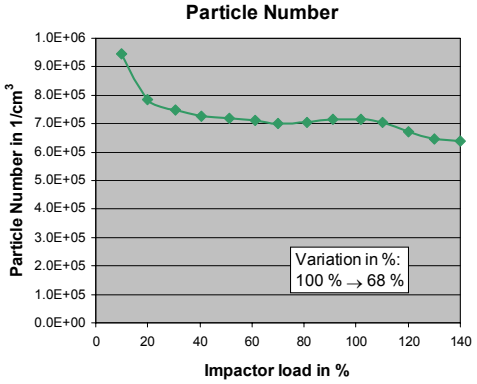
2nd Measurement:
Engine at 2000 rpm, 120 Nm
Sampling after Turbocharger
Dekati – Ejector Dilution (DF = 140)
ELPI with Absolut Filter Stage
Duration of Measurement app. 16 h

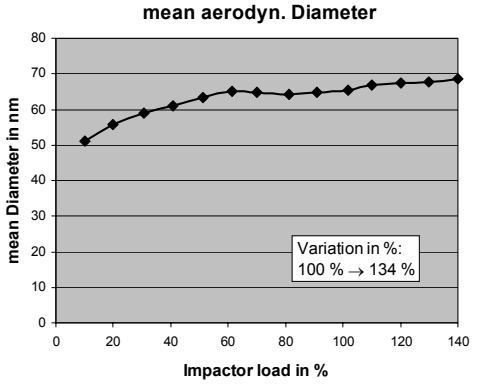
Measurement 2 (27.02./05.03.01)

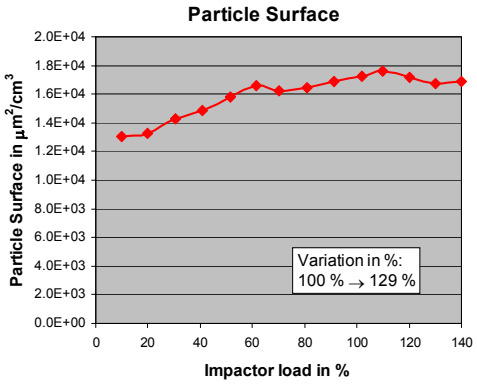


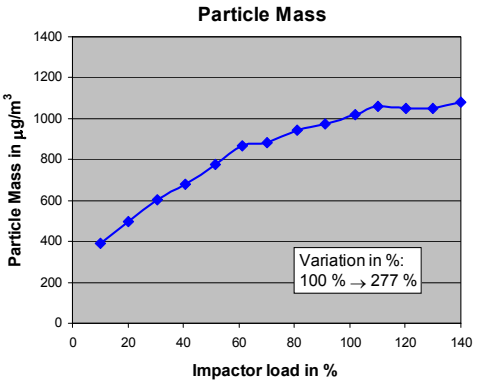












Impactor load value as displayed by ELPI

Fig. 3.2 Influence of the ELPI total Impactor load (2nd measurement)

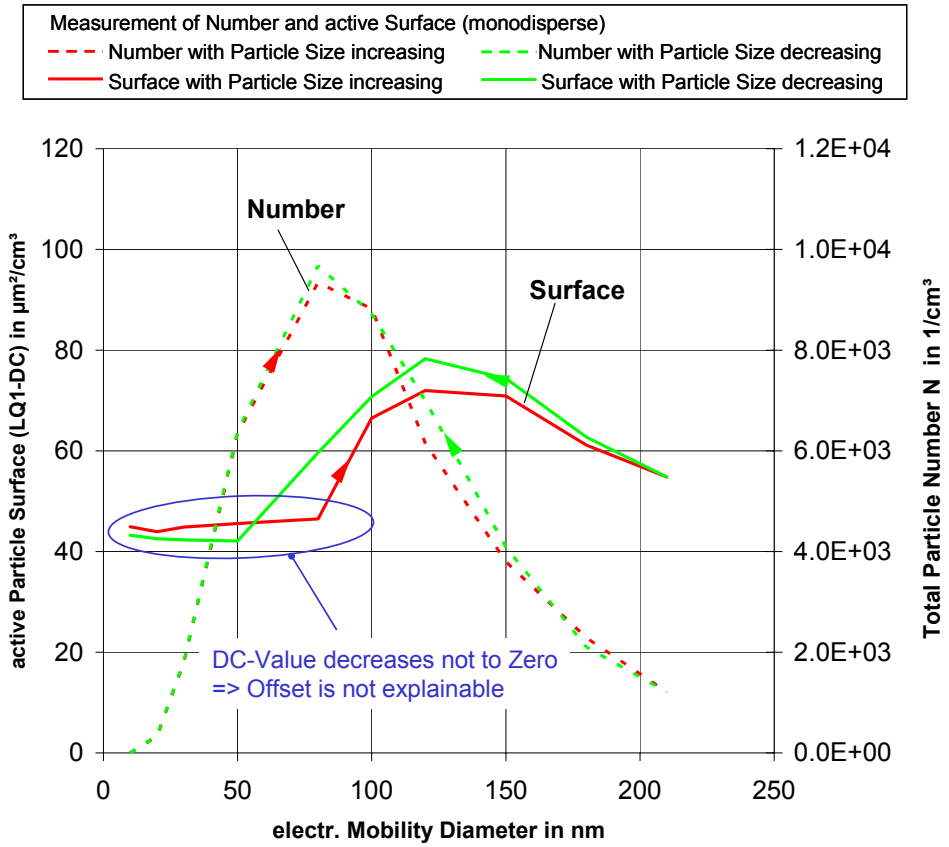


Fig. 3.3 Measurement of active surface area for monodisperse particles
(engine operating point: 2000 rpm, 120 Nm , downstream catalyst, DF = 25)

Contamination of Corona Needle (Electrostatic Air Cleaner after 180 h in Use)

(Air contains Cyclomethicone, which is often used in deodorant sprays)

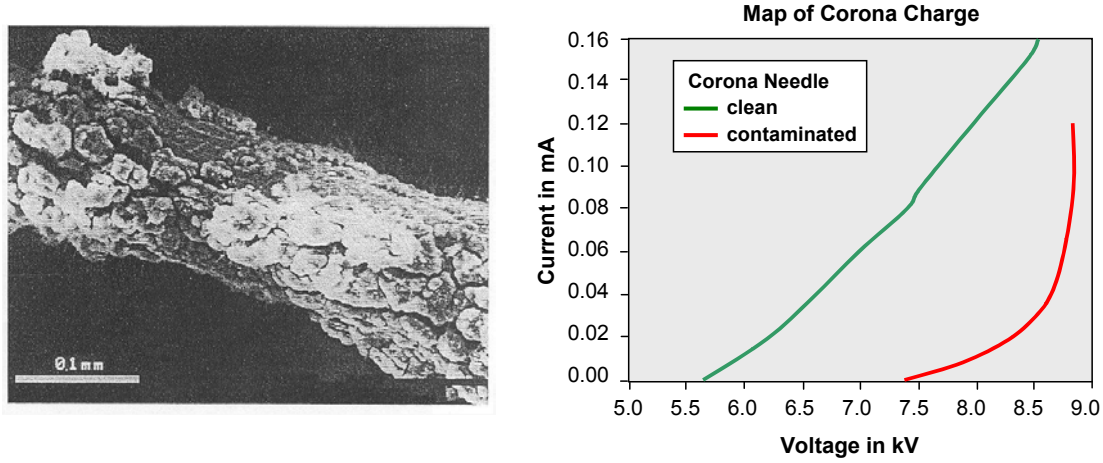


Fig. 3.4 Contamination of the corona needle of an electrostatic air cleaner

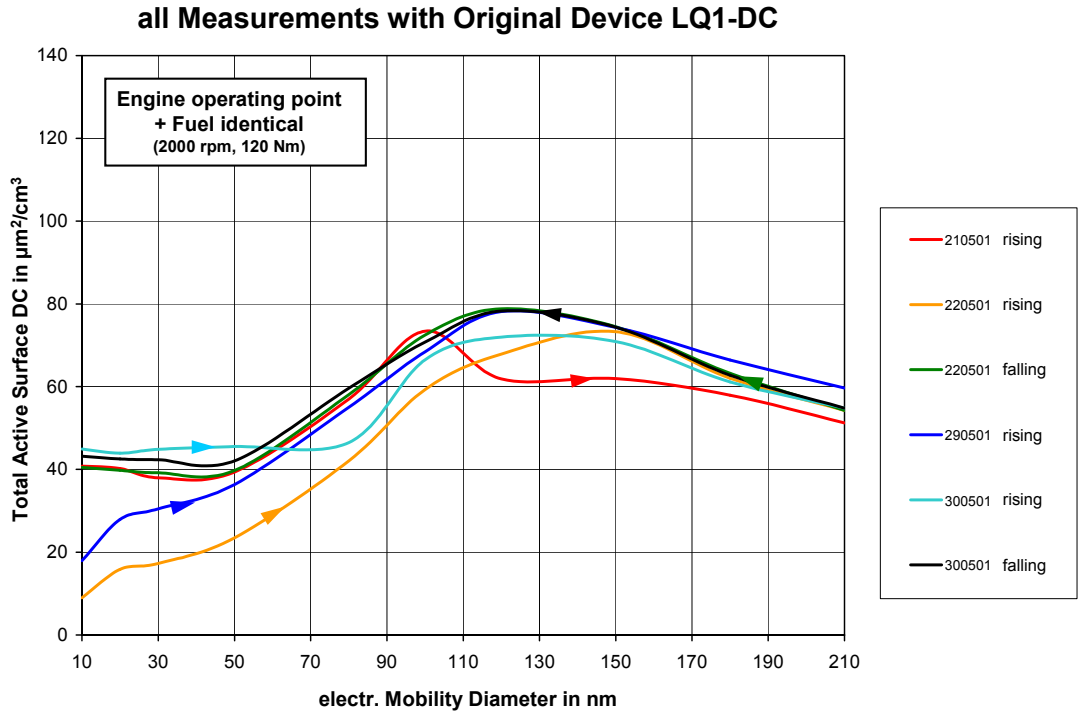


Fig. 3.5 Surface area measurements with LQ1-DC
(original device without corona current control)

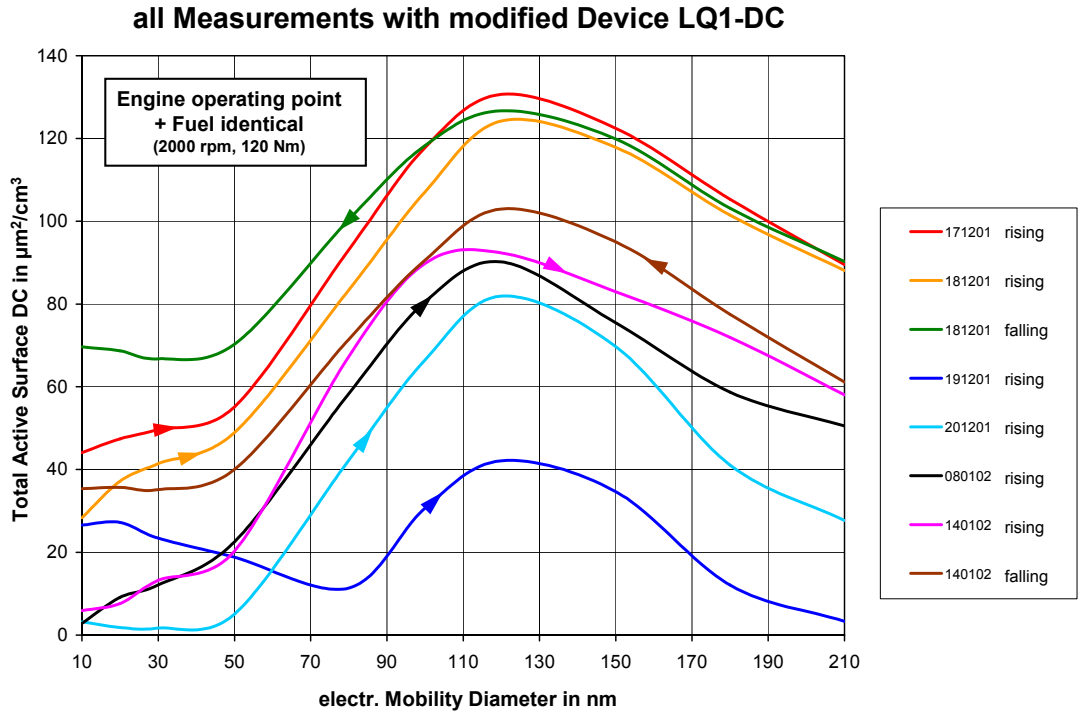


Fig. 3.6 Surface area measurements with LQ1-DC
(modified device with corona current control)

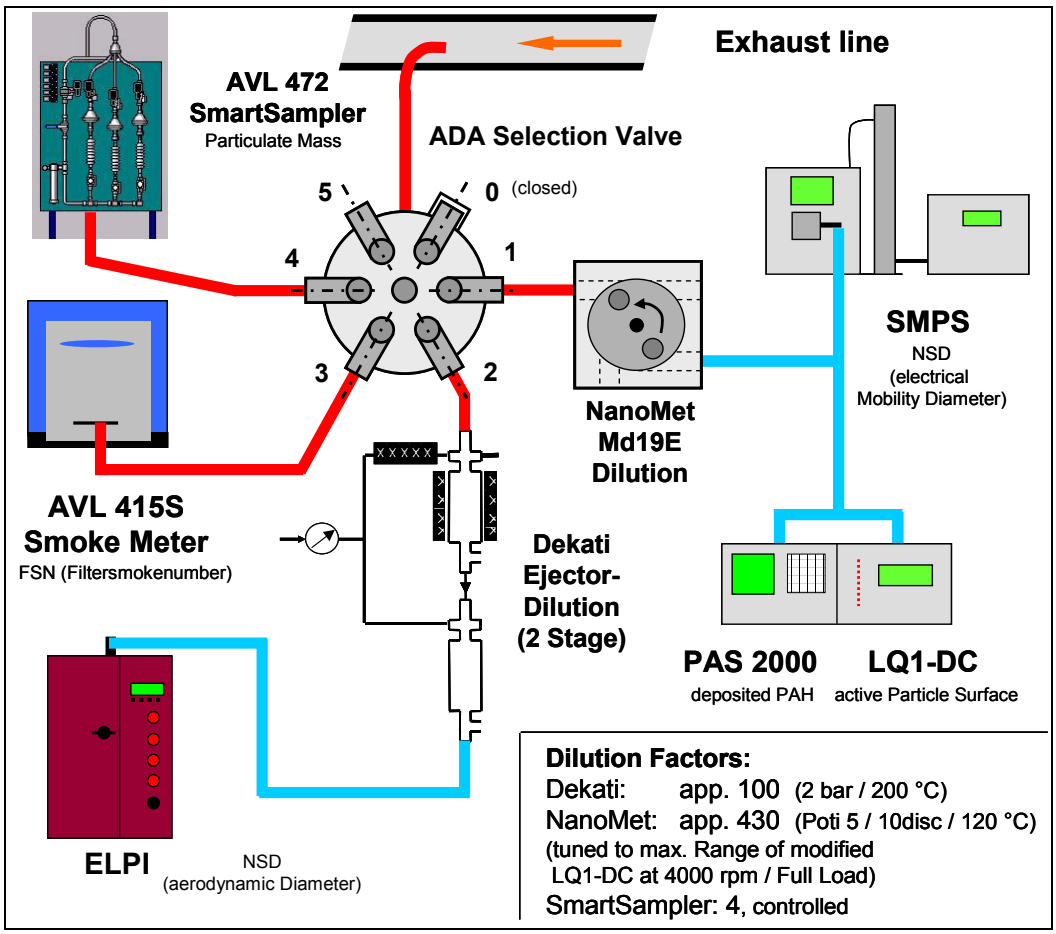


Fig. 4.1 Measurement set-up for correlation measurements

Method	direct Variables / derived Variables		
	Surface	Mass	Particle Size
SMPS (DMA+CPC)	Surface[1] "Mobility" [µm²/cm³]	Mass[2] "Mobility" [µg/cm³]	mean[4] electrical Mobility Diameter [nm]
ELPI	Surface[1] "Aerodynamic" [µm²/cm³]	Mass[2] "Aerodynamic" [µg/cm³]	mean[4] aerodynamic Diameter [nm]
LQ1-DC	active Surface [µm²/cm³]		
PAS 2000	Value of deposited Polyaromatics PAH [fA]		
AVL 415 S Smokemeter	FilterSmokeNumber FSN [-]	Mass FSN[3] [mg/m³]	
AVL SPC 472 SmartSampler		Total Mass PM + Mass INSOF [µg/m³]	

1 Spherical Form of Particles assumed
2 Spherical Form of Particles with uniform Density 1,2 g/cm³ assumed
3 Calculation based on AVL Statement
4 arithmetic mean

Table 4.1 Direct and derived variables for correlation measurements

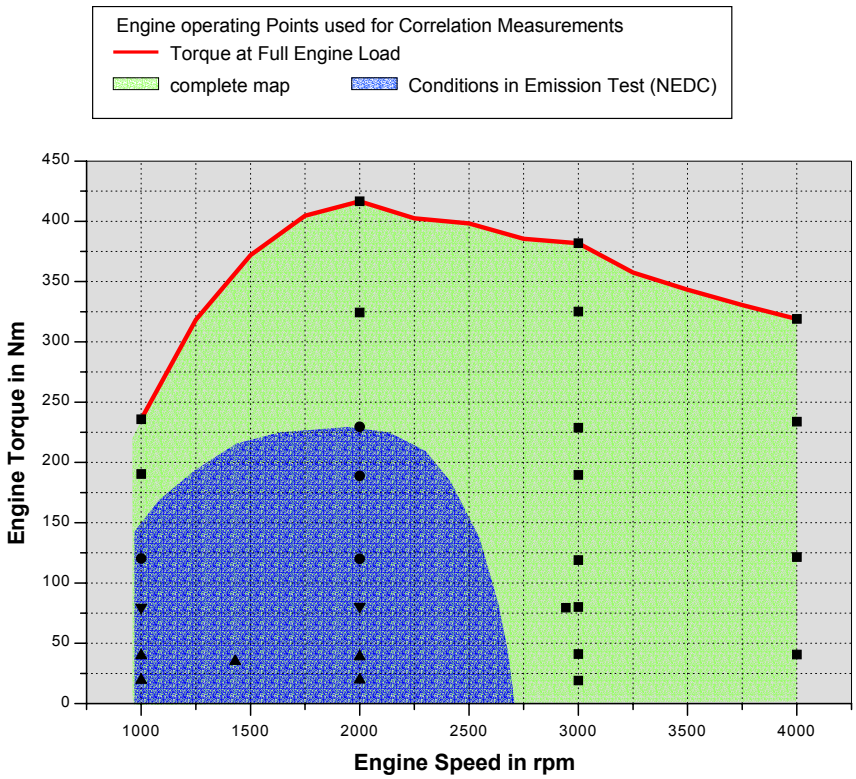


Fig. 4.2 Position of the selected engine operating points in the engine map

Correlation Matrix of the Measurement Methods (Selection)

Coefficients of Determination due to assumed linear Correlation
(Measuring Conditions: BMW 3.0 CR, stationary Engine Test Bench, ADA Selection Valve)

	ELPI				LQ1-DC		PAS 2000	
	Surface (NSD aerodyn. Ø)		Mass (NSD aerodyn. Ø)		active Surface		deposited PAH	
LQ1-DC	0.74	0.86	0.54	0.75	x		x	
active Surface	0.90	0.97	0.59	0.64				
PAS 2000	0.84	0.93	0.59	0.83	0.76	0.93	x	
deposited PAH	0.67	0.35	0.32	0.04	0.71	0.46		
SmartSampler	0.74	0.78	0.82	0.70	0.49	0.73	0.56	0.82
Total Mass PM	0.78	0.76	0.93	0.88	0.53	0.71	0.36	0.11
SmartSampler	0.81	0.92	0.87	0.88	0.64	0.81	0.61	0.90
Mass INSOF	0.76	0.73	0.92	0.85	0.55	0.70	0.32	0.12

Correlation

high	$R^2 > 0.90$
middel	$0.70 < R^2 < 0.90$
low	$0.50 < R^2 < 0.70$
no	$R^2 < 0.50$

Measuring Conditions

all operating points	only upstream Catalyst
only downstream Catalyst	only Emission Test Conditions (downstr. Cat., EGR)

Table 4.2 Correlation matrix of the measurement methods (coefficients of determination R^2)

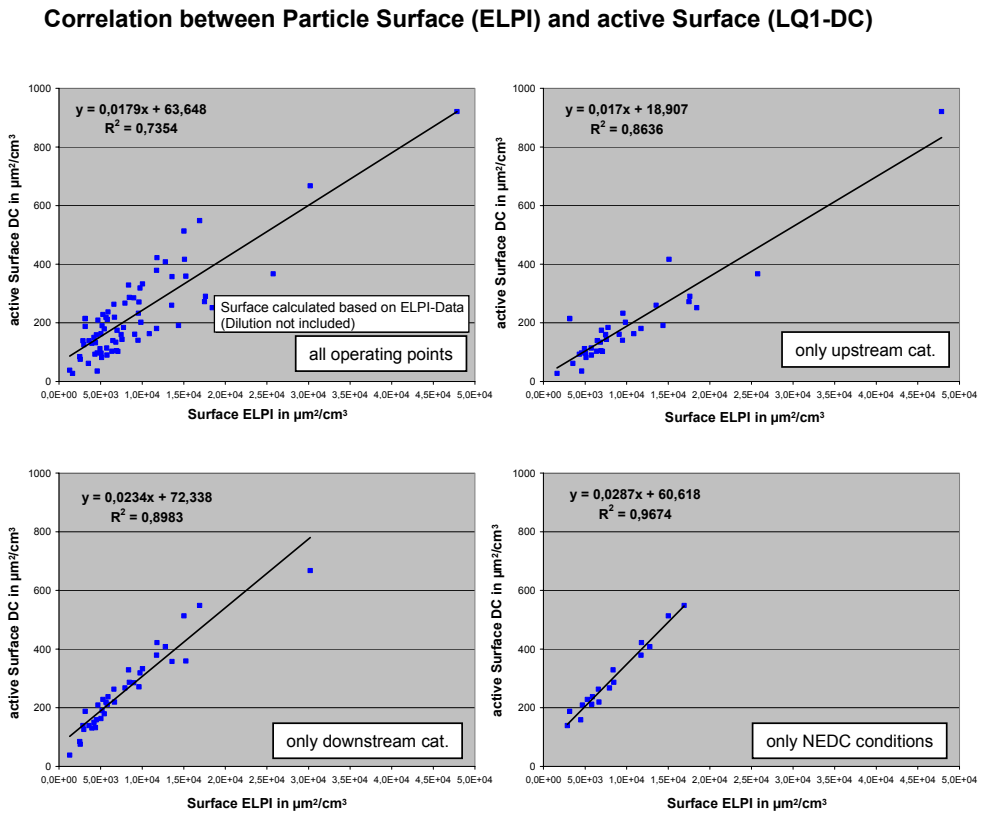


Fig. 4.3 Correlation between the particle surface area concentration (ELPI) and the active surface area (LQ1-DC)

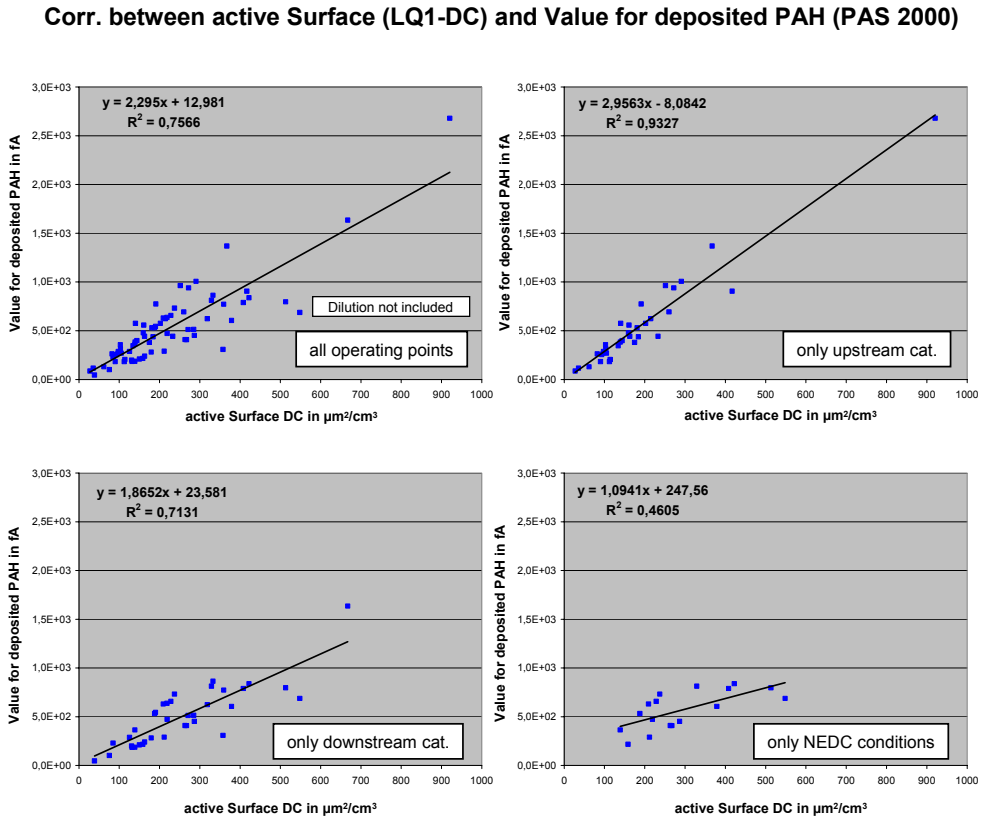


Fig. 4.4 Correlation between the active surface area concentration (LQ1-DC) and the measured value for deposited PAH (PAS 2000)

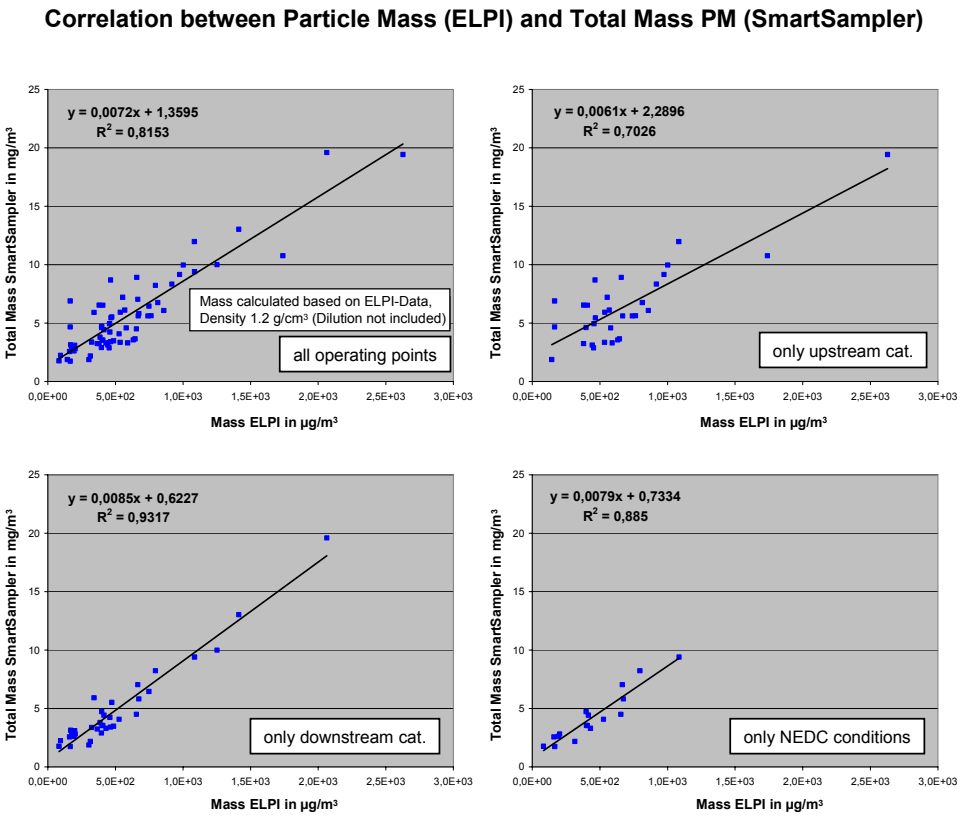


Fig. 4.5 Correlation between the mass concentration (ELPI) and the total particle mass (SmartSampler)

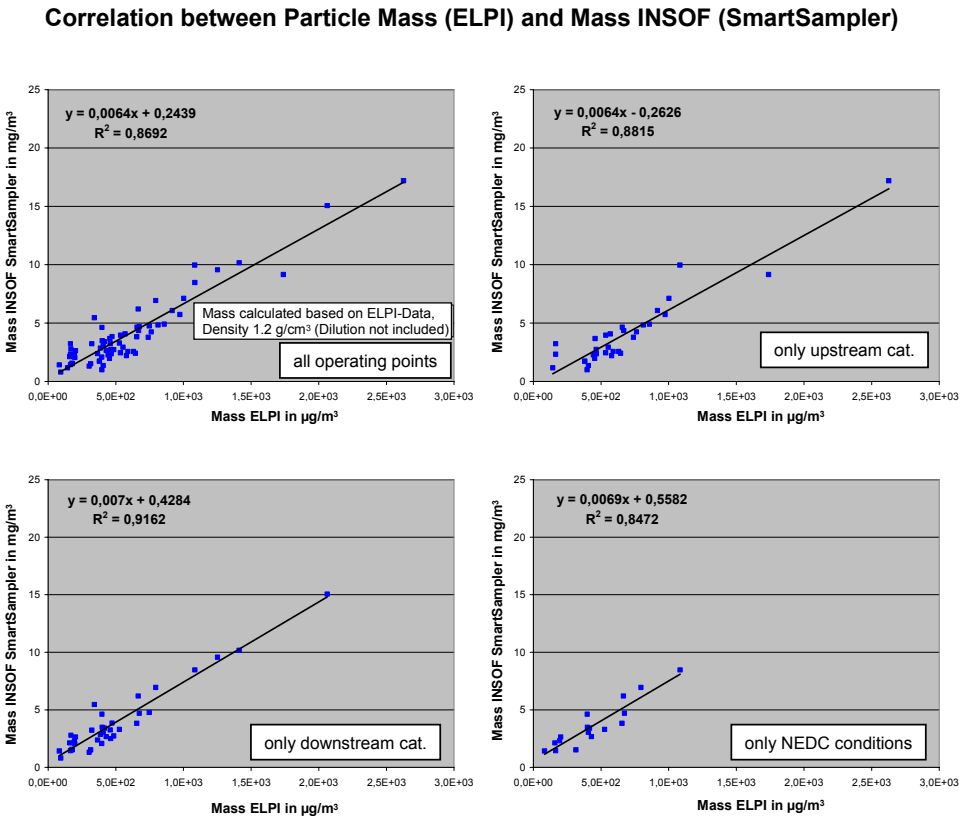


Fig. 4.6 Correlation between the mass concentration (ELPI) and the particle mass INSOF (SmartSampler)

BMW Dieselmotorenentwicklung

Some aspects for future particulate measurement

1. Gravimetric mass measurement

2. Particulate size distribution
   some influences on the test results

Gerhard Resch, Reinhold Töper

Steyr, 20.Oktober 2002

Some aspects for future particulate measurement

1. Gravimetric mass measurement

By our experience the gravimetric mass measurement is quite good for being used at emission levels of EU-4 and below. To estimate the lower limit of this method BMW did the following investigation.

To get a very low particulate loading, blank-test had been carried out. Instead of sampling the exhaust of a vehicle the air of the test-cell had been sampled during a MVEG test. The results are shown in Figure 1 - each five tests had been made on two chassis dynos. As the patterns show the emission decreases with increasing testnumber. We assume that particles are removed from the surface of the sampling system and in time this “particle-source” decreases.

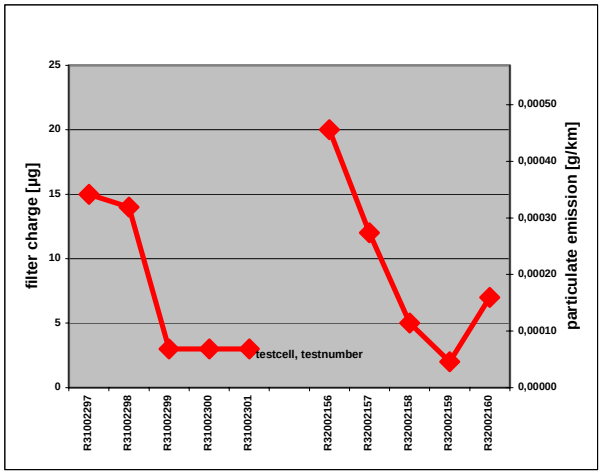


Figure 1: Blank-tests on two chassis dynos

The mean value of all 10 tests is 0,0002 g/km with a standard deviation of 0,00015 g/km. One part of this relatively high standard deviation results from the decreasing “particle-source”. Compared with the EU-4 limit of 0,025 g/km this standard deviation of 0,00015 g/km is less than 1% of that limit value. Tests with very low emission vehicles had smaller standard deviations of about 0,0001 g/km.
The evaluation of the daily weighted reference filters and reference mass results in a deviation of +/- 0,005 mg, this is 2% of a low filter loading of 0,25 mg.
These results corresponds well with the results of Volkswagen AG [1], so we can confirm the statements of this paper regarding the gravimetric mass measurement.

Statement

By our point of view the gravimetric measurement of the particulate mass emission is up to now the only one method, which is suitable to limit values of EU-4.
With some improvements e.g. filter balance with more accuracy, higher gas velocity across the filter, we see a potential for even a lower measuring range.

Reference:

[1]: Bechmann, Carli, Engeler, Garbe, Lach, Ryan, Schindler
Particulate emissions and their measurement in practice: Today and in future
Forum Partikelemissionen 24./25.10.2002, Nürnberg p. 33-51

2. Particulate size distribution - some influences on the test results

BMW had made investigations for the determination of particulate size distributions. In the following figures some effects are shown how test results may be influenced by

- Nucleation
- Sulphur content of the fuel
- Sampling system and samplingpoint

The particulate size distribution was measured with a twin SMPS with a Faraday-Cup Electrometer from the University of Vienna, Prof.Reischl.
Tests had been carried out on an engine test bed with a BMW Diesel engine M47 (2 lit., 110 kW / 4000 rpm). The operating point was 2400 rpm and 7 bar pme corresponding to a vehicle speed of 120 km/h.

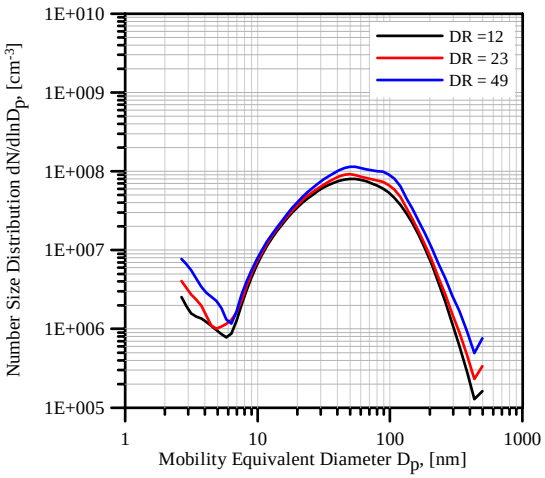


Fig.2: variation of dilution ratios, sampling point in front of catalyst, temperature 40°C, 210 ppm sulphur

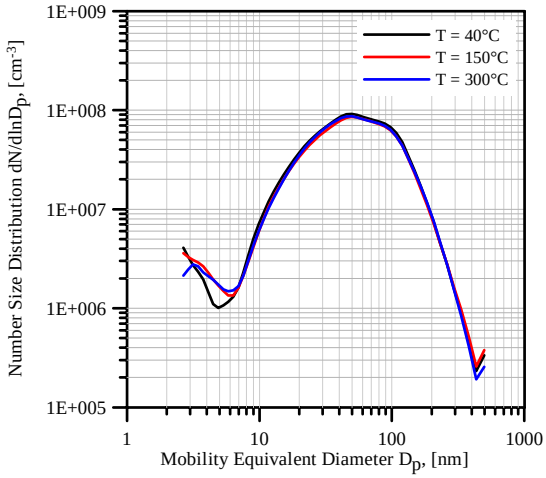


Fig.3: variation of temperature, sampling point in front of catalyst, dilution ratio 23, 210ppm sulphur

Figure 2 shows the size distribution with the sampling position in front of the catalyst, the fuel is standard diesel with 210 ppm sulphur. The measurements had been made with three different dilution ratios of 12, 23 and 49. It can be seen, that the three results are nearly the same and that there is no influence of the dilution ratio.

Figure 3 shows the result of the same setup with a dilution ratio of 23 but varying the sample temperature of 40°C, 150°C and 300°C. The results are identically, that means that in this case there is no influence of the sampling temperature.

In Figure 4 the sampling position is behind the catalyst. The monomodal distribution changes to a bimodal distribution with a sharp peak in the range of 5 to 20 nm. Additionally the shape of this peak depends on the dilution ratio.

Figure 5 has the same setup as Figure 4, but at these tests the sampling temperature was varied at constant dilution ratio of 23. In this case, the shape of the peak depends on the sampling temperature and the nucleation process becomes more complex.

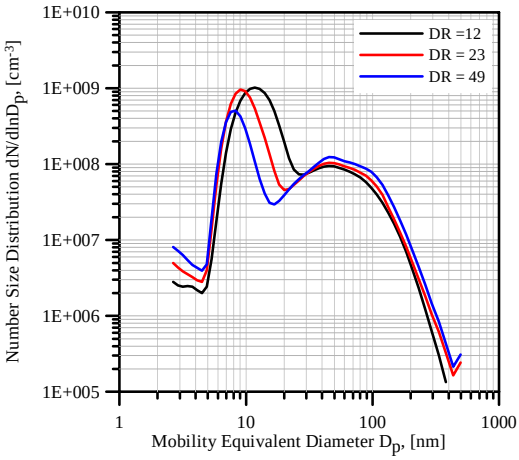


Fig.4: variation of dilution ratios, sampling point behind catalyst, temperature 40°C, 210 ppm sulphur

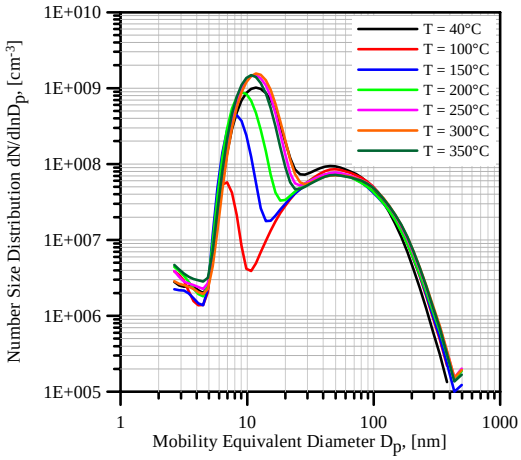


Fig.5: variation of temperature, sampling point behind catalyst, dilution ratio 23, 210ppm sulphur

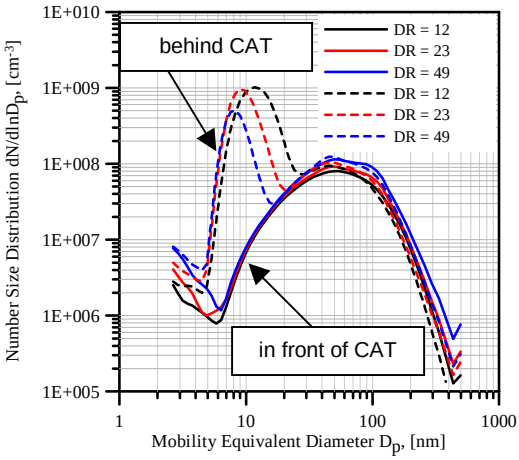


Fig.6: variation of dilution ratios, sampling point in front and behind catalyst, temperature 40°C, 210 ppm sulphur

Figure 6 shows the results of Figure 3 and Figure 4 for an easier comparison. In the range above 30 nm the shapes of sampling in front and after the catalyst are nearly the same, below 30 nm the nucleation effect can be seen very clearly.

Figure 7 has the same setup as Figure 4 but using a low sulphur diesel with 10 ppm. Though the sampling position is behind the catalyst in this case no nucleation can be observed.

Figure 8 shows a variation of sampling temperature. In this case there is also no nucleation being observed.

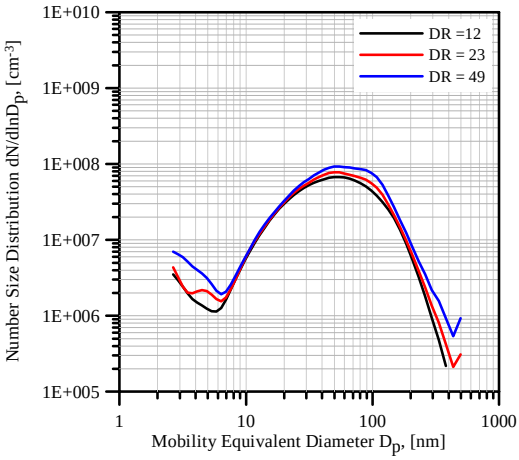


Fig.7: variation of dilution ratios, sampling point behind catalyst, temperature 40°C, 10 ppm sulphur

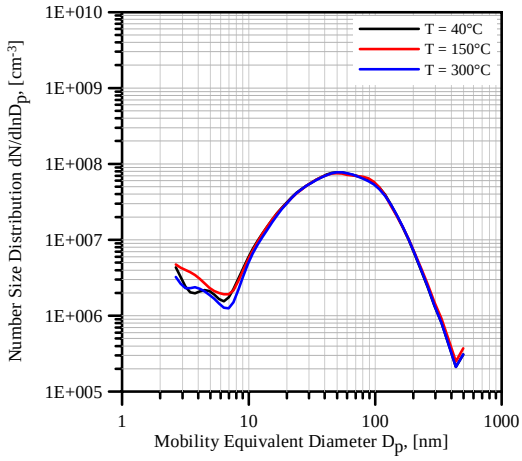


Fig.8: variation of temperature, sampling point behind catalyst, dilution ratio 23, 10ppm sulphur

sampling position / catalyst	dilution ratio	sampling temperature	sulphur in the fuel	Fig. No.
in front	12, 23, 49	40 °C	210 ppm	Fig. 2
in front	23	40, 150, 300 °C	210 ppm	Fig. 3
behind	12, 23, 49	40 °C	210 ppm	Fig. 4
behind	23	40 to 300 °C	210 ppm	Fig. 5
in front / behind	12, 23, 49	40 °C	210 ppm	Fig. 6
behind	12, 23, 49	40 °C	10 ppm	Fig. 7
behind	23	40, 150, 300 °C	10 ppm	Fig. 8

Table 1: Test-Matrix

Conclusion

The determination of particulate size distribution may be affected by

Nucleation
This effect arises at sampling positions behind the catalyst and can be observed at the exhaust tailpipe and also at the standard particulate sampling position of a CVS-System.

Sulphur
Especially those fuels with higher sulphur content cause the nucleation process. This influences the shape of the size distribution dramatically and increases the total number of particulates being measured.

Sampling system
Sampling position, sampling system, sampling temperature and dilution ratio may affect the shape of the size distribution and the total number beeing measured.

Statement

By our point of view are systems for particulate size determination **not suitable** for a **quantitative determination** of the particulate emission in connection **with legal limit values**.
The reasons for this statement are

- as shown above, the results may be affected e.g. by nucleation, fuel, sampling system
- today there is no method known for an absolute calibration of particulate size distribution measurement systems.

In our opinion the determination of the particulate size distribution is a good procedure in the **development process** of diesel engines for the **qualitative** assessment of measures in the field of the particulate emission.

Von	Bearbeiter	Telefon-Durchwahl	Telefax-Durchwahl	Schwieberdingen
FV/SLE	Khatchikian	0711/ 811-24923	0711/ 811-1686	11.11.2002

Dependence of particle size distribution on injection pressure

Summary

The influence of the injection pressure on the particle size distribution has been measured with a SMPS and a one stage ejector dilution unit. Measurement were carried out on a stationary test bench with a 3 l, 6 cyl., common rail direct injection engine from a passenger car, by varying the pressure in the rail. The sulphur content of the diesel fuel was < 10 ppm, and the sampling point was the tailpipe or the outlet of a transfer line.

First of all, the size distribution had been measured with the standard engine setting. In a second step, only the torque had been set to the value of the original operating point (the one with the original rail pressure, etc.) after changing the pressure. This had been done by adapting the end of injection. In a third step, the engine had also been set to the emission level of the original application by varying the EGR rate to set the soot emission (Bosch Smoke Number), and the start of injection for the NOx level. Finally, the size distribution had been measured in this configuration, but with the sampling point at the outlet of a transfer line.

When the original injection pressure of 550 bar is varied in a range of 250...1600 bar and only the engine torque is kept at 82 Nm, a slight decrease in the count median diameter (CMD) with increasing rail pressure can be found; on the other hand, the total number concentration (N) is reduced quite significantly. In the step three configuration (same emission as original application) both particle size and concentration are almost constant with changing injection pressure. When the residence time of the aerosol prior to dilution is increased by employing a transfer line, a smaller number of slightly larger particles can be measured.

With the test procedure and measurement conditions used in this investigation, no negative effect of high injection pressure on the particle size distribution could be found.

Introduction

The development of new diesel injection systems and components in the last decade has lead to a steep decline in soot emission levels. Most of this success is due to the introduction of direct injection systems, and the steady increase of the injection pressure. Since only the soot mass emission is relevant

for legislation, whereas recent publications indicate a correlation between the number concentration and the carcinogenic effect, a discussion on the size distribution of aerosols from diesel engines arose.

This section is a report on the measurement of the particle size distribution with different levels of the injection pressure.

Measurement setup

All measurements were performed with a scanning mobility particle sizer (SMPS) in a dual path configuration. Both paths have an identical arrangement with a DMA and a CPC, only that in one path the aerosol is heated upstream of the DMA. The heating section is not a thermodenuder, because there is no vapour adsorbing agent in it.

Dilution was achieved with a one stage (1:10) ejector system close to the sampling point, which could not be heated. For the calculation of the particle concentration, the measured dilution ratio was used (CO_2 balance). There are further dilution stages within the SMPS. The aerosol was taken from the tailpipe, or from the outlet of a transfer line (5 m length, 70 mm in diameter).

Test engine

A standard passenger car engine on a stationary test bench was employed for the measurements. Only the electronic control unit was a modified Bosch EDC 16 device, that allowed for tuning the engine parameters. Besides that, the EDC software was standard.

Some engine specifications:

- 3 l, 6 cylinder, direct injection, 150 kW
- Common-rail injection system (Bosch), with a CP 3 pump and a maximum rail pressure of 1600 bar
- Turbo charger with variable nozzle turbine (VNT)
- Cooled charge air and exhaust gas recirculation (EGR)
- Euro 3 emission standard

The engine was operated with low sulphur diesel fuel (< 10 ppm), which is probably the reason for the absence of a nucleation mode in all of the measured distributions.

Procedure

When the injection pressure is modified, a number of parameters like torque, NOx emission, soot emission and fuel consumption will also change. One can take this phenomenon as given, or one can try to tune the engine to get these parameters as close as possible to their original value. There are pros and cons to both approaches, so both were realised in the experiments. The measurement procedure was:

1. Setting the engine operating point and waiting for stationary conditions. The operating point was chosen to match a vehicle speed of 100 km/h: n = 2000 1/min; M = 82 Nm; q_air = 100 m3/h; p_rail = 550 bar.
   – Measuring the particle size distribution.

2. Changing the pressure in the rail. The adaptation of the torque is done automatically by the EDC 16 by changing some parameters, especially the end of injection.
   - Measuring the particle size distribution.

3. Changing the EGR rate, until the Bosch Smoke Number (SN) equals the value of the standard setting.
   Changing the start of injection to set the NOx level to the standard value.
   - Measuring the particle size distribution.

4. Switching from the sampling probe in the tailpipe position to the one behind the transfer line.
   – Measuring the particle size distribution.

Results

All of the measured size distributions have a log-normal shape without a nucleation mode. The difference between the curves from the heated and the cold path is quite small, which is probably due to the low sulphur fuel and to the low HC emission level of the engine. Therefore, the results can be discussed in terms of the count median diameter (CMD) and the total number concentration (N).

Measurements of CMD and N for a range of the injection(rail-) pressure are shown in **Fig. 1**. When only the torque is kept at the original value, there is a decrease in particle size with increasing injection pressure. On the other hand, the number of particles is reduced quite significantly. The change in the combustion process induced by the variation of pressure

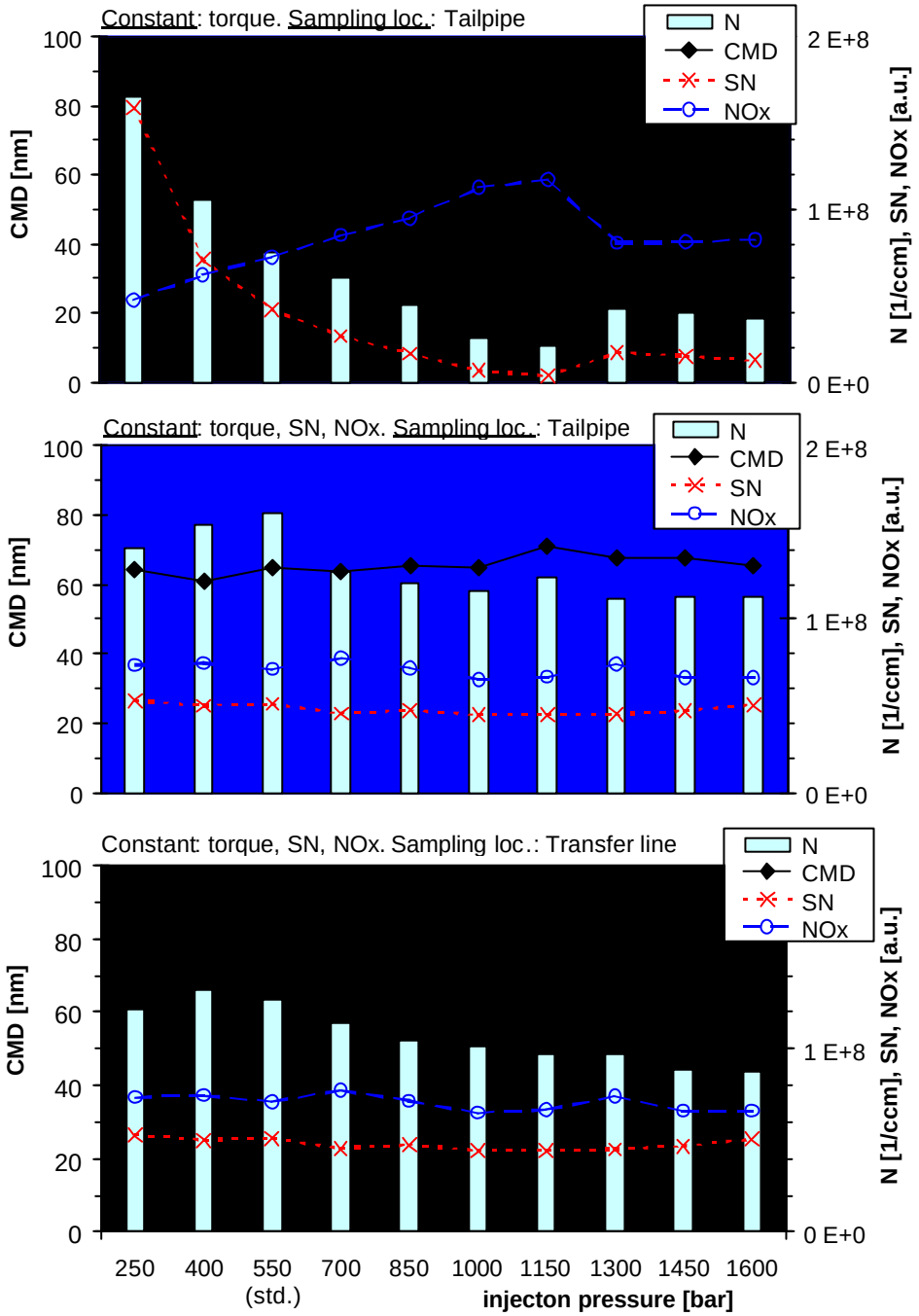


Fig. 1: Particle size (CMD), number concentration (N), smoke number (SN) and NOx level versus injection pressure; n = 2000 1/min, Torque = 82 Nm (v = 100 km/h). The standard injection pressure is 550 bar for this engine speed and load.
Top: Torque set to standard value.
Middle: Torque, Smoke and NOx set to standard value.
Bottom: Like middle, but sampling behind transfer line.

and injection timing leads to a remarkable modification of the emission behaviour of the engine. This is also shown in the figure. The rise in particle emission from 1300 bar on is caused by the electronic control unit, which automatically increases the exhaust gas recirculation rate. It should be pointed out here that neither the injection system, nor the software in the EDC are designed for an injection pressure in this range at this engine operation point. For example, the standard design sets a rail pressure of 1300 bar at n = 2500 1/min, mep = 15 bar, and 1600 bar at n = 4000 1/min, mep = 12 bar.

When the NOx and smoke levels are set to their standard values as described above, no clear correlation between particle size and number concentration and the injection pressure can be observed. With the same measurement procedure, but the sampling probe at the outlet of a transfer line, a smaller number of slightly larger particles can be measured.

The smoke number (SN) measures the amount of soot in a specified volume; it does not contain any information on the exhaust gas flow rate. Therefore, the volume related number concentration is shown in the figure. The course of the distance related number concentration N [1/km] differs from it, because the EDC reduces the intake air flow with rising injection pressure. This leads to a clear decrease of N [1/km] with increasing injection pressure, especially in the measurements with constant smoke number and NOx level.

In the process of applying an injection system and an electronic control unit to an engine, the parameters like EGR, injection timing, and so on are set in order to reach a certain trade-off concerning smoke emission, NOx emission and fuel consumption. Therefore, it seems useful and necessary to set the engine to the original emission levels after changing the injection pressure – the same would be done in an application process.

The transfer line is only a very rough approximation to the agglomeration processes, that occur in the atmosphere behind the tailpipe. Nevertheless, the measurements with the transfer line indicate that the influence of the injection pressure on the atmospheric aerosol is even lower, than the tailpipe measurements show.

In summary it may be said, that with the test procedure and measurement conditions used in this investigation, no negative effect of high injection pressure on the particle size distribution could be found.

Investigation of Alternative Methods to Determine Particulate Mass Emissions

Dr. Oliver Mörsch
Petra Sorsche
DaimlerChrysler AG

Background and Executive Summary

Currently alternative particle measurement techniques for the type approval of exhaust emissions of vehicles in addition to the actual gravimetric procedure are considered within UNECE/WP.29/GRPE due to the ongoing discussion on health effects of fine particles. In this context novel, unconventional particle characteristics like number, size and surface are focussed as measurand as well as the mass of black carbon or the solid particle fraction.

To date still many uncertainties concerning the evidence, strength and kinds of health effects of particles exist and also an alternative health-related particle dose measure besides the traditional mass metric could not yet be proven causally. The introduction of an additional type approval method is therefore questionable, risk of losing consistency in exhaust gas improvements and misguided engine developments must be taken in account. As the limit of detection of the actual type approval procedure is also suitable for future regulatory demands no additional certification testing technique is required.

DaimlerChrysler was motivated to investigate some of the discussed alternative measure-ment methods for elemental carbon due to their potential to act as development tool. Thereby the main quality characteristics and the suitability for practical use of the measurement systems "laser-induced incandescence (Li^{2}sa)" and "photoacustic sensor (PASS)" in comparison to the standard gravimetric procedure and the actually utilized real time measurement tool (opacimetry) have been the examination items. Measurements were performed with current mass production diesel and gasoline vehicles of different manufacturers.

Both measurement systems for the determination of the mass emission of elemental carbon offered excellent quality characateristics for engine exhaust developmental purposes:

- The correlation to gravimetrically determined particle emissions is significant (regression coefficient = 0,98). For modern vehicle concepts the results of these systems account for about 80 % of total particulate mass.
- The limit of detection is at least one order of magnitude better than this of the standard procedure.
- Because of a time resolution ? 5 Hz particle formation during engine combustion could be cause studied.
- Cross interferences to other exhaust components are not given.
- System calibration is performable via coulometry.

It should be mentioned, that Li^{2}sa measurements revealed a non-linear relationship between soot mass and signal value. As the PASS system shows additionally advantages regarding practical routine application it seems to be the more preferable technique and has the potential to substitute the actually utilized opacimeter as online development tool.

Li2sa-determined primary particle diameters of different engine concepts did not offer notable size differences, the expressiveness of this measurand is questionable so.

Experimental

Investigations were carried out on a diesel test cell equipped with twin roller chassis dynamometer and a CVS system with diesel particulate tunnel. Several methods were applied in parallel (Figure 2).

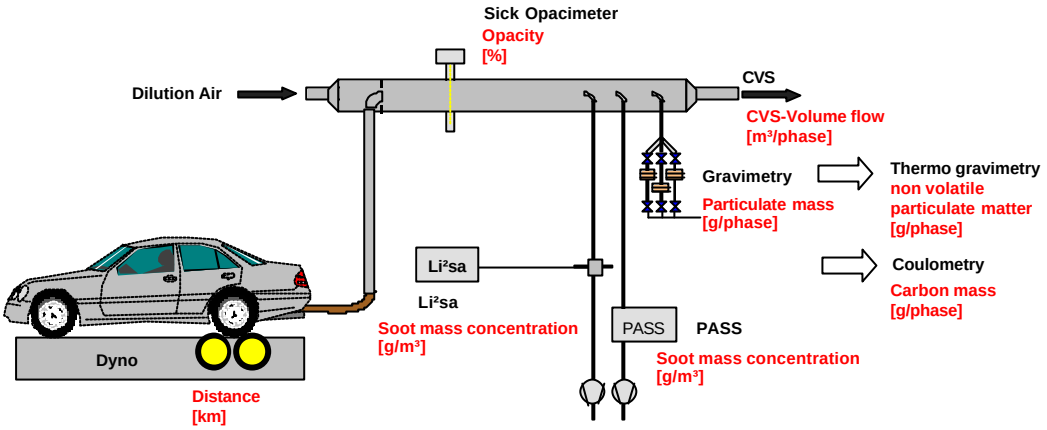


Figure 1: Experimental setup

Applied Methods:

Gravimetry: Standard filter method as described in the regulations
Thermo-gravimetry: After the weighing the standard teflon coated filters are heated to 250 °C for a defined time to eliminate volatile matter (mainly fuel and oil constituents). After this treatment the filters are weighed again and the amount of non volatile particulate matter is calculated.
Coulometry: Special filters (pretreated quartz fiber) are loaded according the standard procedure and are analyzed after the test by coulometry for the total carbon mass.
Opacimetry: The opacity is measured across the tunnel.
Li²sa (laser induced incandescence soot analyzer): A small sample is taken iso-kinetically and delivered to the measuring chamber of the device.
PASS (photo acoustic soot sensor): A small sample is taken iso-kinetically and delivered to the measuring chamber of the device.

Method	sampling	analysis	measured value	# of phase results
Gravimetry	iso-kinetic	off-line	particulate mass on filter	101
Thermo-gravimetry	iso-kinetic	off-line	non volatile particulate mass on filter	62
Coulometry	iso-kinetic	off-line	carbon mass on filter	12
Opacity	in-situ	continuous	opacity	101
Li²sa	iso-kinetc	continuous	soot concentration	101
PASS	iso-kinetc	continuous	soot concentration	76

Table 1: Characteristics of the investigated systems

Testing program

During the evaluation period 47 tests were run, most of which European driving cycles. 8 Tests were conducted at constant speed (50, 100 and 120 km/h).

Vehicle	# of Tests
Diesel (EU2)	3
Direct injection diesel (EU3-4)	27
Gasoline (EU4)	3
Gasoline direct injection (EU4)	14
Blank test	2

Table 2: Tests conducted during testing period

Calibration of Opacimeter

From the opacity T a mass concentration of particulate matter can be calculated according to:

$c = k * \ln(100/(100-(T-T_0))$

with
c = mass concentration [g/m³]
k = calibration factor [g/m³]
T = opacity [%]
T_0 = opacity value at zero concentration [%]

Experiments showed very good correlation of opacity data with thermo-gravimetric results. The calibration factor k was determined according figure 3 to k = 0,2381.

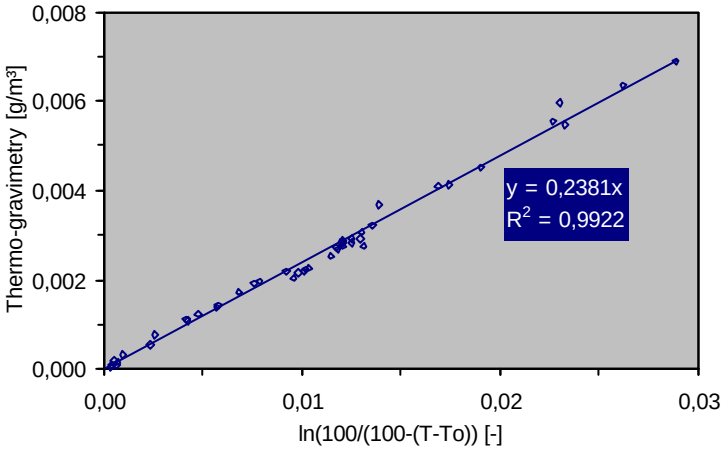


Figure 2: Calibration of opacimetry

Calibration of Li²sa and PASS

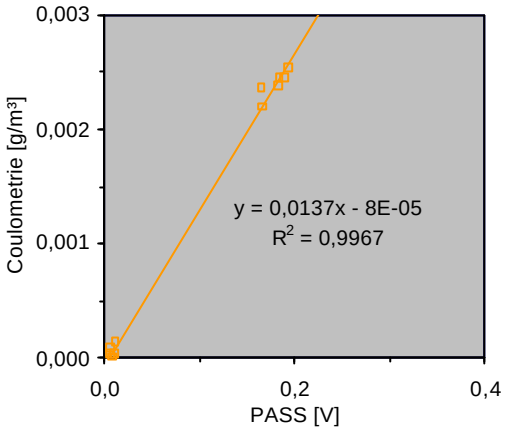


Figure 3: Calibration of the PASS with results from coulometry

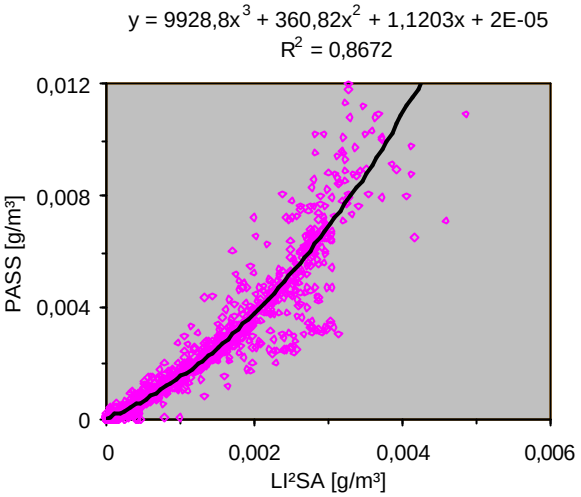


Figure 4: Third order calibration of Li²sa using calibrated values from PASS

The PASS system was calibrated using coulometric results (see figure 4). A linear calibration was applied, since PASS and thermo-gravimetric results showed a good linear correlation.

The Lisa system was calibrated using the calibrated PASS data. This was necessary because of an assumed non-linear relation between soot mass and Lisa signal. Since only few points with coulometric results were available, these were not sufficient for a non linear calibration.

Correlation to standard gravimetric procedure (with/without volatiles)

Figure 6 shows the correlation of the results from the different systems with the standard gravimetric method. Each point represents the average concentration of one phase. As to be expected, the gravimetric method yields the highest results, since all other methods register only part of the particulate matter on the filter. Li²sa, PASS and coulometry give the amount of soot or elementary carbon respectively. In the tests conducted soot was typically about 80 % of the total gravimetric mass. Results from opacimetry and thermo-gravimetry are slightly higher and typically reach values around 90 %.

As can be seen from figure 6, opacimetry, Li²sa and PASS show a very strong correlation to thermo-gravimetric results with coefficients of variation of 0,97 to 0,99.

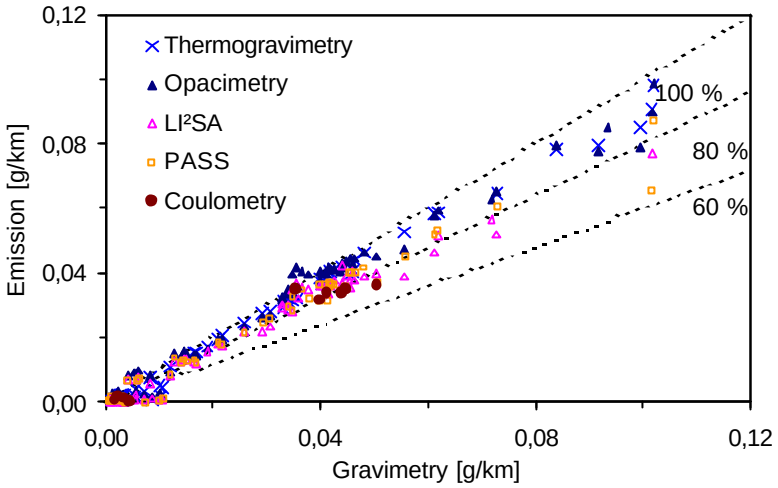


Figure 5: NEDC-Phase average emissions plotted over results from gravimetry

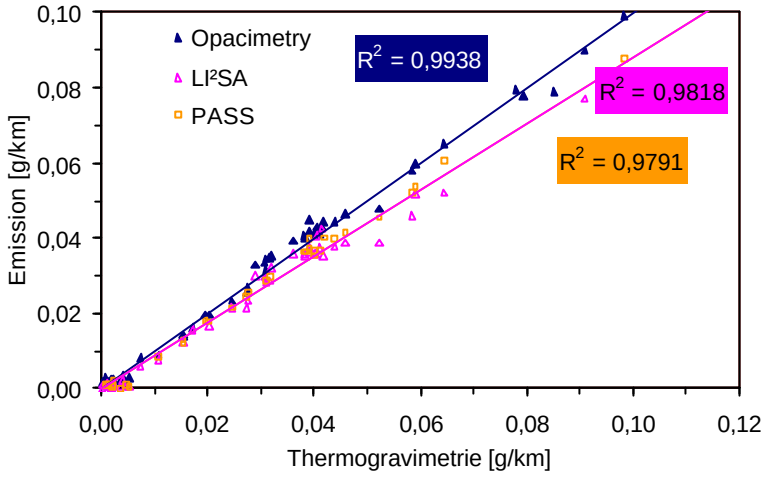


Figure 6: Correlation of mass emissions calculated from opacity, Li²sa and PASS with thermo-gravimetry (NEDC)

At very low emission levels Li²sa and Pass still show a reasonable correlation. This confirms that Li²sa and PASS are applicable for emission levels far below the Euro 4 level.

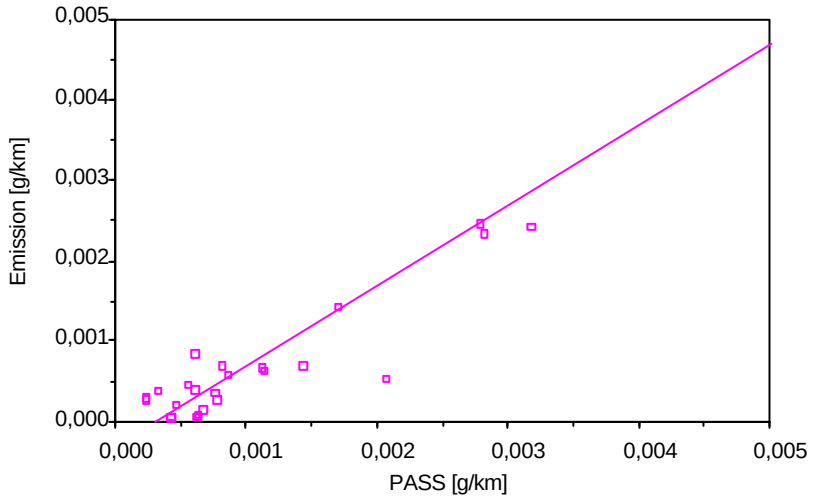


Figure 7: Correlation of opacity, Li²sa, thermogravimetry related mass emissions with PASS results at low emission levels

Time resolution

For development purposes time resolution is an important issue. Figure 9 shows a comparison of the time resolved mass emission during the NEDC. In the investigated setup the opacimeter has the best time resolution since it is directly applied to the bulk gas flow. For the Li²sa and PASS system small samples are extracted and a delay time depending on length of sample line and sample flow can be observed. The Li²sa system at the time of this experiments featured only a sampling rate of 0,5 Hz. This is the reason why the peak at 120 s is not fully resolved. In the meantime a sampling rate of 20 Hz is available. The PASS has a sampling rate of 5 Hz, however, T90-time is in the order of 1 s. Therefore, time resolution is not as good as for the opacimeter, however, it is sufficient for development purposes.

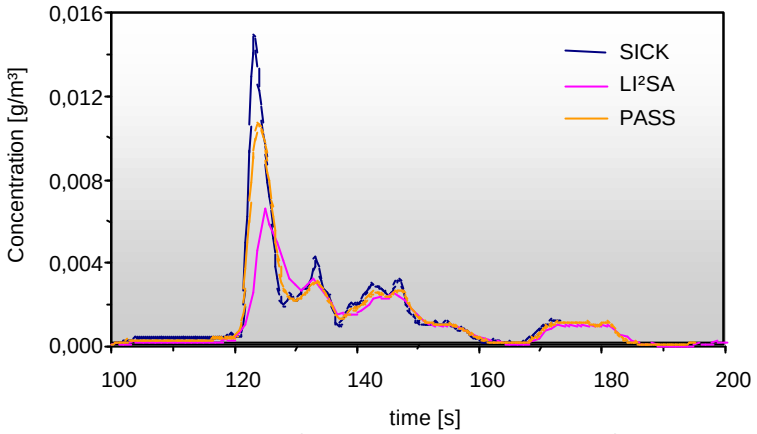


Figure 8: Comparison of time resolution (section of an NEDC)

Signal noise and limit of detection

To study the limit of detection of the measurement methods, blank tests (emission test without vehicle) were carried out. In the case of the gravimetric method these tests indicate the limit of detection of the entire process (weighing, filter handling, loading, weighing). Figure 1 shows the difference in weighing before and after test. The zero scatter (standard deviation ?) is +/- 0,8 mg. Therefore, the LOD (3 * ?) is estimated to be 0,025 mg. This is equivalent to approximately 1 mg/km in an NEDC which is 4 % of the Euro 4 emission limit. By optimization of the gravimetric method (optimized flow, micro balance with increased accuracy) it will be possible to decrease the LOD to approximately 0,01 mg/filter.

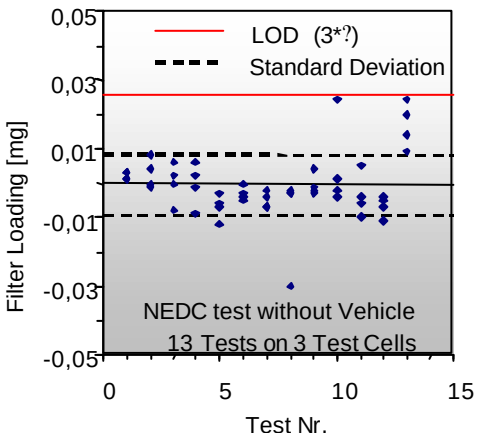


Figure 9: Determination of LOD of gravimetric method by blank tests

For the continuous measurement techniques signal noise and stability of the base line are important criteria for the achievable limit of detection. Figure 10 shows the signals during a blank test. The opacimeter has the highest signal noise. In addition a baseline drift can be observed. PASS has a very low signal noise and offers the highest potential for low emission measurement. The offset of opacimeter and PASS is due to contamination (see below). For the repeatability and accuracy of test results the scatter of the phase average is incisive.

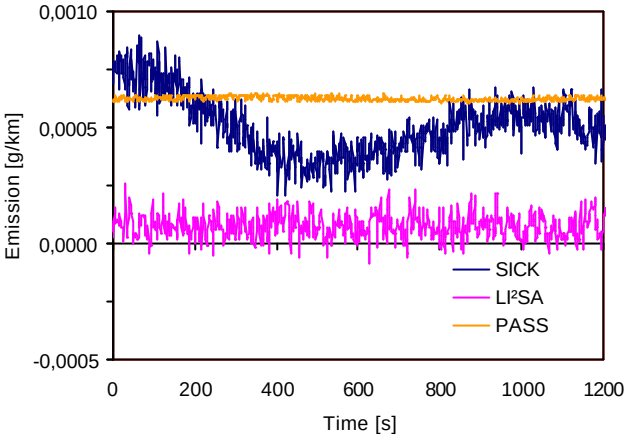


Figure 10: Signal noise during blank test

Zero drift

In figure 11 the zero signal prior to each test is shown. A pronounced increase of the zero signal due to fouling of the optical interface can be observed for the opacimetry. The PASS also shows an increasing zero signal, although fouling is much less pronounced. The zero signal of Li²sa is very stable. No influence from fouling can be seen. Due to the zero drift opacimetry requires a zero correction. This is done by the determination of T_0 prior to each test. The same is possible for the PASS system.

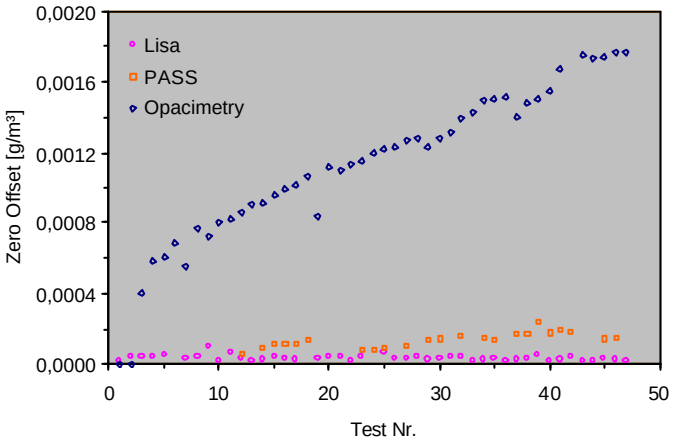


Figure 11: Zero drift due to fouling

Cross interference

It is known that the opacimetry suffers a slight cross interference from NO_2. For vehicles with high NO_2 and low particulate emissions results are influenced noticeably (Figure 13). A NO_2 concentration of 100 ppm causes an interference of 4 mg/m³. For Li²sa and PASS no cross interference was observed.

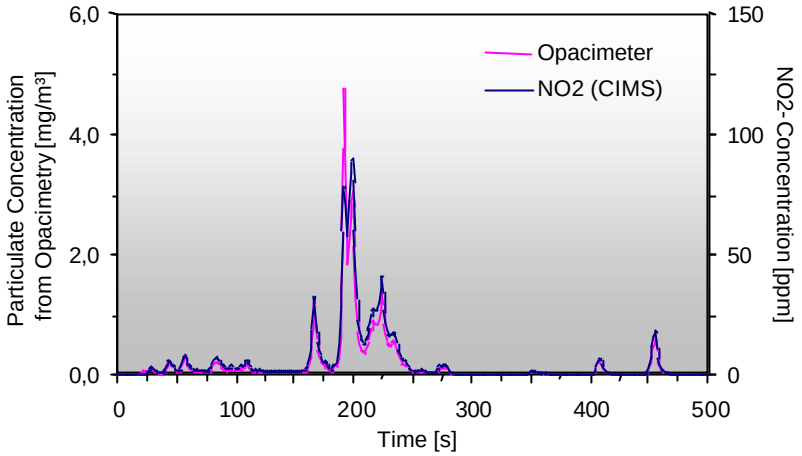


Figure 112: NO_2 interference of Sick opacimeter

Measurement of primary particle diameter with Li²sa

The Li²sa system offers the possibility to determine the primary particle diameter of the soot particulate. As figure 13 shows, this diameter is independent on particle concentration (and thus engine load) and combustion principle. For all investigated vehicles it was in the range of 25 – 35 nm.

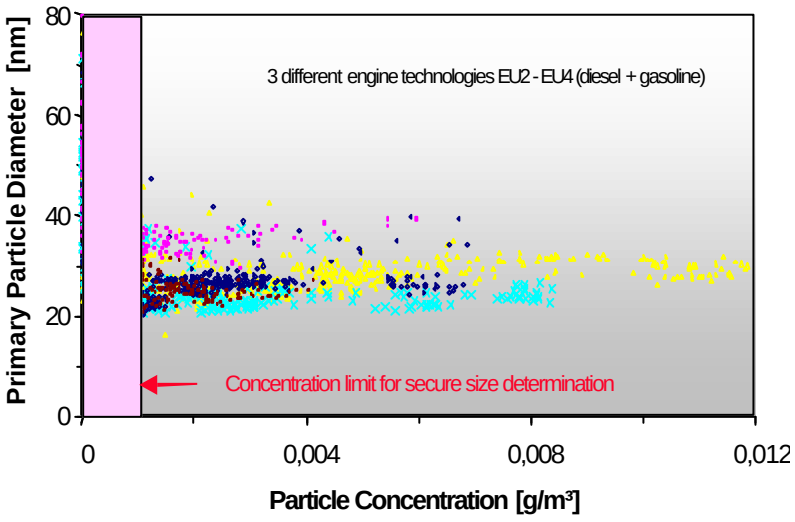


Figure 13: Primary particle size plotted over particle concentration for different vehicles

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Vehicle Exhaust Particle Size Distributions: A Comparison of Tailpipe and Dilution Tunnel Measurements

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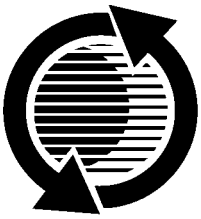

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ABSTRACT

This paper explores the extent to which standard dilution tunnel measurements of motor vehicle exhaust particulate matter modify particle number and size. Steady state size distributions made directly at the tailpipe, using an ejector pump, are compared to dilution tunnel measurements for three configurations of transfer hose used to transport exhaust from the vehicle tailpipe to the dilution tunnel. For gasoline vehicles run at a steady 50 - 70 mph, ejector pump and dilution tunnel measurements give consistent results of particle size and number when using an *uninsulated* stainless steel transfer hose. Both methods show particles in the 10 - 100 nm range at tailpipe concentrations of the order of 10^4 particles/cm^3. When an *insulated* hose, or one containing a *silicone rubber coupler*, is used to test small 4 cylinder gasoline vehicles, a very intense nanoparticle / ultrafine mode at < ~30 nm develops in the dilution tunnel particle size distribution as the vehicle speed is increased to 60 and 70 mph. This nanoparticle mode coincides with a rise of the transfer line temperature to about 180 - 250 °C. It is much less evident for the full size gasoline sedan, which has cooler exhaust. Both tailpipe and dilution tunnel measurements of diesel vehicle exhaust reveal an accumulation mode peak of ~10^8 particles/cm^3, centered at 80 -100 nm. In this case, even with the uninsulated transfer hose an intense ultrafine peak appears in the dilution tunnel size distributions. This mode is attributed to desorption and/or pyrolysis of organic material, either hydrocarbon deposits on the walls of the steel transfer hose or the silicone rubber, by hot exhaust gases, and their subsequent nucleation in the dilution tunnel. This substantially limits the ability to make accurate particle number and size measurements using dilution tunnel systems.

INTRODUCTION

Prompted by potential health concerns, the past few years have witnessed a growing interest in particulate matter (PM) measurements, both ambient and from a wide variety of emissions sources. These measurements are conventionally performed by recording PM mass. The ambient standards are written in terms of mass concentrations, and emission regulations are based on mass rates. However, in order to understand better the nature of the mobile source contribution to ambient PM, many research groups are currently extending their investigations to include measurements of the numbers and sizes of particles in motor vehicle exhaust. Because the standard procedure for tailpipe PM measurements utilizes a dilution tunnel to cool the exhaust and to prevent water condensation, concerns have emerged that the test cell measurements of motor vehicle PM do not reflect the “real world” emissions.

The root of the concern is that vehicle exhaust, a hot, complex, mixture of gaseous emissions and particles, is transformed differently when diluted in a tunnel as compared to the “real world”. Particles are not immutable; they readily undergo transformations, such as coagulation, condensation, and adsorption, and new particles can be created by nucleation of gaseous particle precursors in the diluted and cooled exhaust. Under “real world” conditions, motor vehicle exhaust is diluted rapidly, in less than one second, and by a large amount, a dilution ratio of greater than 100, into air of variable temperature and humidity. In the test cell, the exhaust is conducted to the dilution tunnel, typically by a 10 cm diameter by 5 m long tube, where it is then diluted by a factor of between 5 and 50, depending on test conditions, using dry air at room temperature. This discrepancy between dilution times, extents, temperature, and humidity can potentially lead to significant differences in the nature of the particulate emissions.

Kittelson[1,2] has extensively discussed the possible ways in which coagulation, adsorption, and nucleation can differ between these two dilution scenarios and potentially affect particle number emissions and the nature of the size distributions. However, the interpretation of these processes in a specific situation depends a great deal on the nature of the test vehicle: Does it have a diesel or gasoline engine? Is the fuel conventional or low sulfur? Does the exhaust aftertreatment include a catalyst? A particle trap? For example, ultrafine, or nanoparticles, might be formed by sulfate nucleation in the diluted exhaust from a diesel vehicle using sulfur-containing fuel and incorporating a particle trap. Whereas, in the absence of the particle trap, the sulfates condense on the carbonaceous particles normally formed during diesel combustion, and many fewer ultrafine particles are observed.[3] Similarly, it might be anticipated that removal of gaseous hydrocarbons would make condensation less of a factor for a catalyst equipped vehicle as compared to a non-catalyst vehicle, and that coagulation might be less important in gasoline vehicle exhaust as compared to diesel exhaust, because of the inherently lower gasoline engine PM emissions.

That dilution conditions, such as the dilution ratio, affect particulate mass has been appreciated for some time.[4,5] Recently, the effect of dilution ratio, temperature and humidity on particle size distributions has also begun to receive attention.[2,3,6,7] As seen in the present work, the transit of the hot exhaust through the transfer line to the dilution tunnel further enhances the likelihood that the particle distribution measured in the tunnel does not match what comes out of the tailpipe. Particle number is in principal more sensitive to the dilution process than particulate mass, because coagulation alters the number of individual particles, but not the overall PM mass, and, though nucleation can create large numbers of nanometer size particles, they contribute relatively little to the total PM mass because of their small size.

The purpose of the present paper is twofold: First, it compares two distinctly different combustion particle sampling methodologies, namely the ejector pump and the dilution tunnel. Secondly, whereas previous work[1,2] has emphasized the possibility that dilution tunnel measurements may miss nanoparticles attributable to vehicle exhaust, the present paper explores the complementary issue of particle “artifacts”, i.e., particles not emitted by the tailpipe, but nonetheless recorded in the dilution tunnel. Two sources of artifacts are identified: deposits on the interior walls of the transfer line and shedding of materials used in the transfer line. In a similar vein, Kittelson[1,2] has given examples of long stabilization times needed after transient changes in diesel engine load, and attributed this to the storage and release of volatile particle precursors in the engine and sampling system. In both the previous and present work, these particles are primarily in the ultrafine, or nanoparticle, mode. Whereas these “artifacts” modify the appearance of diesel exhaust particle size distributions, they can completely overwhelm, in terms of particle number, the PM emissions from current model port injection gasoline vehicles. The artificial sources yield higher numbers of particles with an increase in exhaust temperature; thus, they serendipitously mimic the behavior one might expect from increasing vehicle speed or load and can easily be confused as “real” vehicle effects. They may be responsible for some of the comments appearing in the literature that “gasoline vehicles emit less PM mass, but as large a particle number as diesel vehicles”.

EXPERIMENT

PARTICLE SIZE DETERMINATION – Particles, sampled either from the tailpipe or from the dilution tunnel, are analyzed using two model 3934 scanning mobility particle sizers (SMPS) from TSI Inc. Large particles in the sample stream are removed with a 577 nm 50% cutoff impactor. The remaining particles are brought to a Boltzmann charge equilibrium by passing them through a ^{85}Kr bipolar charger and are injected along the outer periphery of a cylindrical cavity that constitutes the differential mobility analyzer (DMA). A voltage applied between the outer wall and the central cylindrical electrode induces a drift of the positively charged particles through the sheath flow and towards the central electrode. Particles exhibiting the correct charge to mobility ratio exit through an aperture at the downstream end of the DMA, are transported to a model 3010-S condensation nuclei counter (CNC), and counted. The size resolution of the instrument typically ranges from ±0.5 nm at 15 nm to ±30 nm at 500 nm at the classifier flow settings used in the present experiments (0.4 L/min aerosol flow and 4.0 L/min sheath flow). A correction for multiply charged particles is applied using the manufacturer provided algorithm.

Two minute scans were used to record particle size distributions simultaneously at the tailpipe and from the tunnel. The scans were performed at approximately 3 - 5 minute intervals. For the gasoline vehicles, the particle emissions are sufficiently small that typically 5 scans are averaged in order to minimize statistical noise that would otherwise result in a “spiky” appearance for the size distributions. Consistency of the two SMPS instruments was confirmed by connecting both instruments to the tunnel and verifying that the size distributions are essentially identical.

Number weighted particle size distributions are plotted as $dN/dlog(D_p)$, i.e., as the number concentration of particles in a given size channel normalized by the logarithmic width of the channel. The values have been appropriately scaled to give tailpipe concentration. These are converted to mass weighted distributions by multiplying by D_p^3 and the particle’s density, either known or guessed. The two types of tailpipe concentrations can be converted further to number or mass emission rates, respectively, by multiplying by the relevant exhaust flow rate. The total number or mass emission rates are then computed by integrating over particle diameter.

TEST VEHICLES – Four vehicles are used in the tests reported here: a small, U.S., 4-cylinder, 1997 model, passenger car equipped with a three-way catalyst (car labeled US4); a European, 4-cylinder, 1997 passenger car, with three-way catalyst (E4); a 1996, full size, 8-cylinder, U.S. car (US8); and a 1998, direct injection, diesel passenger car, with an oxidation catalyst (DV). All are relatively low mileage vehicles that meet the current gaseous and PM emissions standards.

The following fuels are used: California Phase II summer regular grade gasoline for the 4 cylinder U.S. car, European certification fuel for the 4 cylinder European gasoline car, California Phase II summer premium grade gasoline for the 8 cylinder U. S. vehicle, and European certification premium #2 diesel fuel for the diesel passenger car.

DILUTION TUNNEL – The test cell and chassis dynamometer have been described in detail previously[8,9]. Here, it is primarily the dilution process that is of interest. Exhaust gas from the test vehicle is transferred to the dilution tunnel through a corrugated stainless steel tube. Separate transfer tubes, as well as dilution tunnels, are used to test gasoline and diesel vehicles. For the gasoline vehicle tests the transfer tube is 9.1 cm in diameter and 5.8 m long; whereas the diesel transfer tube is 10.4 cm in diameter and 7.6 m long. Table 1 lists the dilution specifications for the various vehicle type and speed combinations that were tested. The exhaust flow rates range from about 0.6 m^3/min for the 4 cylinder gasoline vehicles running at 50 mph to about 1.7 m^3/min for the diesel vehicle and the large gasoline vehicle at 70 mph. Thus, the transit time between tailpipe and dilution tunnel ranges from 1.3 to 3.1 seconds for the gasoline vehicle tests and from 2.2 to 5.7 seconds for the diesel vehicle tests.

Table 1. Test vehicles and exhaust dilution conditions.

Vehicle	Speed (mph)	Exhaust flow (m^3/min)	Tunnel flow (m^3/min)	Primary dilution ratio	Second. dil. ratio	Tailpipe dilution ratio	Transfer hose[a] temperature (°C)
US4	50	0.63	19.8	31.5	1	8	120 – 160
	60	0.85	19.8	23.3	1	8	175 – 215
	70	1.19	19.8	16.6	1	8	260– 300
E4	31	0.44	9.9	22.4	1	8 & 58	~ 113[b]
	44	0.59	9.9	16.6	1	8 & 58	130 – 145
	63	1.00	9.9	9.87	1	8 & 58	160 – 260
US8	50	0.83	19.8	23.7	1	8	~ 113[b]
	60	1.16	19.8	17.1	1	8	113 – 121
	70	1.58	19.8	12.5	1	8	160 – 177
DV	50	0.88	19.8	22.4	8	57	~ 113[b]
	60	1.27	19.8	15.5	8	57	120 – 140
	70	1.78	19.8	11.1	8	57	160 – 180

[a]Applies only to insulated transfer hose; the uninsulated line remains below about 175 °C.
[b]Minimum temperature maintained by heater.

The dilution tunnels are constructed from 30.4 cm diameter electropolished stainless steel tubing. Heated (38 °C), filtered, low humidity (-9 °C dewpoint) dilution air enters at the upstream end through a subsonic venturi (smooth approach orifice). The exhaust gas is introduced in the downstream direction, along the dilution tunnel axis, and just upstream of an orifice plate, which is used to ensure rapid mixing of the exhaust with the dilution air. The tunnel operates in the turbulent regime at a constant total (exhaust + diluent) flow of between 10 and 30 m^3/min. In the present study, vehicles US4, US8, and DV were tested at a tunnel flow of 20m^3/min and vehicle E4 at 10 m^3/min. The corresponding primary dilution ratios, listed in Table 1, range from 10 to 32.

A sample of the tunnel flow is withdrawn at a distance of more than 10 tunnel diameters downstream from the orifice plate. A 0.95 cm diameter, J-shaped, tube pointing upstream parallel to the tunnel axis is used to extract the sample at a flow rate of 0.4 L/min. This sampling is not isokinetic, but for the 10 - 500 nm particle range relevant to exhaust particulate matter, this provides a representative sample regardless. For the gasoline vehicle tests, the sample is directly introduced, using Tygon tubing, into the SMPS. The diesel vehicle particulate emissions are sufficiently high to require secondary dilution. This is accomplished by using an ejector pump to extract a sample from the tunnel via the aforementioned J tube. The output flow from the ejector pump is then sampled at 0.4 L/min into the SMPS for particle size measurements.

As the curve marked “tunnel background” in Figure 1 shows, the filtered dilution air is not entirely free of particles; however, about 90% of the particles have been removed. It is also apparent from the figure that the gasoline vehicle particulate emissions are sufficiently low as to require subtraction of this background signal. After subtraction, there is good agreement between the tailpipe and dilution tunnel measurements of particle size distribution (see also Figures 3 and 4 below). Background subtraction for the ejector pump is not required since it employs particle free N_2 (or air) for dilution.

The tunnel PM measurements are carried out in three configurations: 1) using the corrugated stainless steel transfer tube, 2) insulating and heating the transfer line, and 3) employing a short section of silicone rubber tubing to connect the tailpipe to the transfer tube. The heater only operates during cold start to prevent water condensation; subsequently the exhaust gas is sufficient to maintain the transfer tube to above the dewpoint.

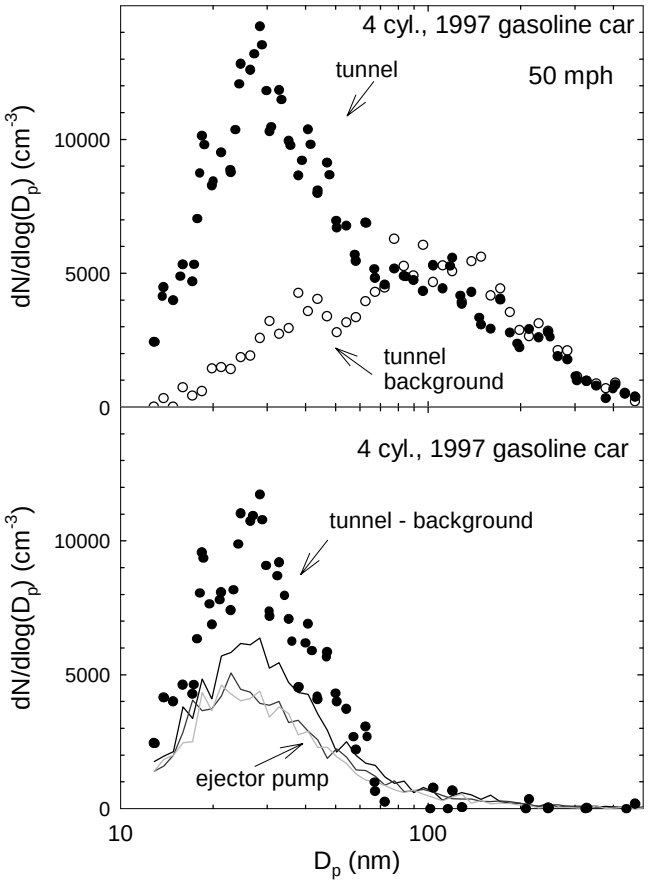

Figure 1. Top panel: Dilution tunnel particle size distributions recorded with and without vehicle (E4) exhaust. The uninsulated transfer tube is used to conduct the exhaust to the tunnel. Bottom panel: Comparison of ejector pump measurements of exhaust particle size with tunnel measurements after subtracting the background. All concentrations are converted to equivalent tailpipe concentrations.

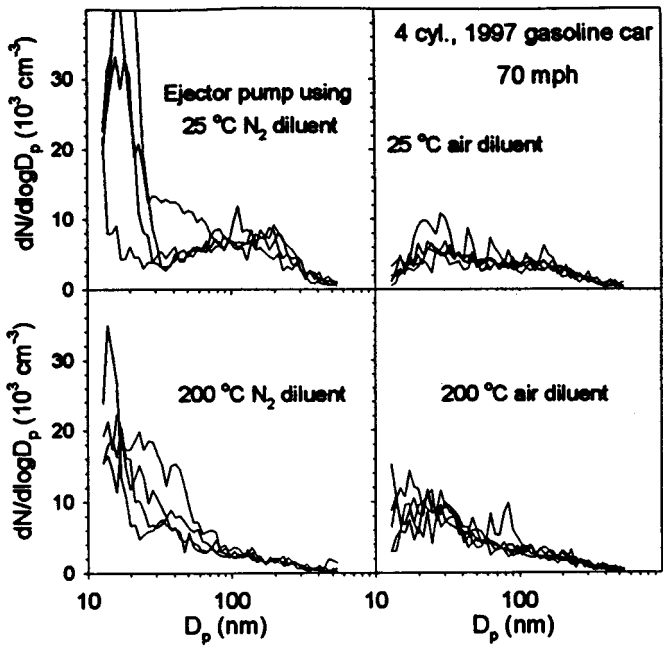

Figure 2. A comparison of ejector pump measurements of tailpipe PM concentration using N_2 and air diluent at either 25 °C or 200 °C. The measurements are made sequentially and are thus subject to fluctuations in the vehicle emissions.

During the 70 mph steady state tests, the exhaust can heat the transfer tube as high as 300 °C. Although at our test facility flanges are added to the tailpipes of test vehicles to enable an entirely metal connection to the tunnel, it is a common practice at many other facilities to employ a flexible silicone rubber coupler to connect the tailpipe to the dilution system, hence the reason for the third test configuration.

EJECTOR PUMP SAMPLING – Ejector pump diluters, from Dekati Ltd., are used to sample vehicle exhaust directly from the tailpipe. The ejector pump is mounted onto the tailpipe with a short, J shaped, 0.6 cm diameter, tube extending into the tailpipe via a compression fitting, and facing open end upstream. Particle free air, or N_2, at 2 atm overpressure is forced at high velocity past a small orifice in the ejector causing a pressure drop, due to the Bernoulli effect, which acts to pump some exhaust from the tailpipe. The same air, or N_2, then serves as the diluent. The dilution ratio for the ejector pump is fixed by the orifice size. It is nominally about 8, but varies from one unit to another due to small differences in orifice size. In these experiments, we use the manufacturer specified dilution ratio. Higher dilution ratios are readily achieved by cascading two or more units.

In our standard approach, we use N_2 as the diluent because of its ready availability. The first ejector stage, as well as the N_2 supplied to it, is heated to about 200 °C. The second stage, when used, remains uninsulated and employs room temperature N_2. In order to ascertain possible effects of this combination of diluent and tempera-

ture on the particle size distribution, the following comparison was performed: the ejector pump was operated with 1) N_2 at 25 °C, 2) N_2 at 200 °C, 3) air at 25 °C, and 4) air at 200 °C. As seen from Figure 2, the temperature of the first ejector stage appears to have little effect on the particle size distribution. Compared to the distributions recorded using air diluent, those obtained with N_2 show higher and more variable particle concentrations in the 10 - 30 nm range. However, relative to the sampling effects that are discussed below, i.e., order of magnitude differences in particle size distribution, the variations between the distributions obtained using N_2 versus air diluent are minor. It is unclear whether they are due to the choice of N_2 versus air diluent, minor examples of the artifacts described below, or simply normal variations in the engine emissions.

RESULTS

GASOLINE VEHICLE: *UNINSULATED* TRANSFER LINE – Prior to a set of steady state tests, each vehicle is warmed up over at least Phase 1 of the FTP drive cycle, followed by 5 or more minutes of steady driving at 50 mph. For many, but not all, of these preparatory drives the exhaust is directed outside the test cell and not into the transfer tube and dilution tunnel. In this case additional time is allowed for the vehicle exhaust to heat the transfer line to above the dewpoint prior to making the particle size measurements.

Figures 3 and 4 compare tailpipe and dilution tunnel measurements of particle size at 50, 60, and 70 mph for vehicles US8 and US4, respectively. These tests utilize the *unheated/uninsulated* exhaust transfer line. Note that the US8 data in Figure 3 are plotted using a linear scale for particle concentration; whereas, the US4 vehicle data are plotted on a logarithmic concentration axis. For vehicle US8, ejector pump sampling at the tailpipe and dilution tunnel measurements are in very good agreement with respect to both the numbers and sizes of the particles. The particle number recorded from the tunnel is perhaps 20% higher than determined by the ejector pump measurement; however, the difference, possibly due to our reliance on the stated ejector pump dilution factors, is comparable to the test to test variation.

The exhaust particle concentration, in Figures 3 and 4, is essentially independent of vehicle speed over the 50 - 70 mph range. This implies that the “efficiency” of forming particles remains nearly constant over the 3 engine rpm/load points corresponding to 50, 60, and 70 mph. Although the exhaust concentration does not change, the particle number emission rate at 70 mph is nearly double that at 50 mph because of the higher exhaust flow. The corresponding PM mass emission rates, as calculated by assuming a particle density of 1 g/cm^3, mass weighting the particle size distributions, integrating over size, and scaling the result by exhaust flow and vehicle speed, are also listed in Figure 3. Note that these are extremely small, on the order of a few micrograms per mile. The 2σ error in the mass emission rate is estimated at ± 50%, originating roughly equally from test to test variability, and the uncertainty in particle density.

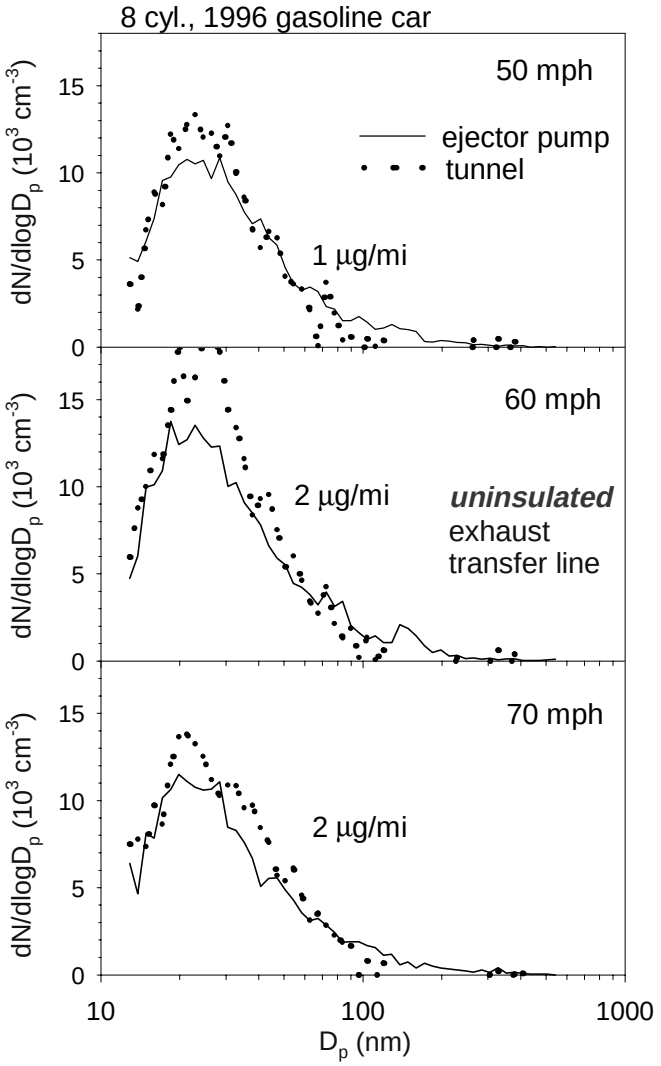

Figure 3. Comparison of ejector pump and dilution tunnel particle size distributions for the 8-cylinder gasoline car at 50, 60, and 70 mph when using the *uninsulated/unheated* transfer line. Note linear concentration axes. The tunnel background has been subtracted. Mass emission rates are estimated from the size distributions.

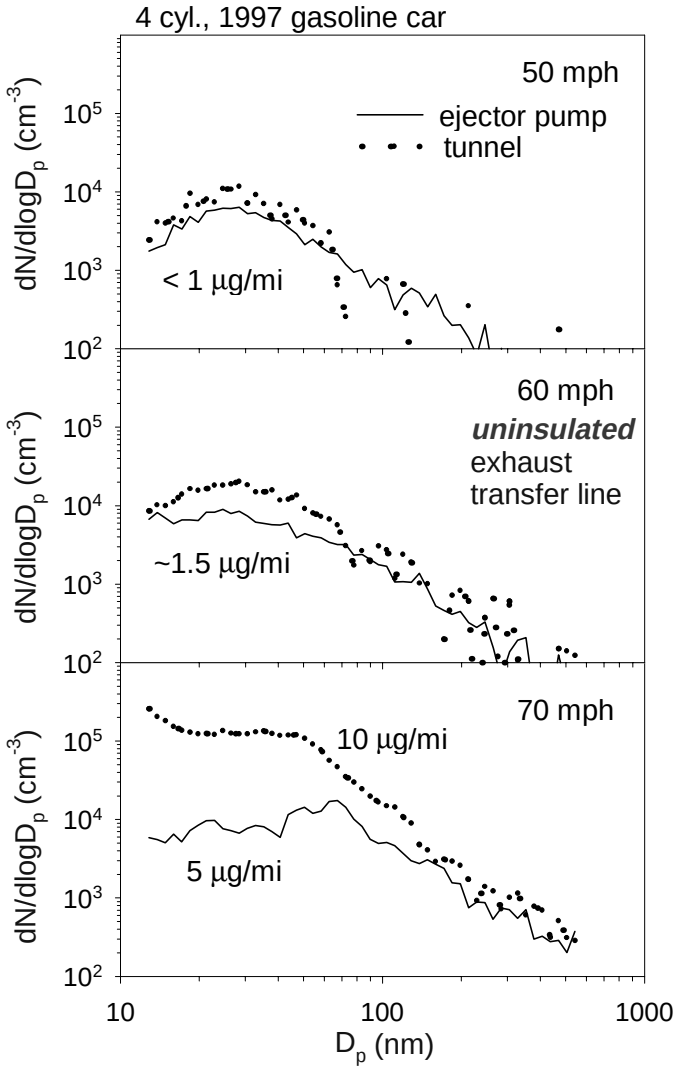

Figure 4. Comparison of ejector pump and dilution tunnel particle size distributions for the 4-cylinder, U.S., gasoline car at 50, 60, and 70 mph when using the *uninsulated/unheated* transfer line. Note logarithmic concentration axes. Mass emission rates are estimated from the size distributions.

At 50 and 60 mph in Figure 4, particle number emissions for vehicle US4 recorded from the dilution tunnel are 1.5 and 2 times the ejector pump results, respectively. Both sampling techniques show similar shapes of size distribution, with particles present primarily in the 10 - 60 nm regime. Tests performed on vehicle E4 at 31, 44, and 63 mph mimic those shown in Figure 4, both with regard to the shapes of the size distributions and the level of agreement between ejector pump and dilution tunnel measurements. As with vehicle US8, PM mass emission rates deduced from these size distributions, and those for vehicle E4, are a few μg/mi. At 70 mph, the particle number recorded from the tunnel exceeds the ejector pump result by an order of magnitude, primarily at the small size end of the distribution. The increase coincides with large variations, by factors > 2, in the scan to scan variability in the size distributions and is attributed to the hydrocarbon storage - release artifacts discussed below.

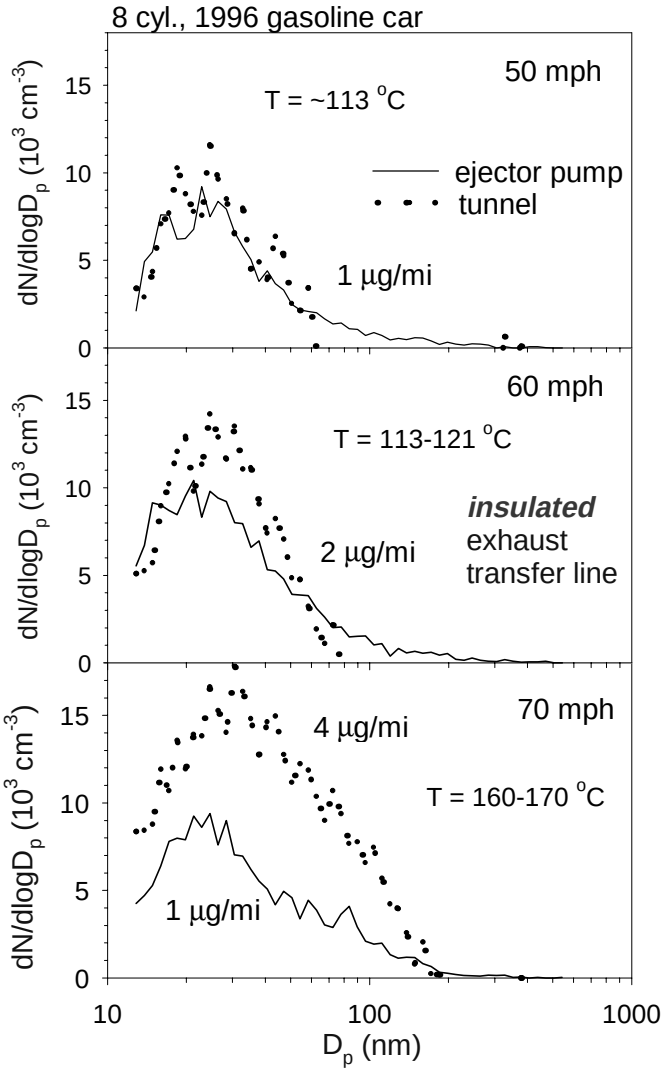

Figure 5. Comparison of ejector pump and dilution tunnel particle size distributions for the 8-cylinder gasoline car at 50, 60, and 70 mph when using the *insulated/heated* transfer line.

GASOLINE VEHICLE: *INSULATED* TRANSFER LINE – The vehicle tests presented in the preceding section were repeated using an *insulated and heated* transfer line, with the heater employed solely to maintain a minimum temperature of 113 °C. In this case agreement, or disagreement, between dilution tunnel and ejector pump measurements depends on the test vehicle and its speed. Figure 5 illustrates agreement within ~20% for vehicle US8 at 50 and 60 mph, which deteriorates to a greater than factor of two disagreement at 70 mph. The particle size distributions, peaking at about 25 nm, are essentially the same at the tailpipe as in the tunnel, both for the uninsulated and insulated transfer tube, except that at 70 mph the tunnel based distribution broadens toward the large diameter side.

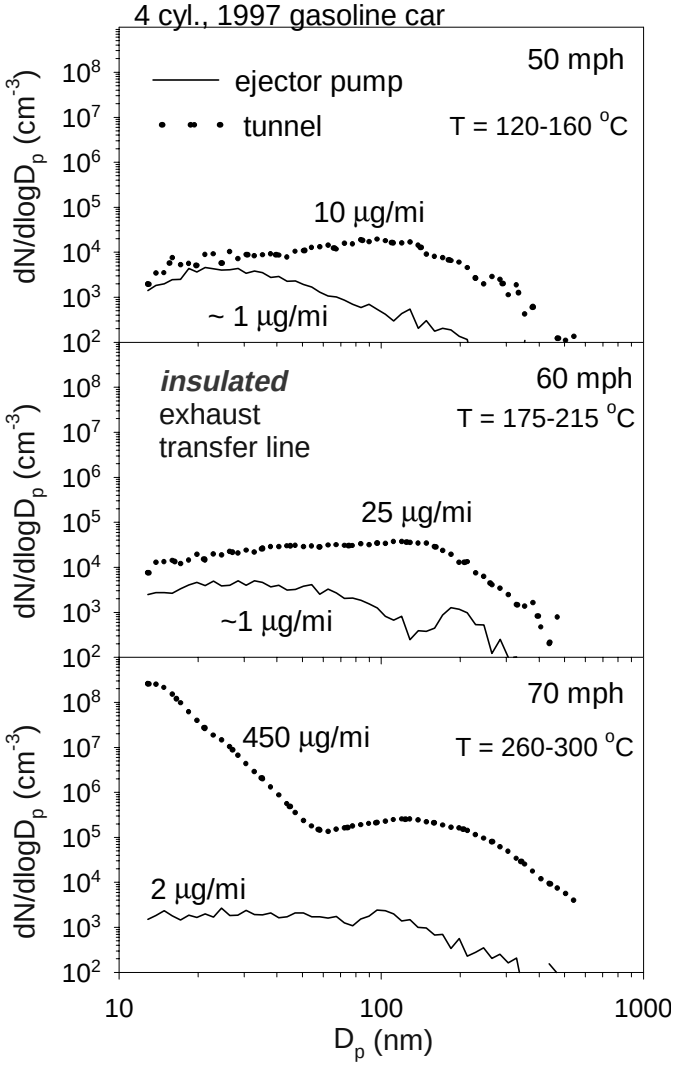

Figure 6. Comparison of ejector pump and dilution tunnel particle size distributions for the 4-cylinder, U.S., gasoline car at 50, 60, and 70 mph when using the *insulated/heated* transfer line.

In contrast, use of the *insulated* transfer line has an enormous effect on the particle number emissions for vehicle US4, as shown in Figure 6. Comparison of the ejector pump based size distributions in Figures 4 and 6 indicates that PM emissions from the vehicle have not changed; they remain broadly distributed over the 10 - 60 nm range. However, the main feature in the tunnel derived size distributions, at 50 and 60 mph, is now an accumulation mode peak at about 100 nm. At 70 mph, an ultrafine particle mode forms at < 15 nm with particle number concentrations 3 - 4 orders of magnitude higher than observed from the ejector pump. Essentially the same behavior is observed for vehicle E4; the differences in ejector pump versus tunnel based size distributions at 31 and 44 mph are smaller than for the 50 and 60 mph tests in Figure 6, but a similar 3 order of magnitude increase in ultrafine particles in the dilution tunnel is found at 63 mph (see Figure 9). For both vehicles US4 and E4, these changes coincide with an increase in transfer line temperature to above roughly 180 °C (this value is likely quite sensitive to the previous testing history), as measured at the middle of the transfer hose (see Table 1). Due to the significantly cooler exhaust, the insulated transfer line only reaches about 170 °C at 70 mph when testing the larger displacement 8 cylinder US car. This is less than the temperature reached for the 4 cylinder vehicle tests at 60 mph; thus, for vehicle US8 the relatively small factor of two increase in particle number observed at 70 mph when using the insulated transfer line (see Figure 5) is consistent with the 4 cylinder vehicle data.

The large increase in ultrafine particles observed when using the insulated transfer tube is not quantitatively repeatable; that is, the increase as compared to the tailpipe measurements can range from a factor of 100 to 10000, the peak in the ultrafine mode can vary from 25 nm to < 10 nm, and the transfer line temperature at which the mode appears can vary from ~160 °C to > 250°C. Size distributions recorded from one series of 70 mph tests on vehicle US4 performed in succession are illustrated in Figure 7. Here, particle number and mean size increase as the temperature rises from 150 °C to about 220 °C, and then subsequently decrease. In other tests, depending on their length and on the previous testing history, only the increase or decrease in ultrafine particles is observed during a specific test sequence.

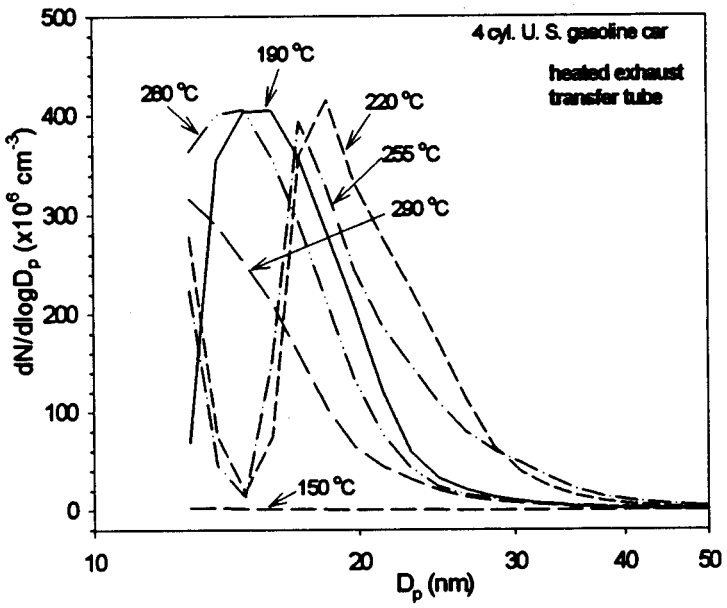

Figure 7. Variation in the ultrafine mode with a sequence of SMPS scans, over which the transfer line temperature climbs progressively higher.

That the intense ultrafine mode is observed in the tunnel, but not at the tailpipe, implies that the transfer line is the source of the particles. That the appearance of this mode is very sensitive to temperature and to the prior history of vehicle tests, suggests that the particles originate from the desorption or pyrolysis of particle precursors from hydrocarbon materials previously deposited on the transfer tube walls. This is corroborated by ejector pump measurements, which in Figure 8 reveal the presence of the ultrafine mode at the downstream end of the *insulated* transfer line just prior to the dilution tunnel. As with the tunnel data, the ultrafine mode is not quantitatively reproducible; rather it depends on the temperature of the tube and the testing history.

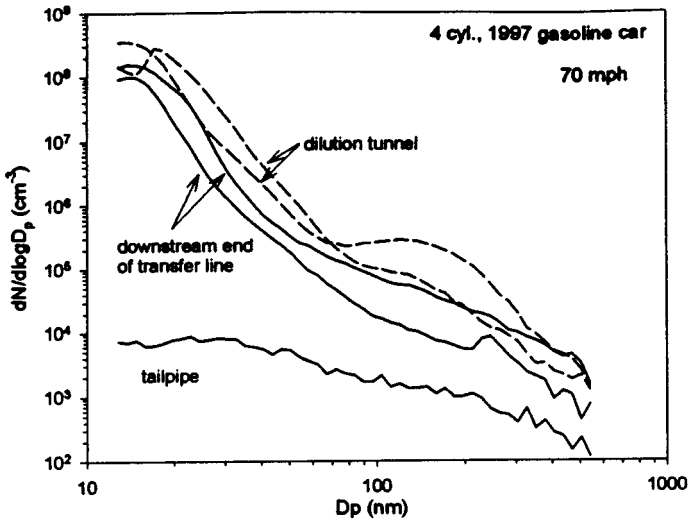

Figure 8. Ejector pump particle size distributions measured at the downstream end of the *insulated/heated* transfer line.

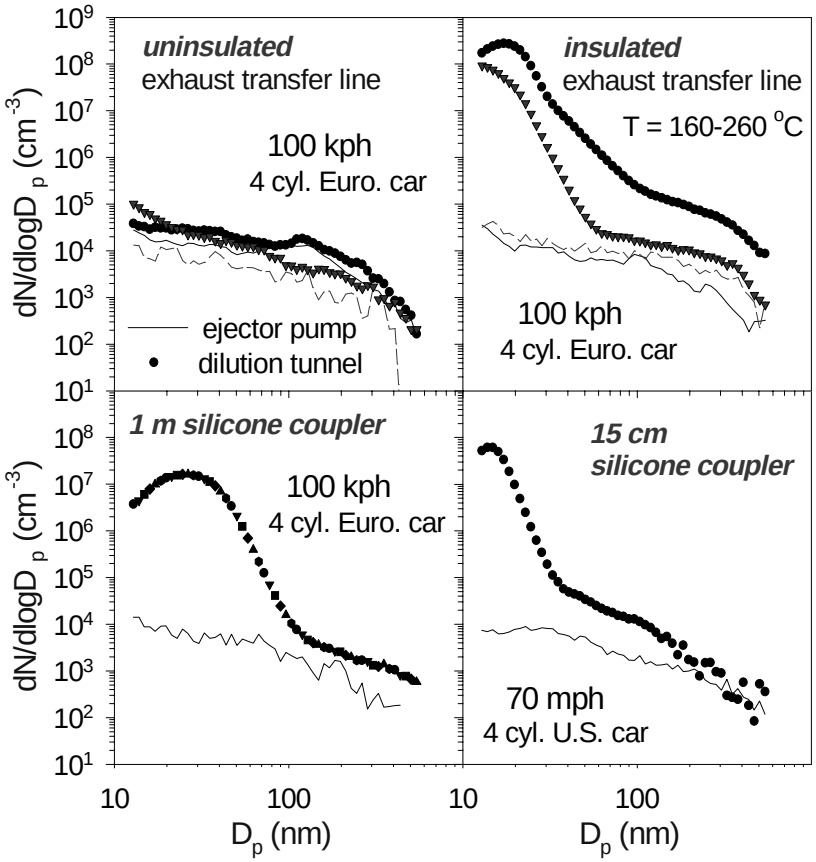

Figure 9. Comparison of particle size distributions for the 4 cylinder European gasoline car taken by ejector pump versus dilution tunnel when using a 1) *uninsulated* transfer line, 2) *insulated* transfer line, 3) *uninsulated* transfer line plus a 1 meter silicone rubber coupler, and 4) *uninsulated* transfer line plus a 15 cm silicone rubber coupler. In the top two panels, two sets of data are compared. Mass emission rates are estimated from the size distributions.

GASOLINE VEHICLE: SILICONE RUBBER COUPLER – The third test configuration utilizes an *uninsulated/unheated* transfer line, but inserts a silicone rubber coupler between the tailpipe and the transfer line. A 1 meter coupler was used in tests at 31, 44, and 63 mph with vehicle E4 and a 15 cm coupler was used in tests at 50, 60, and 70 mph with vehicle US4. Below 60 mph, the dilution tunnel and ejector pump particle size distributions are in good agreement, analogous to what is observed in Figures 3 and 4 without the coupler. In stark contrast, as shown in Figure 9, a very sizable ultrafine mode develops in the tunnel derived size distributions at 63 mph for vehicle E4 and at 70 mph for vehicle US4, although it is not observed in the ejector pump tailpipe measurements. After initially bringing the vehicle speed to 70 mph (or 63 mph for E4), the intensity of this mode increases with time, presumably because the silicone coupler gets hotter. In this case, the ultrafine particles are attributed to desorption / pyrolysis of the silicone rubber material by the hot exhaust gases.

DIESEL VEHICLE – Size distributions of diesel exhaust PM recorded from the tailpipe are compared to dilution tunnel measurements in Figure 10 for the case of the *uninsulated/unheated* transfer line. Each of the distributions, at the various speeds and sampling locations, exhibits an accumulation mode of ~10^8 particles/cm^3 that is centered at roughly 100 nm. At 60 and 70 mph a major discrepancy becomes apparent, namely the tunnel derived distributions are bimodal whereas those from the tailpipe show only the accumulation mode. The ultrafine mode of ~18 nm particles in the tunnel version of the 60 mph test exceeds the accumulation mode by a factor of 10 in particle number. This mode shifts to larger particle size, ~35 nm, and increases another fivefold in intensity in the 70 mph test.

Unlike the accumulation mode, the ultrafine mode is not always stable from one scan to the next. Figure 11 displays a sequence of size distribution scans made after raising the vehicle speed from 50 to 60 mph. The top panel shows the dilution tunnel data, whereas the lower panel gives the corresponding tailpipe measurements. The interpretation is as follows: The accumulation mode represents the distribution of particle sizes actually emitted in the engine exhaust. The increase in exhaust temperature, from raising the vehicle speed, desorbs and/or pyrolyzes hydrocarbon deposits on the j-tube probe used for ejector pump sampling, thereby creating a temporary source of ~20 nm particles. After a short time, the hydrocarbon deposits are “burned off” and this ultrafine mode disappears. The ultrafine mode is not at first observed in the dilution tunnel. It grows in with time as the transfer hose is heated by the vehicle exhaust sufficiently high for the desorption / pyrolysis of the hydrocarbon material to begin. The artifact can persist for a long time because considerable hydrocarbon storage is available in the 7.6 m corrugated hose. It is in principal possible that hydrocarbons stored in the exhaust / aftertreatment systems of the vehicle can also give rise to an ultrafine mode, but in the present situation this is inconsistent with the opposite trends observed for the intensity of this mode in the tunnel versus from the tailpipe.

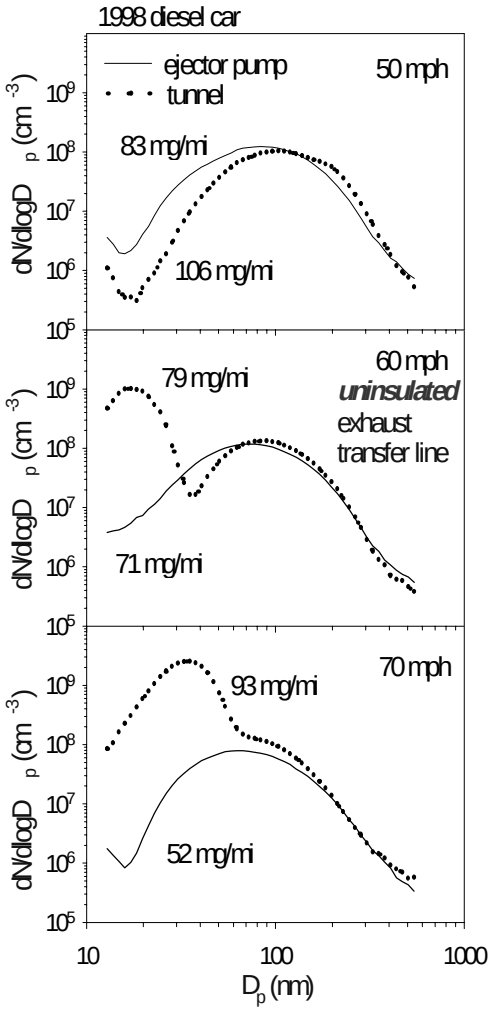

Figure 10. A comparison of diesel vehicle exhaust particle concentration taken with the ejector pump versus dilution tunnel when using the *uninsulated/unheated* transfer line.

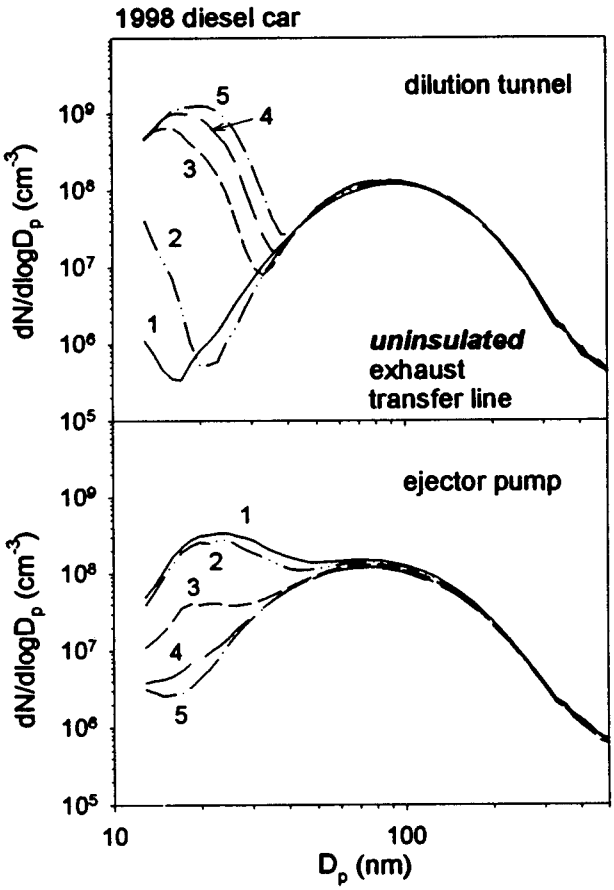

Figure 11. Sequence of size distributions taken at 3 minute intervals following an increase in vehicle speed from 50 to 60 mph. Top panel illustrates the growing in of the 20 nm artifact due to heating of the transfer hose. Bottom panel shows a transient artifact from hydrocarbon build-up that "burns off" of the j-tube sample probe in the tailpipe.

It should be noted that special precautions were observed in these tests for the tailpipe probe. The vehicle was warmed up without the j-tube probe in place. It was stopped and a clean probe inserted into the tailpipe. The vehicle was restarted and taken to the 50 mph, and then 60 mph, test speeds. Hydrocarbons deposited on the probe prior to it reaching the tailpipe exhaust temperature are assumed responsible for the ultrafine particles temporarily observed in the initial few 60 mph size distributions in Figure 11. In other tests, for which the j-tube probe is in place throughout the vehicle warm up cycle, the ultrafine mode can persist for considerably longer than a few scans, presumably from the larger amount of hydrocarbons that deposit during the cold start.

The accumulation mode, both as measured from the tailpipe and dilution tunnel, is reproducible to about ±15%. However, the tailpipe and tunnel versions differ from each other. Examination of Figure 10 shows the accumulation mode to be shifted to smaller particle size by about 25 nm at the tailpipe as compared to the dilution tunnel. Also noticeable is the more rapid falloff of the small diameter side of the distribution in the tunnel measurement. These differences are likely a manifestation of particle coagulation occurring in the transfer hose during transport of the exhaust from the tailpipe to the tunnel.

To get an idea of how important coagulation might be, let us assume that the "typical" particle on the small side of the distribution is 30 nm. An approximate, "hard sphere", rate constant for coagulation between two particles is $k_c = (2)^{-½}\ \sigma\ \langle v \rangle$, where $\sigma = \pi D_p^2$ is the collision cross section between two spherical particles and $\langle v \rangle = (8kT/\pi m)^{½}$ is the thermal mean speed of the particles. Here k represents Boltzmann's constant and m is the particle mass. For particles of unit density at a transfer line temperature of 150 °C, $k_c = 2.1\ 10^{-9}$ cm^3 s^{-1}. Over the 2 - 5 second transit time through the transfer hose, a second order rate law employing this rate constant, and an initial concentration of $5x10^7$ particles/cm^3 (approximate number of particles in the small half of the accumulation mode), predicts that about 1/3 of the "typical" small particles coagulate to form larger particles. This is qualitatively consistent with the shift to larger particles observed in the dilution tunnel.

Because the PM artifacts consist primarily of ultrafine particles, they have negligible, or at least relatively small, effects on PM mass emission rates. This is apparent from comparing the mass emissions that are listed in Figure 10 alongside each size distribution. At 60 mph, the ultrafine artifact, though ten times higher in particle number than the accumulation mode, contributes almost nothing to the particulate mass. At 70 mph, the increase in size of the artifact particles to about 35 nm begins to affect the PM mass emissions; thus, PM mass recorded from the tunnel is 79% higher than what is determined from the tailpipe data. PM emissions measured from the dilution tunnel when using the *insulated/heated* transfer hose lead to qualitatively the same results as observed in Figure 10. The tunnel based size distributions are bimodal at 60 and 70 mph, except that the ultrafine artifact is more pronounced than when using the *uninsulated* hose.

DISCUSSION AND CONCLUSION

The major conclusion to emerge from this study is that hydrocarbon storage in the transfer hose that is used to transport exhaust from the vehicle to the dilution tunnel, and its subsequent release by the hot exhaust gases from the vehicle, can have a profound influence on the number and character of the measured particles. As a result, whether or not one is able to record a representative size distribution using a dilution tunnel depends on a number of factors: Is a gasoline or diesel vehicle being tested? Is the engine displacement large or small? What is the nature of the test: FTP, US06, or steady state? What material is the transfer hose constructed from? And, what is the previous testing history of the transfer hose and tunnel?

Although Kittelson et al.[2,7] has noted occasions when long stabilization periods are needed after switching between diesel engine test modes and attributed this to the release of stored hydrocarbons in the exhaust and sampling systems, the extent to which this can alter the appearance of particle size distributions has not been fully appreciated. Instead, the shortcomings of the dilution tunnel have been seen primarily in terms of how it might limit observation of ultrafine, or nanoparticle, emissions that might occur under “real world” conditions. However, the storage - release artifacts can substantially alter the appearance of vehicle exhaust particle size distributions. In the case of the diesel test vehicle the artifact adds an ultrafine peak to the accumulation mode of diesel exhaust particles producing a bimodal appearance. In the case of recent model gasoline vehicles, the situation is even worse. The artifacts completely overwhelm the exhaust particulate matter. They raise the normal gasoline exhaust levels of 10^4 particles/cm^3 by 3 - 4 orders of magnitude, effectively making the gasoline PM emissions look like those from a diesel vehicle. Moreover, the artifacts can mistakenly be attributed to the test vehicle since they often appear as speed and load are increased, but this is an indirect consequence of the hot exhaust gases.

For recent model gasoline vehicles, as long as the artifacts are avoided, dilution tunnel measurements appear to give accurate renditions of the exhaust particle size distribution. This can be seen from the good, ~20%, agreement between tunnel and tailpipe measurements for vehicle US8 in Figure 3 and at the lower speeds for vehicle US4 in Figure 4, when the *uninsulated* transfer hose is used and remains relatively cool. The high exhaust flow, ~1 m^3/min, and large diameter of the transfer tube, ~ 9 cm, minimize thermophoretic, diffusional, and electrostatic losses en route to the tunnel. Efficient reduction of hydrocarbon emissions by the catalytic converter significantly limits the extent to which adsorption, condensation, and especially nucleation occur. Finally, gasoline exhaust PM concentrations of 10^5 particles/cm^3 are too low for coagulation to be effective. Hence, the agreement between tailpipe and tunnel PM measurements is consistent with the physical characteristics of the dilution tunnel system and the nature of gasoline vehicle exhaust.

Dilution tunnel measurements of transient PM number and size during the FTP, or ECE urban, cycle are likely to be accurate for current model gasoline vehicles. The vehicle speed is moderate, only briefly rising above 55 mph during the FTP, thus limiting the extent to which the transfer hose is heated. One must be more careful with regard to the more aggressive US06 cycle, during which the vehicle speed reaches above 70 mph. Transient measurements of particle number during the US06 cycle reveal the particles to be emitted in a series of narrow peaks in time that coincide with vehicle acceleration.[10] Between these peaks, the particle emissions return to near background levels, suggesting that the artifacts play at most a minor role. In the course of our previous study [10] we sometimes noticed a curious “lifting” of the baseline toward the end of the US06 cycle for small, < ~30 nm, particles, which we now attribute to the hydrocarbon release artifact. Of all the tests, steady state measurements of particle size are the most prone to interference from artifacts, since these are the most likely to be carried out under prolonged high speed or high load vehicle operation.

There are two sorts of difficulties in using a dilution tunnel to measure particle size distributions for diesel vehicles. One is the artifact problem discussed above with respect to gasoline vehicles; the second is coagulation. As with the gasoline vehicles, the artifacts are likely not a problem for FTP or ECE urban drive cycles where high speed driving is not an issue. US06 tests may prove more of a challenge, since the transfer hose for diesel testing is expected to be dirtier than its gasoline vehicle counterpart and, therefore, the stored hydrocarbon material may begin to desorb at a lower temperature. Even if the artifact emissions are avoided, however, dilution tunnel measurements of particle size in diesel exhaust are distorted from what exits the tailpipe. Above tailpipe concentrations of about 10^7 particles/cm^3, particle coagulation begins to play an increasingly important role. Thus, in Figure 10 the mean particle size of 75 nm at the tailpipe grows to about 100 nm by the time the exhaust reaches the dilution tunnel. It can be avoided to some degree by minimizing the length of transfer hose.

In contrast to some reports[11,12] that suggest gasoline vehicle PM number emissions can be nearly as high as those from a diesel vehicle, the present work shows that recent model port fuel injection vehicles have very low particulate emissions, by number and mass, even at high speed operation. This is consistent with the low emissions recently noted during tests over the US06 transient cycle, for which emission rates of < 10 mg/mi were measured.[10] It is also consistent with the very low “baseline” particle emissions observed for a gasoline vehicle by Graskow et al.[13] (however, the random high PM emission “spikes” observed by these researchers were not found for the vehicles in the present study). The present results do not mean that gasoline vehicles never emit high particle concentrations. High PM emissions are readily observed under rich engine operation.[10] They would be expected as well from malfunctioning vehicles, “oil burners”, and perhaps older technology carburetor vehicles.

A number of recommendations regarding motor vehicle exhaust particle measurements are suggested by the present study. 1) The dilution tunnel, transfer hose, and particle sampling probes should be kept clean, especially when measuring newer technology low, and ultralow, emitting vehicles. 2) Separate transfer hoses and dilution tunnels should be used for gasoline and diesel vehicle particle number measurements. While one might argue that a single dilution tunnel may be adequate for PM mass measurements, since the ultrafine mode artifact contributes relatively little mass, this arrangement is certainly not legitimate for particle number measurements.

3) The temperature of the transfer line should be monitored. A temperature of greater than 100 °C is desirable to prevent water condensation and to reduce hydrocarbon vapor deposition; however, temperatures above about 180 °C (perhaps even lower depending on the condition of the transfer hose) are sufficiently high to desorb or pyrolyze stored organic material. 4) Silicone rubber and other similar materials should be avoided. Clean stainless steel is preferable. Even with these precautions, however, it appears that artifacts will be hard to avoid when measuring particle number and size at high speeds and loads.

ACKNOWLEDGMENTS

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Nanoparticle formation in diesel vehicle exhaust: A comparison of laboratory and chasing experiments

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Introduction

The currently ongoing public debate on the emission of particulates is focused around air quality and health concerns. Sources of particulates include industrial processes, road transport, and natural
emissions from primary sources and secondary particle formation. Regarding diesel particle emissions there are still large uncertainties during the measurement of particle number/size. It is clear that diesel particles consist of EC, OC, sulfuric acid, and some metal ash. The largest uncertainty is the formation of ultrafine particles of 10-20 nm

size.

Open questions include:
How does exhaust dilution effect PM size distribution?

What is the effect of the fuel sulfur and oxidation catatalyst?

Abstract

Exhaust particle size distributions from a diesel passenger car operated on a chassis dynamometer were measured with a scanning mobility particle sizer (SMPS). The exhaust was either sampled after secondary dilution from the dilution tunnel, or was directly taken from the tailpipe using two mini-diluter systems. The influence of the dilution ratio, the relative humidity of the dilution air, and the residence time of the diluted exhaust has been studied with a special emphasis on the formation of condensed particles.

One important question is how well the exhaust dilution in the emission laboratory reflects real atmospheric dilution? To address real world dilution the Ford Mobile Laboratory (FML) was used. This is a "state of the art" laboratory based on a Ford Transit. While carefully following vehicles under controlled conditions, air from their exhaust plume is continuously sampled and analyzed inside the mobile laboratory. Exhaust particle size distribution data together with exhaust gas concentrations are collected and is compared with measurements obtained in the emission test laboratory.

The test vehicle is a current production turbo charged DI Diesel passenger vehicle with oxidation catalyst which was operated with 350 ppm fuel sulfur. To investigate the effect of the oxidation catalyst and fuel sulfur some chasing experiments were conducted with low (10 ppm S), or with normal S fuel and without oxidation catalyst. Significant effects on the nucleation mode particles were observed, depending on the presence of fuel sulfur and the oxidation catalyst.

Dynanometer exhaust dilution & sampling

Fig. 1: Dynanometer exhaust dilution & sampling. For direct tailpipe sampling two ejector-pump diluters or a rotating disk diluter (Matter Engineering AG) were used.

Effect of residence time

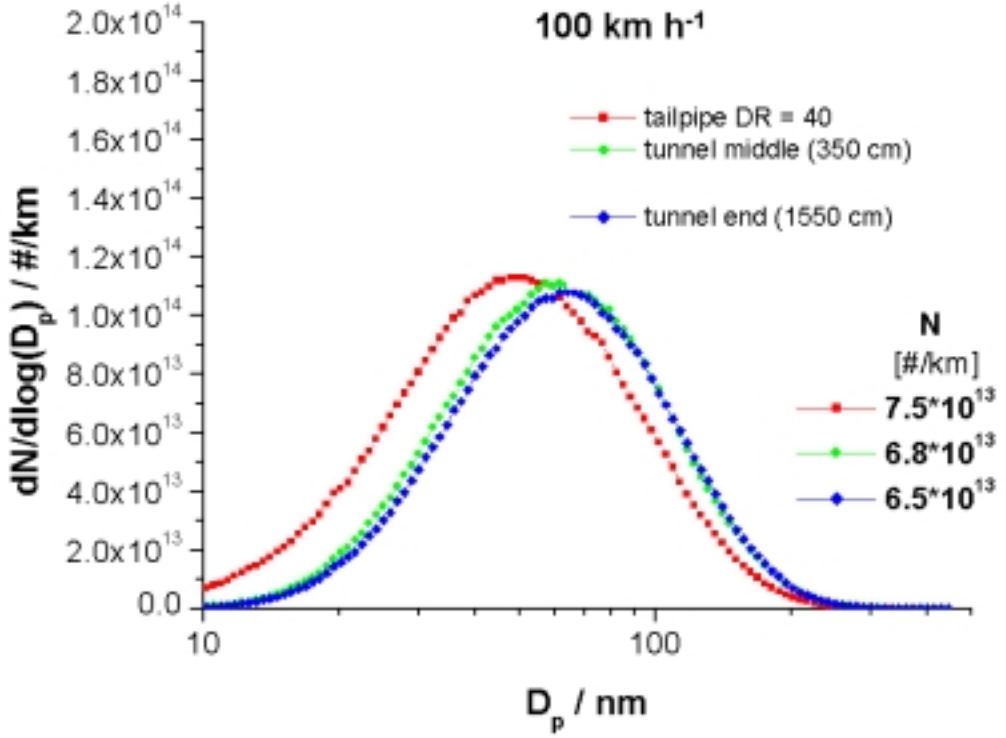

Fig. 2 Comparison of particle size distribution measured at three sampling location with the Matter diluter. The diesel vehicle was running at constant speed of 100 km h^{-1}. The Matter diluter was set to a dilution ratio of 1:40. At the tunnel the total dilution ratio was 1:440.

Effect of residence time

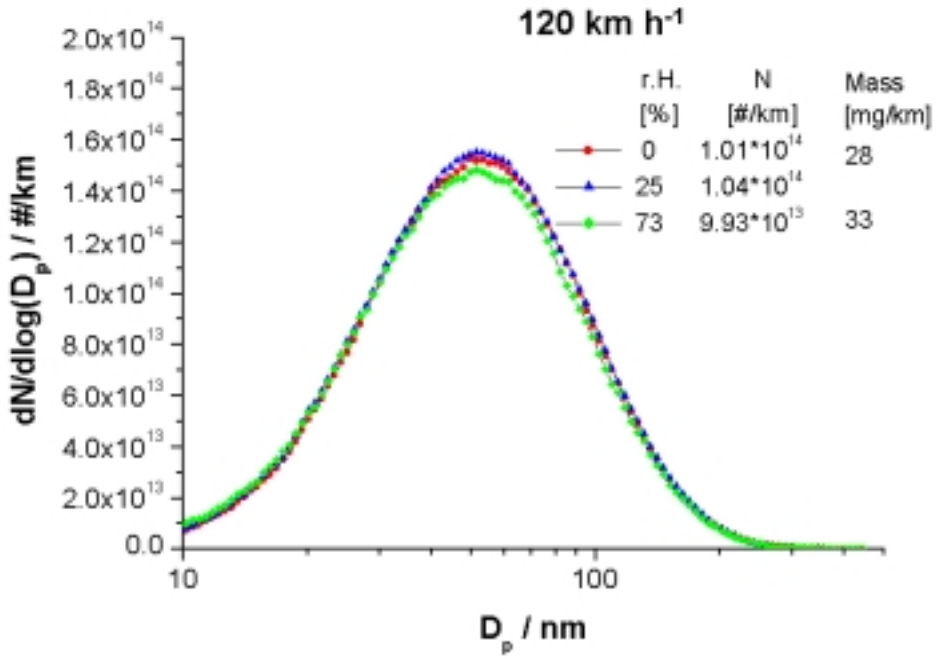

Fig. 3: Comparison of particle size distribution measured with the Matter diluter at the tailpipe of the diesel vehicle. The short sampling line was heated and the exhaust was diluted with humidified synthetic air at the given relative humidity (r.H.) values

On-road chasing of exhaust plume

Fig. 4. Chasing of exhaust plume with Ford Mobile Laboratory

Exhaust chasing of diesel vehicle

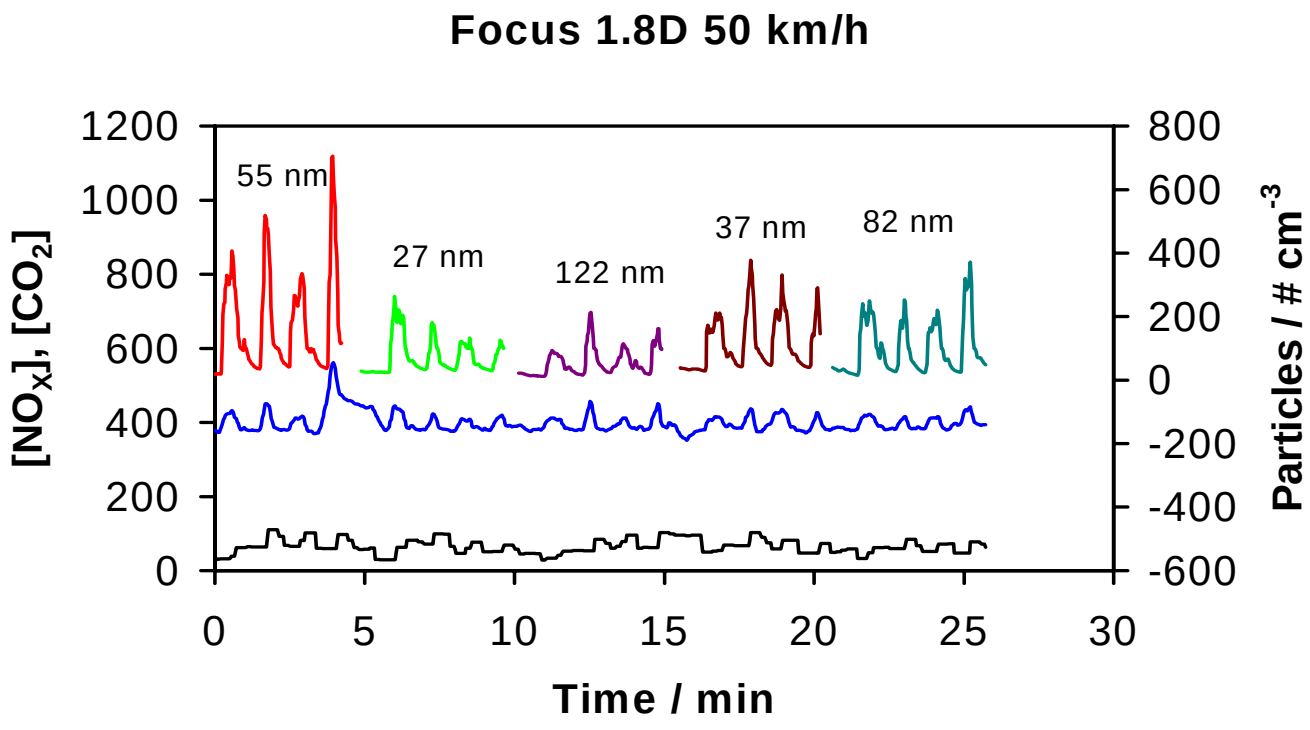

Fig. 5. NO_x, CO_2 and particles measured at a fixed SMPS size bin while drive in and out of the exhaust plume of the diesel test vehicle.

PM size distribution during chasing of diesel vehicle

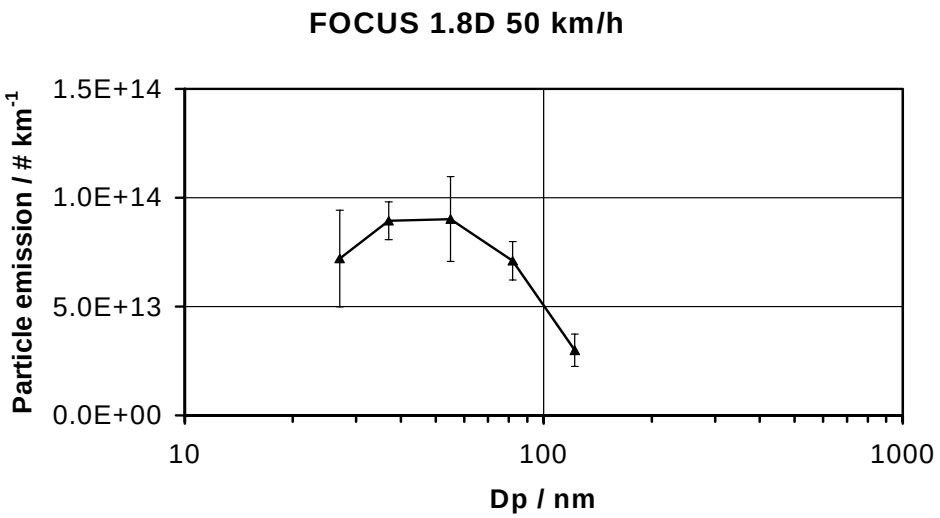

Fig. 6. Constructed size distribution from chasing experiments. The dilution ratio is calculated from the measured NO_x and CO_2 concentration and the known NO_X and CO_2 emission at constant speed.

PM size distribution during chasing at different speeds

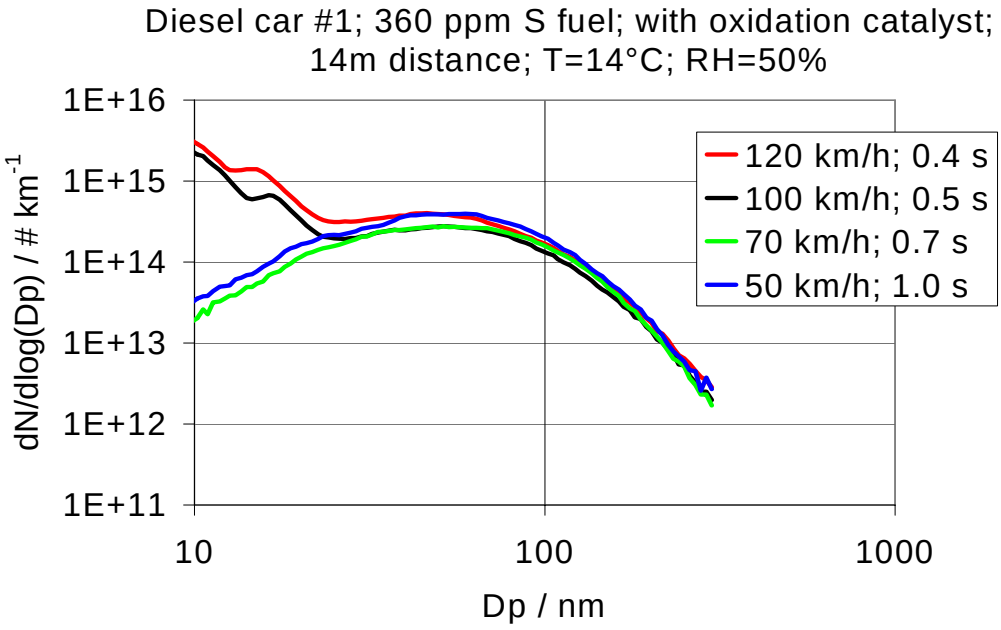

Fig. 7: Size distributions measured at different speeds in the exhaust plume of the test vehicle. running on 360 ppm S fuel and oxidation catalyst.

PM size distribution during at different speeds at dynanometer

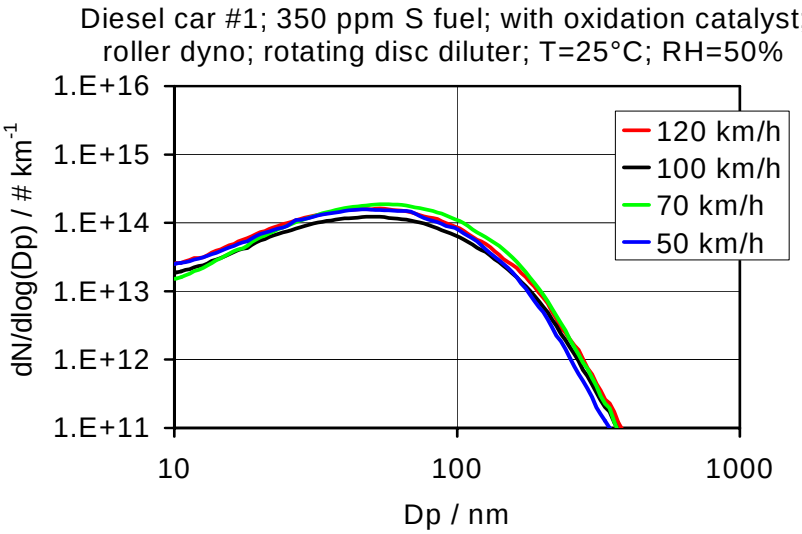

Fig. 8: Same test vehicle as Fig 7 operated at different speeds at chassis dynanomter. No nucleation mode particles were observed with rotating disc diluter.

PM size distribution during chasing at different speeds: no oxidation catalyst

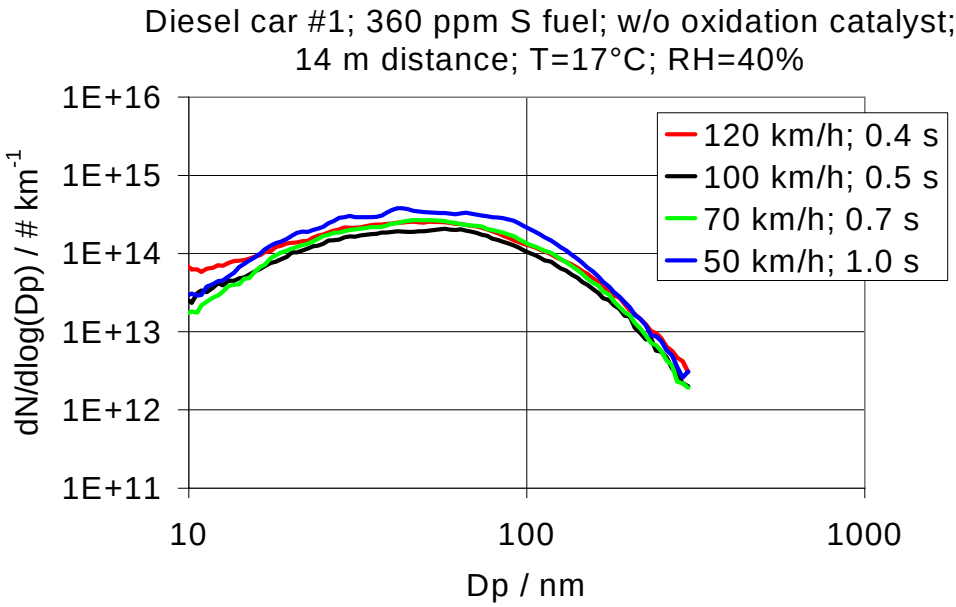

Fig. 9. PM size distributions measured in exhaust plume of test vehicle with 360 ppm fuel S and no oxidation catalyst.

Fuel-S and oxidation catalyst effect

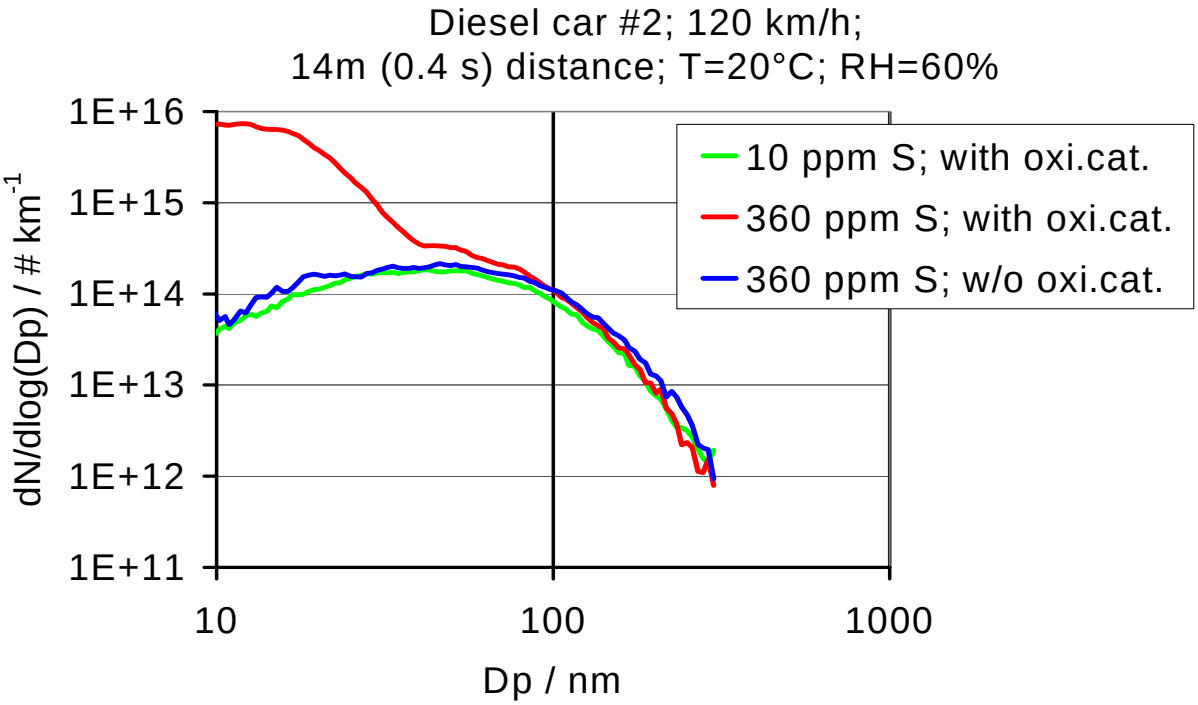

Fig. 10. PM size distributions measured in exhaust plume of test vehicle with different S fuel, with and w/o oxidation catalyst

Time evolution of nucleation mode particles

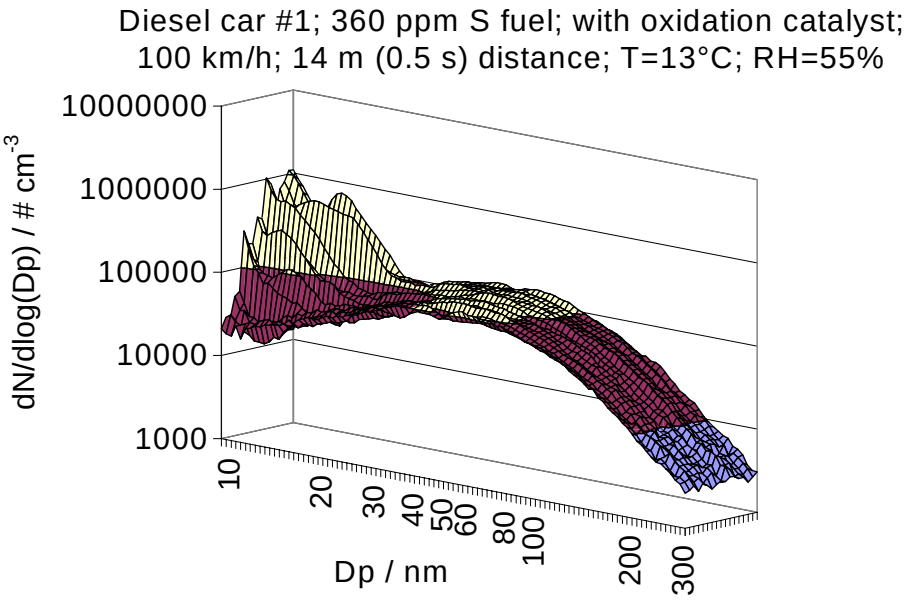

Fig. 11. Evolution of nucleation mode in PM size distribution during 40 min chasing at 100 km h^{-1}.

Evolution of nucleation mode particles and vehicle parameters

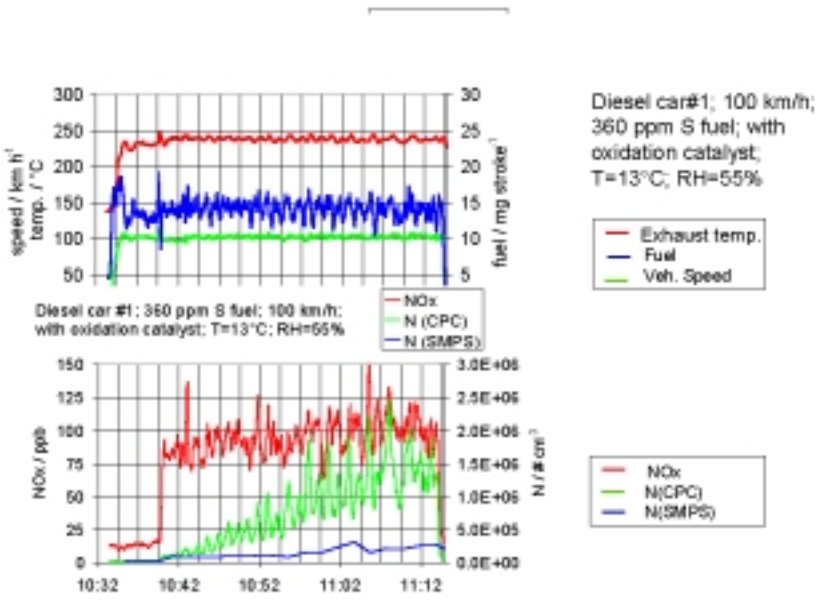

Fig. 12. Evolution of number emission (CPC and integrated SMPS) in PM size distribution during 40 min chasing at 100 km h^{-1} and fuel consumption, exhaust temperature and vehicle speed.

Summary

- Diesel vehicle particle size distributions measured at the dynanometer were unimodel (340 ppm S; with oxidation cat)

- Number/size distribution varied depending on sampling condition

- Good agreement of tailpipe sampling and exhaust chasing for soot mode particles

- Nucleation particles occur during atmospheric dilution only at 100 and 120 km h^{-1}, if 360 ppm S fuel and oxidation catalyst are used

-

- Using 10 ppm S fuel, no nucleation particles were observed

R. Vogt and V. Scheer "Particles in diesel vehicle exhaust: A comparison of laboratory and chasing experiments".
Proceedings of the 11th International Symposium Transport and Air Pollution ,
Graz 19-21.6.2002, pp 79-84, Univ.-Prof. Dr. R. Pischinger, Graz, ISBN 3-901351-59-0.

Particles in diesel vehicle exhaust: A comparison of laboratory and chasing experiments

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ABSTRACT

Exhaust particle size distributions from a diesel passenger car operated on a chassis dynamometer were measured with a scanning mobility particle sizer (SMPS). The exhaust was either sampled after secondary dilution from the dilution tunnel, or was directly taken from the tailpipe using two mini-diluter systems. The influence of the dilution ratio, the relative humidity of the dilution air, and the residence time of the diluted exhaust were studied with a special emphasis on the formation of condensed particles.

To address real world dilution a mobile laboratory was used. While carefully following a test vehicle under controlled conditions, air from the exhaust plume is continuously sampled and analyzed inside the mobile laboratory. Exhaust particle size distribution data together with exhaust gas concentrations were collected and are compared with measurements obtained in the emission test laboratory. First results show good agreement for soot mode particles measured in the exhaust plume, if compared with the emission lab. However, significant differences were observed for nucleation mode particles, which occur only under real atmospheric dilution conditions, depending on the presence of the oxidation catalyst, fuel sulfur content and the vehicle speed.

Key words: Diesel particles, size distribution, exhaust dilution, real world dilution, oxidation catalyst, fuel sulfur

1. INTRODUCTION

The current public debate on the emission of particulate matter is focused on ambient air quality and health concerns. Sources of particulates include industrial processes, road transport, and natural

emissions from primary sources and secondary particle formation. Regarding diesel particle emissions there are still large uncertainties on the measurement of number/size distributions. It is well understood that diesel particles consist of elemental carbon, organic carbon, sulfuric acid, and some metal ash. While it is widely established that the number/size distribution of the soot mode particles has its maximum at a mobility diameter of 50-80 nm and that the particle mean diameter is independent of engine technology (ACEA (1999); Maricq et al. (1999)), a large uncertainty remains with the occurrence of ultrafine particles of 10-20 nm

size. Close to an urban street, or at a parking lot next to an Autobahn, the number/size distribution is often dominated by particles in the 10-30 nm size range (Wahlin et al. (2001); Wehner et al. (2001)). However, it was shown that this size mode is made of volatile material, which may be evaporated using a thermodenuder and that the particles do not have a solid core (Wehner et al., (2001).

It has been suggested that the dilution conditions applied in the emission test laboratory have a significant influence on the presence of nucleation mode particles in the 10-30 nm size range (Shi & Harrison (1999); Abdul-Khalek et al. (1999)). Here we investigate under carefully defined conditions the influence of parameters like the dilution method, dilution time and relative humidity of the dilution air on the measured size distribution. The next important question is, how well the exhaust dilution applied in the emission laboratory

reflects real atmospheric dilution? Measurements using the Ford Mobile Laboratory which closely followed the exhaust plume of a diesel passenger car are presented.

2. EXPERIMENTAL METHODS

Test were performed with a European model diesel passenger car (1.8l turbo-charged DI and oxidation catalyst, EURO 3) and regular sulfur fuel (approx. 350 ppm S). The vehicle was warmed up at a chassis dynamometer for 10 min at constant speed. Subsequently, three size scans (each 5 min measurement and 2 min SMPS down scan) were measured in conjunction with three gas bag samples and three filters for PM mass. As stated below some experiments were conducted with low sulfur fuel (10 ppm S), or with the oxidation catalyst removed.

2.1. Exhaust Sampling in the Emission Laboratory

Two types of diluters were explored: the ejector diluter (Dekati Inc.) and the rotating disk diluter (Matter Engineering AG). Both diluters were operated with particle free air and connected through a 10-15 cm stainless steel line (6mm diameter) directly to the tailpipe. In order to avoid artifacts through evaporation of condensed material this sampling line was regularly cleaned and heated to 220°C. Two ejector diluters (dilution ratio of about 1:9 each) were cascaded, connected by a reservoir volume which inserted 2 s residence time in order to provoke nucleation. The diluters were not heated.

The rotating disk diluter was operated at a dilution ratio between 40 and 100. For some experiments the dilution air was humidified between 0 % and 73 % relative humidity. The test vehicle exhaust is conducted via an insulated and heated corrugated stainless steel hose (6 m length) to a stainless steel dilution tunnel. Particles are sampled on paper filters from the tunnel following the legislated procedure. For particle size measurements an ejector diluter is connected at the same position.

2.2. Sampling from the exhaust plume with the Ford Mobile Laboratory

The Ford Mobile Laboratory (FML) was constructed on the basis of a Transit van to operate as a stand-alone experimental platform for the investigation of ambient particles at one location for a given time period. For these experiments an on-board power supply has been installed which allows operation of pumps, SMPS, CO and NO_X analyzers and data acquisition instruments while driving. Sampling is performed through a 6 mm stainless steel inlet and 12 mm sampling line which opens in front of the radiator grill. The FML was driven at varying distances to the same test vehicle which was used in the emission test facility. Tests are performed on a high speed test track in the absence of other vehicles.

3. RESULTS

3.1. Comparison of dilution conditions

In Fig. 1 particle size distributions are shown which were measured with the diesel passenger car running with constant speed at 100 km h^{-1} and 120 km h^{-1}. The Dekati and Matter diluters were connected directly to the exhaust pipe. At 120 km h^{-1} the particle number is somewhat larger (approx. 20 %) than at 100 km h^{-1}, however the Dekati and Matter diluters show the same tendency. The two dilution systems are in reasonable agreement (2-20%), considered that the measurements were done on different days and no absolute calibrations of the diluters or the SMPS were available. During none of the experiments a nucleation mode was observed.

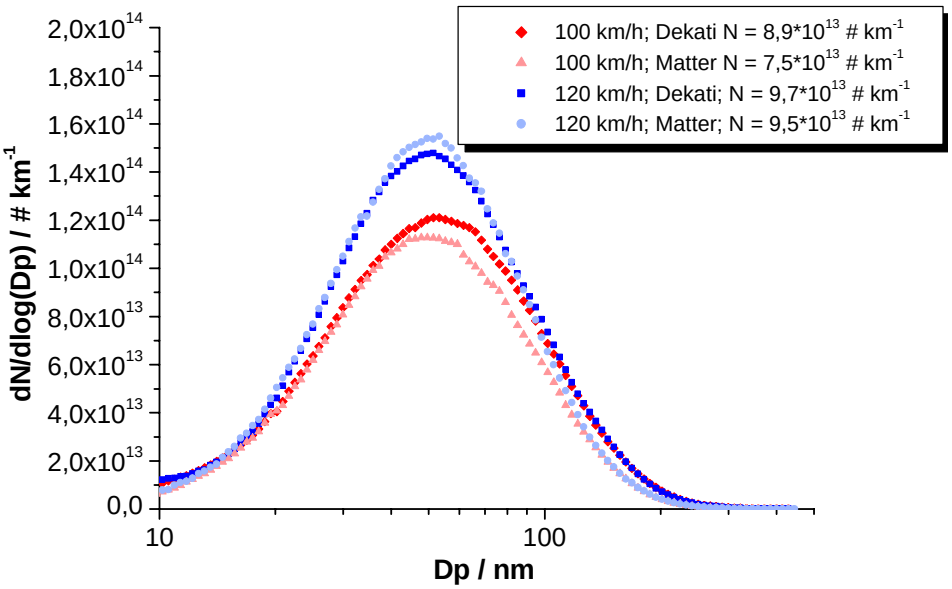

Fig. 1. Comparison of particle size distribution measured after dilution at the tailpipe of the diesel test vehicle with a rotating disk (Matter) and two ejector type (Dekati) diluters at 100 km h^{-1} and 120 km h^{-1}. The Matter diluter was set to a dilution ratio of DR=1:100; two Dekati diluters were cascaded (DR=1:80), connected via a reservoir volume which inserted 2 s of residence time.

In Fig. 2 size distributions are shown which were measured at three different sampling locations: 1.) directly at the tailpipe, 2.) after 6 m of heated and insulated transfer hose sampled at the tunnel middle at 3.5 m, and 3.) after 6 m of heated and insulated transfer hose sampled at the tunnel end at 15.5 m. Depending on the residence time of the particles in the transfer line and dilution tunnel the maximum of the size distribution is shifted towards larger particle diameters. Due to coagulation the integrated particle number decreases with increasing residence time in the dilution system.

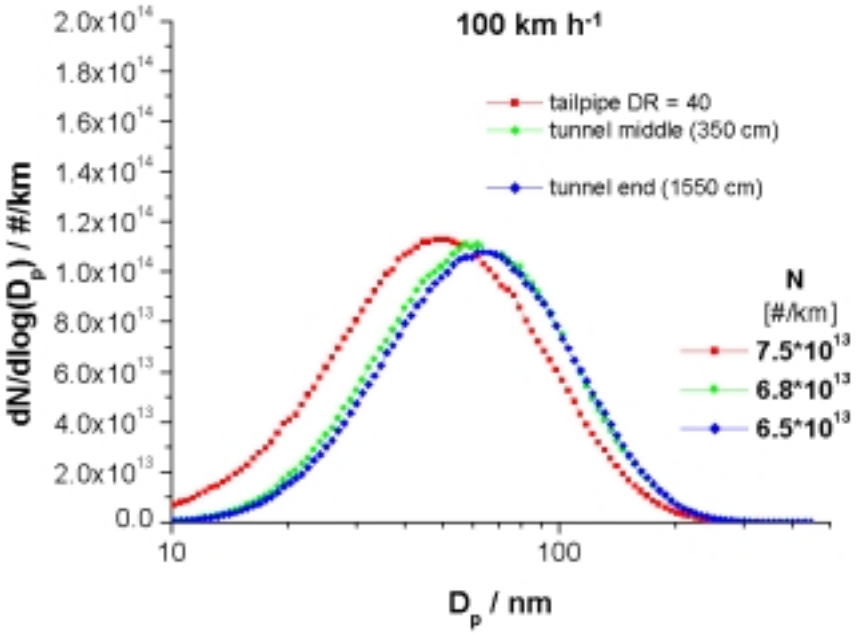

Fig. 2. Comparison of particle size distribution measured at three sampling location with the Matter diluter. The diesel vehicle was running at constant speed of 100 km h^{-1}. The Matter diluter was set to a dilution ratio of 1:40. At the tunnel the total dilution ratio was 1:440.

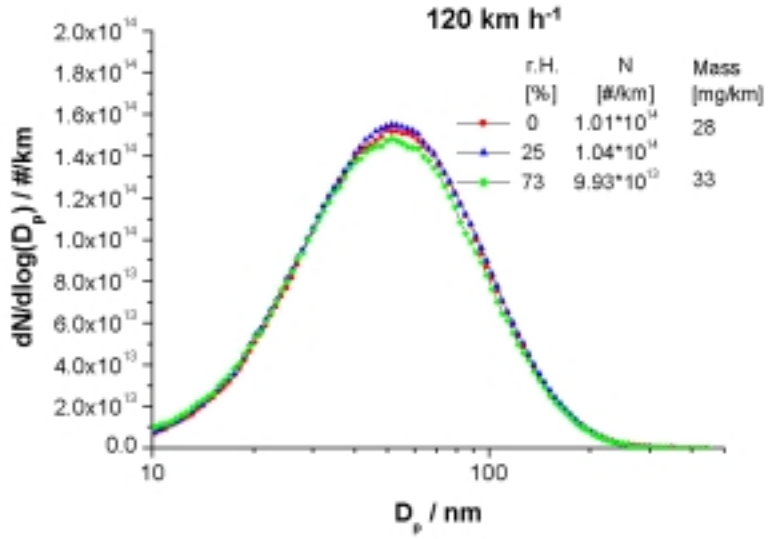

Fig. 3. Comparison of particle size distribution measured with the Matter diluter at the tailpipe of the diesel vehicle. The short sampling line was heated and the exhaust was diluted with humidified synthetic air at the given relative humidity (r.H.) values.

A dilution parameter which may have an impact on the measured exhaust particle size distribution is the relative humidity of the dilution air. Higher relative humidity could lead to particle growth, or restructuring (Weingartner et al. (1997)), or could enable particle nucleation and subsequent growth to a detectable size range. A dilution air humidifier was constructed and connected to the Matter diluter which was applied to the tailpipe. The diesel test car was operated at 120 km h^{-1}. Independent of the relative humidity all size distributions were alike and had the maximum around 50-60 nm. No particle mode around 10-20 nm was observed which would have indicated formation of secondary particles (Fig. 3).

3.2. Real world particle emissions

The Ford Mobile Laboratory (FML) was utilized to measure the particle size distribution in the exhaust trail of the same diesel vehicle previously tested in the emission lab. The measurements were performed on a high speed test track at 14 to 100 m distance to the test vehicle. Clearly, exhaust particles and gases, i.e. NO_x, CO and CO_2 could be measured, if the FML was inside the exhaust plume. From the known NO_x emission of the test vehicle and the measured concentration inside the plume the atmospheric dilution ratio of 1000 to 9000 was calculated. As in the emission laboratory the maximum of the size distribution was found around 50-60 nm. The total amount of particles emitted agrees well with the number determined on the chassis dynamometer. No second mode of smaller particles was observed at 50 km h^{-1} and 70 km h^{-1} (Fig. 4). However, at 100 km h^{-1} and 120 km h^{-1} additional 10 - 20 nm particles became apparent, which is in contrast to the observations at tailpipe dilution, or in the dilution tunnel. The bimodal size distribution indicated the presence of nucleation particles in addition to the soot mode. If the chasing distance was increased from 14 m (0.5 s) to 100 m (3.7 s) the bimodal shape was not effected.

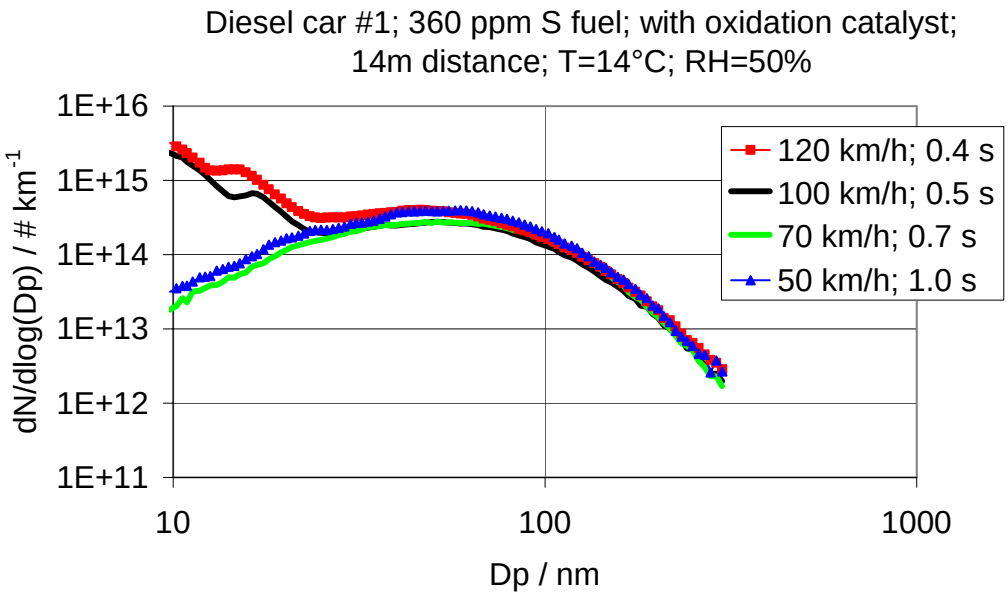

Fig. 4. Size distributions measured at different speeds in the exhaust plume of the test vehicle. running on 360 ppm S fuel and oxidation catalyst.

3.3. Fuel sulfur and oxidation catalyst effect

To further explore the formation conditions of the nucleation mode and the role of fuel sulfur the diesel passenger car was operated on low (10 ppm S) sulfur fuel and the particle size distribution measured with the FML chasing the exhaust plume. As shown in Fig. 5 even at 120 km h^{-1} a uni-modal size distribution and no nucleation mode particles were observed.

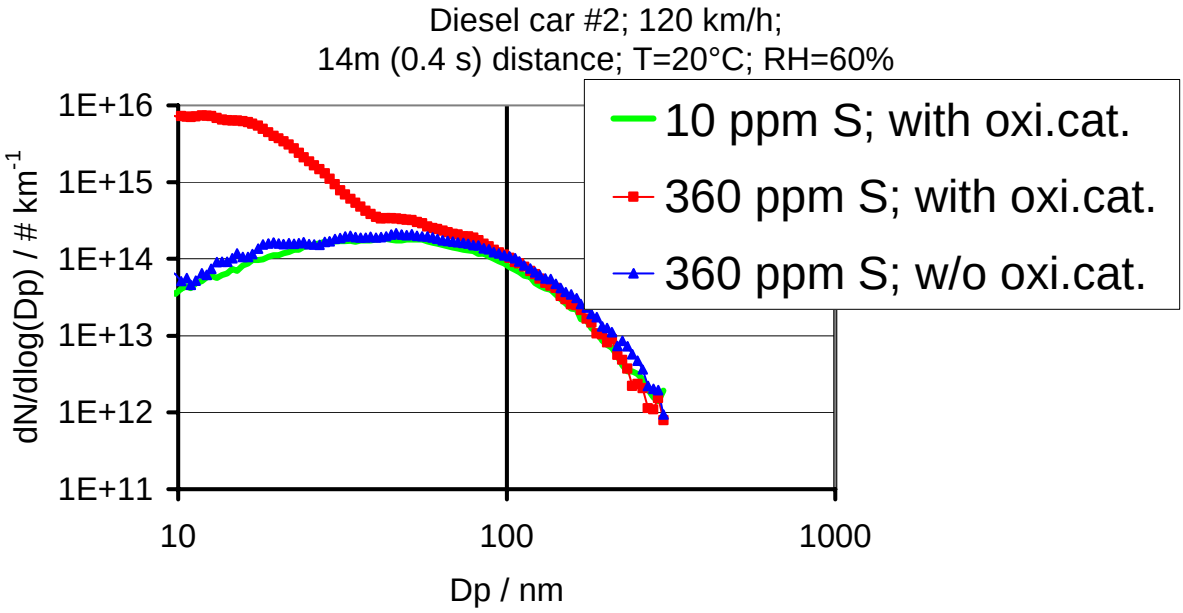

Fig. 5. PM size distributions measured in the exhaust plume of a test vehicle with different S fuel, with and w/o oxidation catalyst.

In the next experiment the fuel was changed back to regular sulfur content (360 ppm S), and a similar bimodal size distribution was observed as shown in Fig. 4. If the oxidation catalyst was removed the nucleation mode was absent and a size distribution very similar to the experiment with the 10 ppm S fuel and oxidation catalyst present.

These experiments show that the presence of fuel sulfur and of the oxidation catalyst are necessary to produce nucleation mode particles. It is likely that the fuel sulfur is oxidized to sulfuric acid which would form nucleation droplets in the exhaust plume. If the bulk of the 10-20 nm particle is made of sulfuric acid/water, or if hydrocarbons condense on the sulfuric acid nuclei (Tobias et al. (2001)) remains open.

Conclusions

In this work the effects of exhaust dilution method, sampling location and dilution parameters were investigated under carefully controlled conditions. The emphasis of the work is to better understand dilution processes and to define laboratory conditions which most reliably reflect real world emission and exhaust dilution. Particle size distributions measured in the exhaust of a diesel passenger car (EURO 3; 340 ppm fuel sulfur content) under laboratory conditions were uni-modal with a maximum of the particle mobility diameter around 50 to 70 nm. Depending on the sampling position (tailpipe versus different positions at the dilution tunnel) and on the residence time the maximum of the size distribution shifted to a larger particle diameter and the total number decreased. This is consistent with particle coagulation occurring during the residence in the sampling line and dilution tunnel.

The different tailpipe dilution systems were in reasonable agreement; no nucleation mode was observed despite introducing a residence time between primary and secondary dilution, or dilution with humidified air.

Particle size distributions were measured in the exhaust plume of the same diesel passenger car at a high speed test track using a Mobile Laboratory. The measurements showed good agreement of the size and number of the soot mode particles. However, at 100 and 120 km h^{-1}, using 360 ppm sulfur fuel and the regular oxidation catalyst mounted, an additional nucleation mode at 10-20 nm was observed. Using low sulfur fuel (S<10 ppm) this nucleation mode disappeared which is strong evidence for the fact that fuel sulfur is oxidized to sulfuric acid which forms efficiently particle nuclei.

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Dr.rer.nat. Olaf Bechmann, Dr.Ing. Stefan Carli, Werner Engeler, Dr.rer.nat. Thomas Garbe, Dipl.Chem. Gerhard Lach, Lisa Ryan (M.S.), Dr.rer.nat. Klaus-Peter Schindler,
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Partikelemission und -messung aus Sicht des Anwenders: heute und morgen

Particulate emissions and their measurement in practice: Today and in the future

Kurzfassung

Die Dieseltechnologie ist ein wesentlicher Bestandteil der Strategie zur Erfüllung der CO_2-Reduktionszusage, zu der sich die europäische Automobilindustrie verpflichtet hat. Der Diesel erfreut sich einer wachsenden Akzeptanz bei unseren Kunden. Er steht aber auch unter steht politischem Druck zur weiteren Minderung der Partikelemissionen. Da belastbare Daten fehlen, wird als Begründung der Aspekt der gesundheitlichen Vorsorge herangezogen. Für diese Diskussion ist eine zuverlässige Messung der Partikelemission von entscheidender Bedeutung. Parallel wird über eine Änderung der Partikelmesseigenschaft und –methodik für zukünftige Zulassungsmessungen nachgedacht.

Um die Partikelmessung diskutieren zu können, wird zuerst dargestellt, wie Partikel entstehen und welche Parameter zur Messung genutzt werden können. Weiterhin werden die Mindestanforderungen an die Partikelmesstechnik formuliert. Aus einer breiten Analyse von 22 Messverfahren zeigt sich, dass für die Messung der Masse nur die Gravimetrie direkt kalibrierbar ist. MassMo-, Li^{2}SA-(EC), Streulicht- und QCM-Verfahren sind indirekt über die Gravimetrie oder Coulometrie kalibrierbar. Eine Kalibrierung zur Messung der Partikelanzahl oder –oberfläche ist zur Zeit nicht möglich. Außerdem stellen die Wiederholbarkeit und die Reproduzierbarkeit, also die Stabilität der Messtechnik, die für Zulassungsmessungen von entscheidender Bedeutung ist, große Hürden für die meisten Methoden dar.

Somit hat der derzeitige Stand der neuen Messtechnik nur den Status der Gewinnung von qualitativen Aussagen zu Partikelanzahl und Größenverteilung erreicht, ist jedoch von der Möglichkeit der quantitativen absoluten Messung dieser Eigenschaften weit entfernt. Durch geeignete Wahl der Testbedingungen kann die Partikelanzahl praktisch beliebig manipuliert werden. Grundsätzlich sollte eine zukünftige Methode aber die Qualitätsanforderungen des derzeitigen Verfahrens zur Bewertung der Partikelemission erfüllen können. Deshalb liegt in der Weiterentwicklung der Gravimetrie das höchste Potential.

Abstract

Diesel technology is the cornerstone of the Volkswagen strategy to fulfil the CO_2 commitment made by the European automobile industry. It is also increasing in popularity with customers. Political pressure is driving the further reduction of particulate emissions as a health precautionary measure, although the scientific evidence is not yet complete to date. A reliable particle measurement procedure is essential for this discussion. Currently there is interest in developing new particle measurement instruments and techniques for future certification procedures.

Before particulate methodology can be discussed, it was necessary to explain the formation of particles and the available measurement parameters. The minimum requirements for any particle measurement system were defined and quantified. An analysis was undertaken of 22 particulate measurement instruments on the market or under development. For mass measurement it was discovered that only the gravimetric method can be directly calibrated, however the systems MassMo, Li^2SA (EC), light scattering and QCM can be indirectly calibrated using gravimetric or coulometric procedures. No particulate number or surface area measurement instrument can be calibrated absolutely. The repeatability and reproducibility, the stability of the measurements, of the new instruments also represent a hurdle for certification tests still to be overcome.

The new measurement instruments can as yet only be applied for the qualitative assessment of particulate number and size distribution as a relative comparison, but are still far from achieving the absolute quantitative measurement of these parameters. By appropriate choice of test conditions the particle number can be manipulated easily. Any new particle measurement methodology should fulfil the same quality criteria as the current one. Therefore gravimetric measurement is viewed to hold the most potential for future development.

1. Die Partikeldiskussion

Der moderne Dieselmotor ist das Antriebsaggregat mit dem besten Wirkungsgrad. Dem Vorteil des geringen Verbrauchs und damit geringen CO_2-Emissionen stehen im Vergleich zum Ottomotor mit Katalysator höhere NO_x- und Partikelemissionen gegenüber. Da bei der Nutzung von Verbrennungsmotoren Forderungen nach dem Schutz der Umwelt Eingang finden, ist die Verringerung dieser Abgasemission des Dieselmotors ein wichtiges Ziel bei dessen Weiterentwicklung.

Die wichtigsten Rahmenbedingungen für die heutigen Fahrzeuge - und damit auch für den Diesel - sind die ACEA[1]-Zusage zur CO_2/Kraftstoffverbrauchsminderung und die Abgasgesetzgebung:

1. Für das Jahr 2005 hat die deutsche Automobilindustrie in 1993 zugesagt, den Flottenverbrauch ihrer Neufahrzeuge um 25% bezogen auf das Jahr 1990 abzusenken. Auf europäischer Ebene hat der europäische Automobilverband ACEA in 1995 ebenfalls eine Zusage abgegeben, im Jahr 2008 den durchschnittlichen CO_2-Ausstoß der Neufahrzeuge auf 140g/km CO_2 zu reduzieren. Dieses entspricht ebenfalls einer 25%igen Minderung. Diese Zusage (Abb. 1) ergänzt die des VDA [1]. Das Monitoring zeigt, dass ACEA auf dem richtigen Wege ist, dieses Ziel zu erreichen. Allerdings ist der Diesel eine unbedingte Voraussetzung. Zum bisher Erreichten hat er bereits einen wesentlichen Beitrag geleistet. Sein Anteil wird auch künftig wichtig sein, da in den noch verbleibenden Jahren bis zum Ablauf der Selbstverpflichtung das Tempo der Verbrauchssenkung deutlich erhöht werden muss.

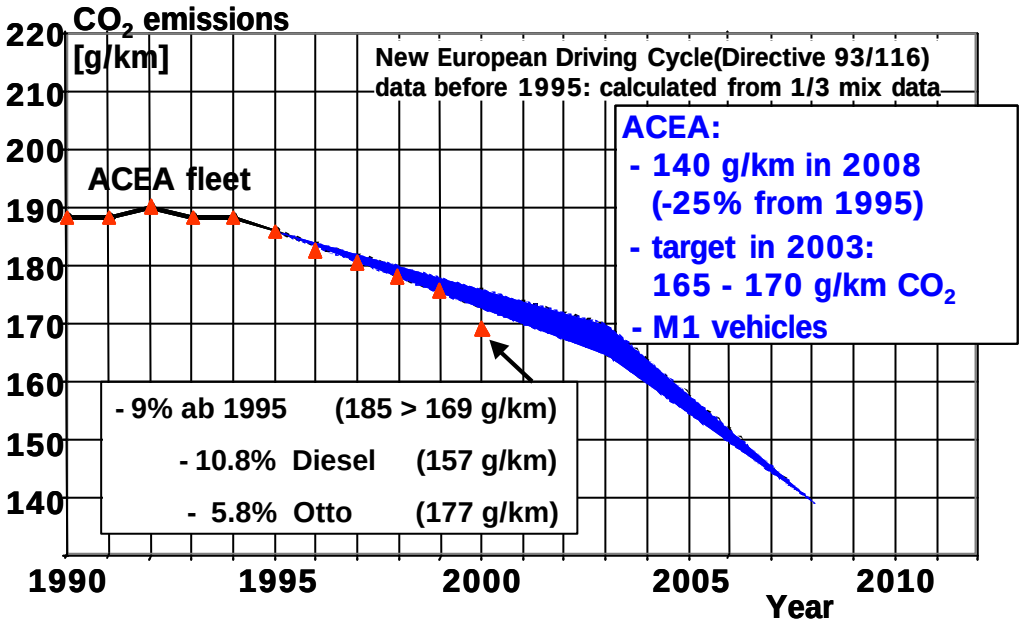


Abb. 1: Vereinbarung zwischen der EU-Kommission und ACEA zur CO_2-Minderung der Neuwagenflotte

Fig.1: Agreement between the EU Commission and ACEA to reduce the CO_2 emissions of the new vehicle fleet

2. Abgasgesetzgebung: Minderung der Partikelemissionen um mehr als 90% seit Einführung der Partikelgesetzgebung (Abb. 2). Die Euro 4-Grenzwerte, die ab 2005 Pflicht werden, bedeuten für den Diesel eine Minderung von Partikeln und NO_x um ca. 70% gegenüber Euro 2, also 1996.

[1] ACEA = Verband der europäischen Automobilhersteller, Brüssel, Belgien

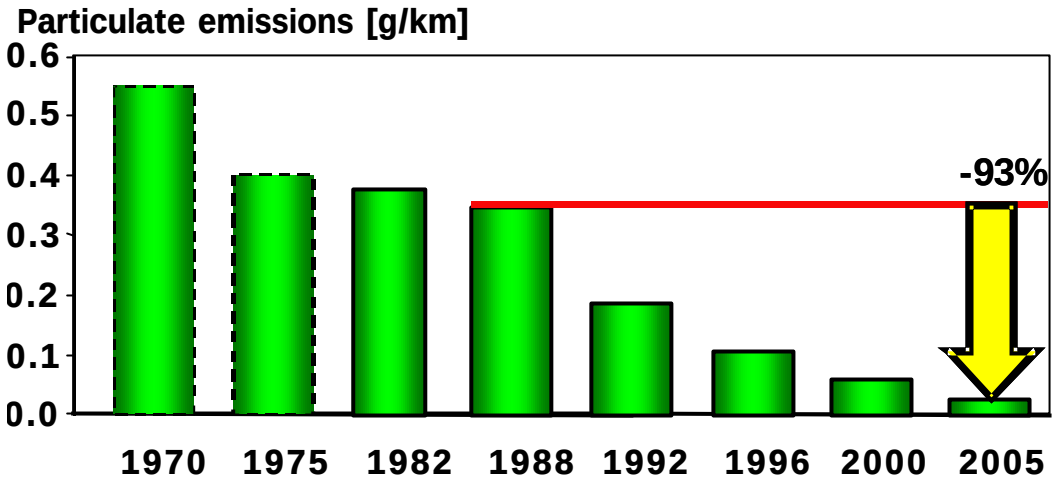


Abb. 2: Reduktion der Partikelemissionen seit Einführung des Partikelgesetzgebung

Fig. 2: Reduction of particulate emissions since the introduction of particulate emissions legislation

Die ersten Untersuchungen (vor ca. 20 Jahren) zur möglichen Gesundheitsgefährdung von Dieselpartikeln wurden mittels toxikologischer Untersuchungen durchgeführt; übrigens mit Unterstützung der Automobilindustrie. Die Resultate zeigen, dass Tierexperimente nicht auf den Menschen übertragbar sind [6]. Vergleichende Untersuchungen zwischen Ratten und Affen bewiesen zudem, dass ein völlig unterschiedliches Ablagerungsverhalten der Partikel in den Lungen vorliegt [8]. In Affenlungen, die der menschlichen Lunge sehr ähnlich sind, werden Partikel überwiegend in den Gewebe- und Zellzwischenräumen abgelagert, ohne dass es zu den für eine häufig den Tumorbildungen vorausgehenden Entzündungen kommt. Bei Ratten hingegen werden diese Partikel überwiegend in den Lungenbläschen gefunden und rufen dort entsprechende Gewebeveränderungen und Entzündungen hervor. Die Tierversuche zur gesundheitlichen Gefährdung von Dieselmotor-Abgasen gelten daher in der internationalen wissenschaftlichen Diskussion derzeit als nicht auf den Menschen übertragbar. Sie sind als Grundlage für eine Risikoabschätzung für den Menschen ungeeignet.

Die Ergebnisse der dann durchgeführten epidemiologischen Untersuchungen sind nicht eindeutig genug, um sichere Aussagen geben zu können [7]. Den Studien liegen bis auf wenige Ausnahmen - wenn überhaupt - Messungen der Exposition nur in Form von Angaben zur Gesamtpartikelmasse zugrunde. Hier ist weiterer Klärungsbedarf vorhanden, bevor der Gesetzgeber weitere Regulierungen erläßt.

Das unabhängige HEI[2] stellt fest [2], dass die Ergebnisse einer umfangreichen Studie "indicate that epidemiologic evidence of PM's effects on morbidity and mortality persist even when the alternative explanations have been largely addressed".

[2] HEI = Health Effects Institute, Cambridge MA, USA (www.healtheffects.org)

Obwohl HEI in diesem Zusammenhang extra auf die Notwendigkeit

- ?? weiterer Forschung zur Klärung der Wirkungsmechanismen der Gesundheitseffekte und
- ?? der Beobachtung der Verwendung der Ergebnisse im politischen Bereich

hinweist, wird die obige Aussage isoliert genutzt und mit Hilfe des Vorsorgearguments die sofortige drastische Minderung der Partikelanzahl oder -oberfläche gefordert.

Grundsätzlich geht Volkswagen deshalb davon aus, dass die schrittweise vollzogene und die künftig noch mögliche Verringerung von Partikeln als Beiträge zum vorbeugenden Gesundheitsschutz zu werten sind. Gleichwohl käme eine generelle Forderung nach Partikelfiltern einer unzulässigen Technologievorschrift gleich.

Nach der Richtlinie 98/69/EC muß die EU Kommission das heutige Partikelmessverfahren (siehe Richtlinie 70/220/EG) untersuchen. In Brüssel wird deshalb das ‚Particulates' Programm[3] durchgeführt. Ziel ist die Erarbeitung eines Vorschlages für eine neue Methodik für den Zeitraum nach 2005.

Im Rahmen der UN ECE GRPE[4] soll parallel dazu bis Anfang 2003 eine alternative Methode zur Messung von Dieselpartikeln im Rahmen der Typprüfung erarbeitet werden. Dazu wurde das PMP[5] eingesetzt. Man geht davon aus, dass die heutige Meßmethode (Gravimetrie) nicht mehr empfindlich genug für zukünftige Gesetzesanforderungen ist. Zudem werden die Partikelanzahl und -größe sowie teilweise die Partikeloberfläche als wirkungsrelevantere Eigenschaft der Partikel diskutiert. Auch die PMP-Ergebnisse sollen Grundlage für eine neue Abgasstufe nach 2005 werden.

Deshalb stellen wir uns der Diskussion der Partikelemissionen aus motorischer Verbrennung.

2. Was sind Partikel und wie entstehen sie?

„Partikel" ist ein Überbegriff für alle Teilchen, fest oder flüssig, die mit dem Gasstrom getragen werden. Diejenigen Partikel, die aus der dieselmotorischen Verbrennung stammen, sind neben den Rußpartikeln noch Tröpfchen aus Kohlenwasserstoffen oder Säuren, Aschepartikel und Metallabrieb. Die Verschiedenheit der Partikel in Form, Größe und Zusammensetzung erschwert eine einheitliche Begriffsbildung für die Partikel. Die häufig verwendeten Bezeichnun-

[3] 'Particulates' = Characterization of Exhaust Particulate Emissions from Road Vehicles, European Research Programme, sponsored by DG TREN (2000-2003)
[4] UN ECE GRPE = UN Economic Commission for Europe, World Forum for Harmonisation of Vehicle Regulations (WP.29), Working Party on Pollution and Energy
[5] PMP = GRPE ad hoc group – Particle Measurement Programme

gen „Nanopartikel“, Feinpartikel“ o.ä. für Partikel aus verschiedenen Größenbereichen sind nicht standardisiert. Im weiteren werden folgende Bezeichnungen benutzt:

- d < 50 nm: Nanopartikel,
- d < 100 nm: Ultrafeine Partikel,
- d < 2,5 µm: Feinpartikel (PM2.5),
- d < 10 µm: Feinpartikel (PM10),
- d > 1 µm: Grobpartikel,
- d < 50 nm: Nukleationsmodus,
- 50 nm < d < 1 µm: Akkumulations- oder Agglomerationsmodus.

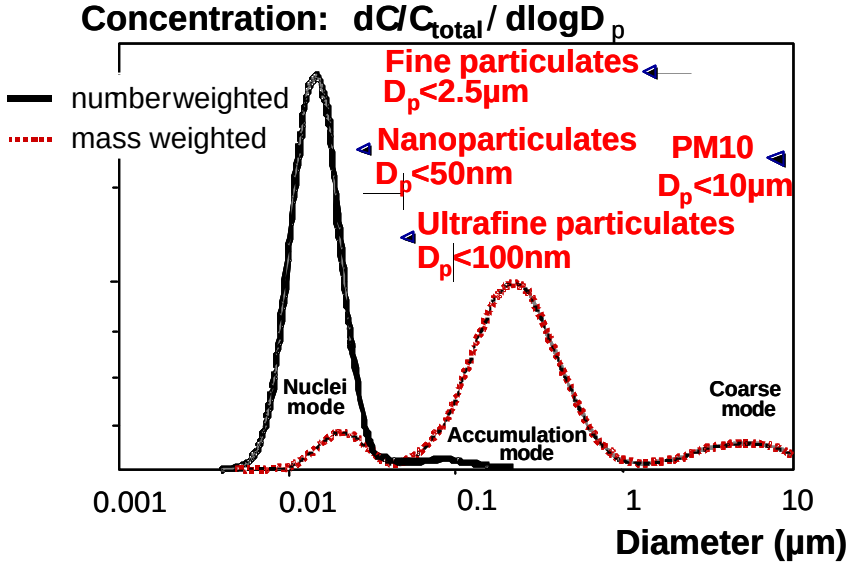


Abb. 3: Verteilung von Partikeln in der Atmosphäre nach Kittelson [5]

Fig. 3: Distribution of particles in the atmosphere, proposed by Kittelson [5]

Abb. 3 zeigt eine idealisierte, dreimodale und logarithmisch normalverteilte Dieselpartikelmassen- und Anzahlgrößenverteilung [5]. Der größte Teil der Partikelmasse bewegt sich im sog. Akkumulationsmodus zwischen 0,05 bis 1,0 µm Partikeldurchmesser. Dabei handelt es sich hauptsächlich um die typischen Rußagglomerate. 5 – 20 % der Partikelmasse machen die sog. Grobpartikel aus, die entstehen, wenn Rußwandablagerungen in der Abgasanlage wieder in den Abgasstrom gelangen. Der Nukleationsmodus besteht aus Partikeln im Größenbereich zwischen 0,005 – 0,05 µm. Diese Partikel setzen sich hauptsächlich aus schwefelhaltigem sowie löslichem organischem Material zusammen. Die hier gezeigte Größenverteilung repräsentiert die Situation bei der Verbrennung von Dieselkraftstoffen mit einem Schwefelgehalt von einigen 100 ppm. Unter diesen Bedingungen kann der Nukleationsmodus bis über 90% der Partikelanzahlverteilung ausmachen. Bei Verwendung von schwefelfreiem Dieselkraftstoff verschwindet der Nukleationsmodus nahezu vollständig.

Ein erheblicher Teil der Partikelmassenemission ist auf Ruß zurückzuführen. Ein zentrales Problem bei der Weiterentwicklung des Dieselmotors ist daher die Rußbildung und -oxidation. Abb. 4 zeigt ein typisches Rußpartikel, wie es bei der Verbrennung erzeugt wird. Es ist ein Agglomerat aus Primärpartikeln, die während der Verbrennung des Kraftstoffes im Brennraum entstehen.

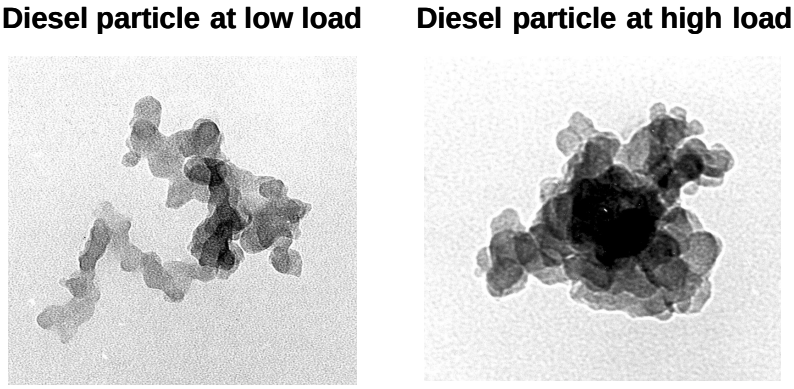


Abb. 4: TEM Analyse der Morphologieänderung der Partikel im Teil- und Volllast.

Fig. 4: TEM analysis of the morphology change of diesel particulate at high and low loads .

Der Rußbildung und -oxidation im Dieselmotor sind die einzelnen Vorgänge der dieselmotorischen Verbrennung - Luftzufuhr, Einspritzung, Zündung, Flammenausbreitung - überlagert. Ein besseres Verständnis dieser Abläufe kann nur durch den Einsatz moderner Meßverfahren und Simulationsmethoden erreicht werden. Dabei müssen die einzelnen Stufen der Rußbildung, deren geschwindigkeitsbestimmende Schritte sowie das Zusammenwirken von simultaner Bildung und Oxidation in diffusionskontrollierter nicht vorgemischter Verbrennung von Kohlenwasserstoffen untersucht werden.

Bei der dieselmotorischen Verbrennung wird der Kraftstoff in die verdichtete Verbrennungsluft eingespritzt. Abhängig vom Zündverzug und der Einspritzrate liegt der Kraftstoff bis zum Zündpunkt als gasförmiges Gemisch mit Luft vor. Messungen der Ausbreitung des Brennstoffstrahls und seiner Vermischung bestätigen, daß die erste Zündung in Zonen mit Luftverhältnissen um etwa 0.7 auftritt [3]. Die sich in der ersten Phase ausbreitende Flamme führt zur Verdampfung des restlichen Kraftstoffs und zu dessen Vermischung mit verbrannten Gasen und Verbrennungsluft. Die Verbrennung des Kraftstoffs in der zweiten Phase findet in partiell vorgemischten Diffusionsflammen statt. Der gesamte Kraftstoff verbrennt also wie eine gasförmige, geschichtete Gemischwolke, in der Bereiche mit unterschiedlichsten Luftverhältnissen vorliegen. Die Ausdehnung dieser Bereiche ist vom Zündverzug und Einspritzverlauf abhängig.

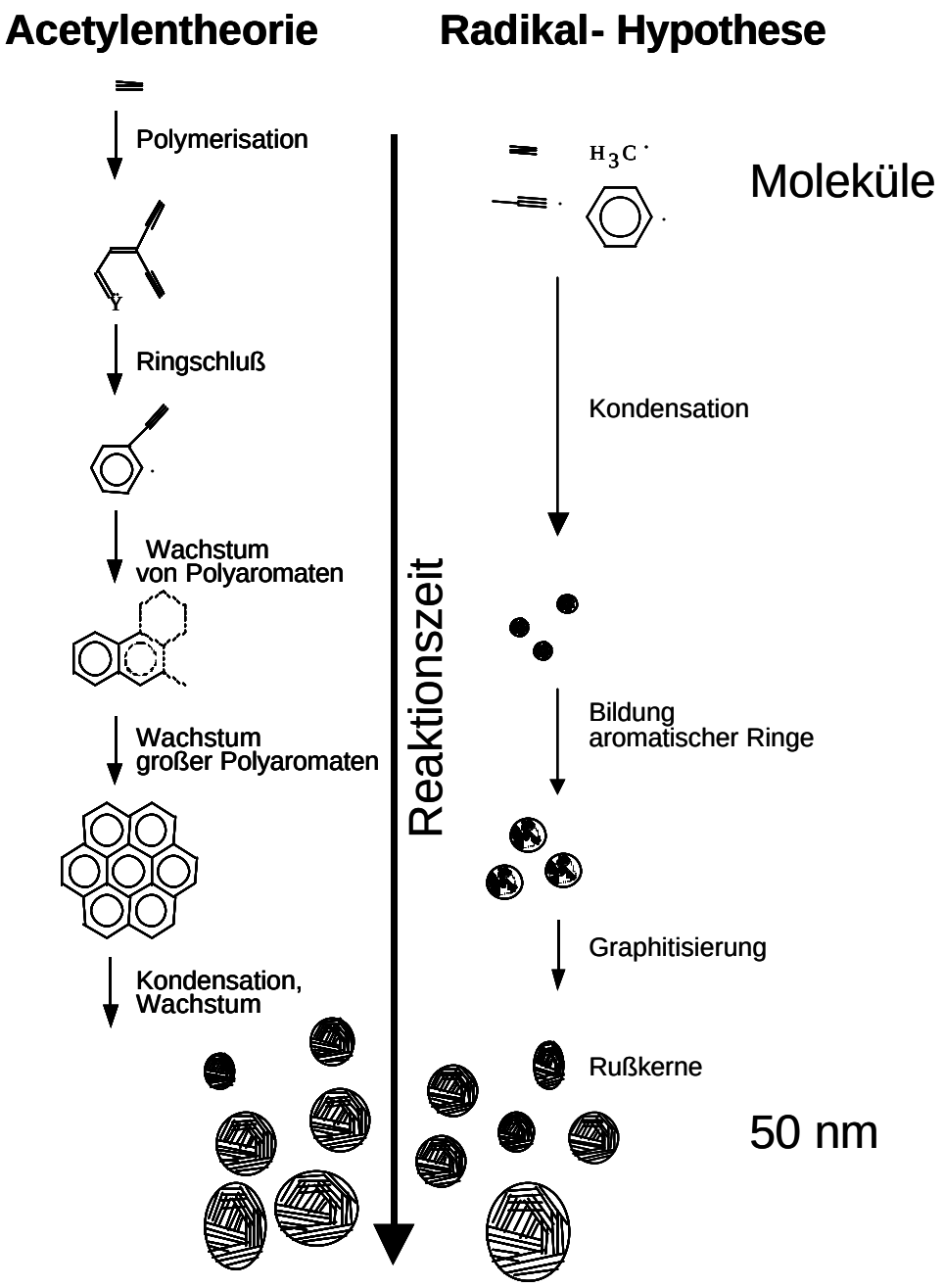


Abb. 5:2: Alternative Mechanismen der Partikelbildung
Fig. 5:2: Mechanisms for particle formation.

Die Rußbildung ist dabei in Teilchenneubildung, Teilchenkoagulation und Oberflächenwachstum sowie Oxidation der Rußteilchen zu unterteilen [4]. Diese Prozesse laufen teilweise simultan ab.

Der Entstehungsmechanismus ist noch nicht genau bekannt, es existieren aber verschiedene Hypothesen, nach denen diese Rußvorläufer, meist aromatische Kohlenwasserstoffe, gebildet werden. Die geläufigsten sind die Acetylen- [9] und die Radikalhypothese [10]. Nach der Acetylenhypothese werden die Brennstoffmoleküle zunächst oxidativ abgebaut. Dabei entsteht Ethin (Acetylen), das den Ausgangspunkt für die Bildung höherer Kohlenwasserstoffe und (alkylierter) Aromaten bildet. Letztere wachsen planar durch einen H-Abstraktions-Ethin-Additionsmechanismus weiter (Abb. 5). In der Radikalhypothese wird davon ausgegangen, daß kleine Radikale unabhängig von ihrer Beschaffenheit zu großen, verzweigten Kohlenwasserstoffketten kombinieren, welche umgehend kondensieren. Intramolekular kommt es nun zu Ringschlußreaktionen. Als Nebenprodukt werden durch Bindungsspaltung aromatische Kohlenwasserstoffe abgeschieden, welche teilweise verdampfen, teilweise am Rußkern gebunden bleiben.

Das räumliche Wachstum erfolgt durch die Zusammenlagerung größerer polyzyklischer aromatischer Kohlenwasserstoffe. Das Volumen der entstehenden Aggregate nimmt durch weitere Koagulation und Oberflächenwachstum zu. Für letzteres wird oft ein Mechanismus analog zum planaren Wachstum der polyzyklischen Aromaten angeführt.

Neben und in Konkurrenz zu diesem Mechanismus laufen natürlich als hauptsächlicher Kanal die Reaktionen zur Verbrennung des Kraftstoffs und der intermediär gebildeteten Kohlenwasserstoffe in die Hauptreaktionsprodukte ab. Die Oxidation der Rußteilchen ist der maßgebliche Prozess für die zweite Phase der dieselmotorischen Verbrennung, in der die gebildeten Rußteilchen durch die Vermischung der Verbrennungsprodukte mit Verbrennungsluft in sauerstoffreiche Umgebung gelangen.

Die Rußvorläufer lagern sich dann zu Graphitkristalliten zusammen. Hat der Kristallkern eine bestimmte Größe erreicht, lagern sich die weiteren Kristallplättchen parallel zur Oberfläche des Primärpartikels an, so daß ein kugelförmiges Gebilde entsteht. In der frühen Phase der Verbrennung wachsen diese Primärpartikel zu Kugeln von typischerweise 30 nm Durchmesser heran. Beim Abklingen der Temperaturspitzen im Brennraum agglomerieren die Primärpartikel zu den traubenförmigen Partikeln, die allgemein als „Ruß“ bezeichnet werden (s. Abb. 4). Diese Partikel erreichen typische Durchmesser von 70-100 nm. Mehr als 80 % der so gebildeten Rußteilchen werden während des Arbeitstaktes im Brennraum wieder verbrannt.

Weitere Abkühlung, insbesondere in der Abgasanlage oder in der Umgebungsluft, führt zur Adsorption oder Kondensation gasförmiger Bestandteile, meist Kohlenwasserstoffe, an den Partikeln. Bei Temperaturen unterhalb etwa 20°C oder bei abrupter Abkühlung können die Kohlenwasserstoffe selber kleine Tröpfchen im Größenbereich bis zu 30 nm (Abb. 6) bilden.

Per gesetzlicher Definition sind alle Komponenten, die aus dem Verdünnungstunnel (Abb. 10) entnommen werden und sich auf den Filtern bei Temperaturen kleiner als 52°C abscheiden, "Partikel". Dieses führt bekanntlich auch zu einer Abscheidung von höhersiedenen Kohlenwasserstoffen, Schwefelverbindungen usw.

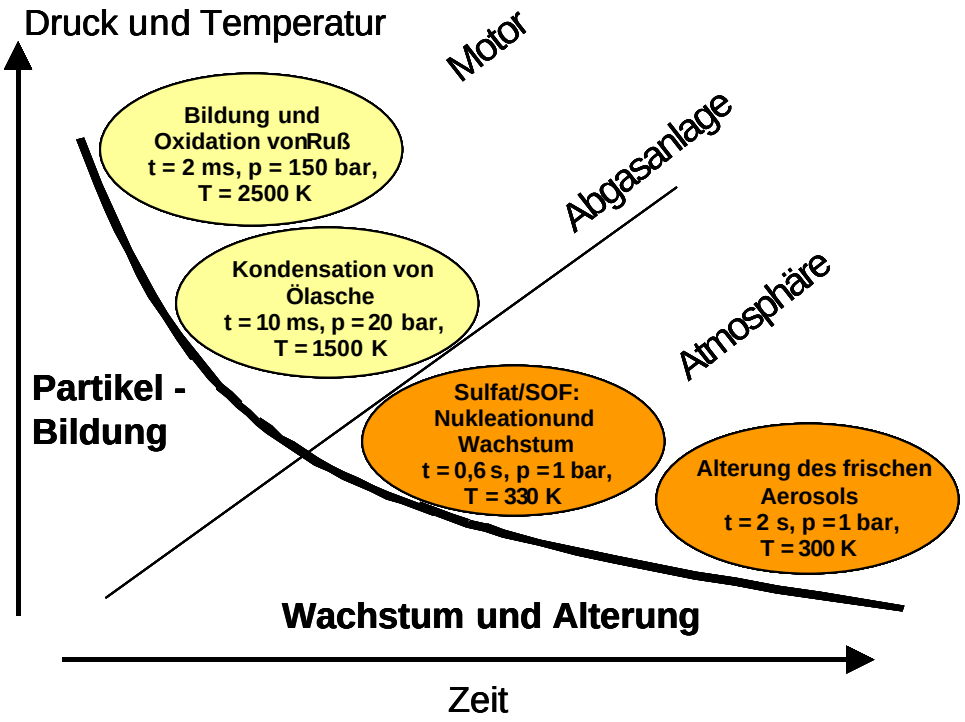


Abb. 6: Darstellung der Bedingungen für Partikelbildung und –wachstum

Fig. 6: Illustration of development of conditions for particle formation and growth

Die während der Verbrennung entstehenden Partikel werden in molekularen Prozessen in der Gasphase gebildet. Messergebnisse von ACEA (Abb. 7) [11] und Volkswagen (Abb. 8) zeigen, daß sich die Partikelgröße bei modernen Dieselmotoren im Vergleich zu älteren Konzepten nicht verändert hat, was bedeutet, daß mit der Verminderung der Partikelmassenemission auch die Partikelanzahl zurückgegangen und damit eine Korrelation zwischen Masse und Anzahl gefunden worden ist (Abb. 7b und 8b). Die Aussage, daß moderne direkteinspritzende Dieselmotoren kleinere und mehr Partikel emittieren als konventionelle Konzepte, ist damit falsch.

Über Veränderungen der Partikel in der Atmosphäre ist bis heute wenig bekannt. Deshalb wissen wir nicht exakt, von welcher Struktur und Zusammensetzung diejenigen Partikel sind, die in die tiefen Bereiche der Lunge gelangen und welches der für ein mögliche Gesundheitsgefährdung wichtige Parameter ist. Damit stellt sich die Kernfrage der Partikeldiskussion: Welches ist der Bewertungsmaßstab? Sollte sich herausstellen, daß die Anzahl die wichtige Größe ist, reicht auch weiterhin die Messung der Gesamtmasse aus, da Masse und Anzahl korrelieren.

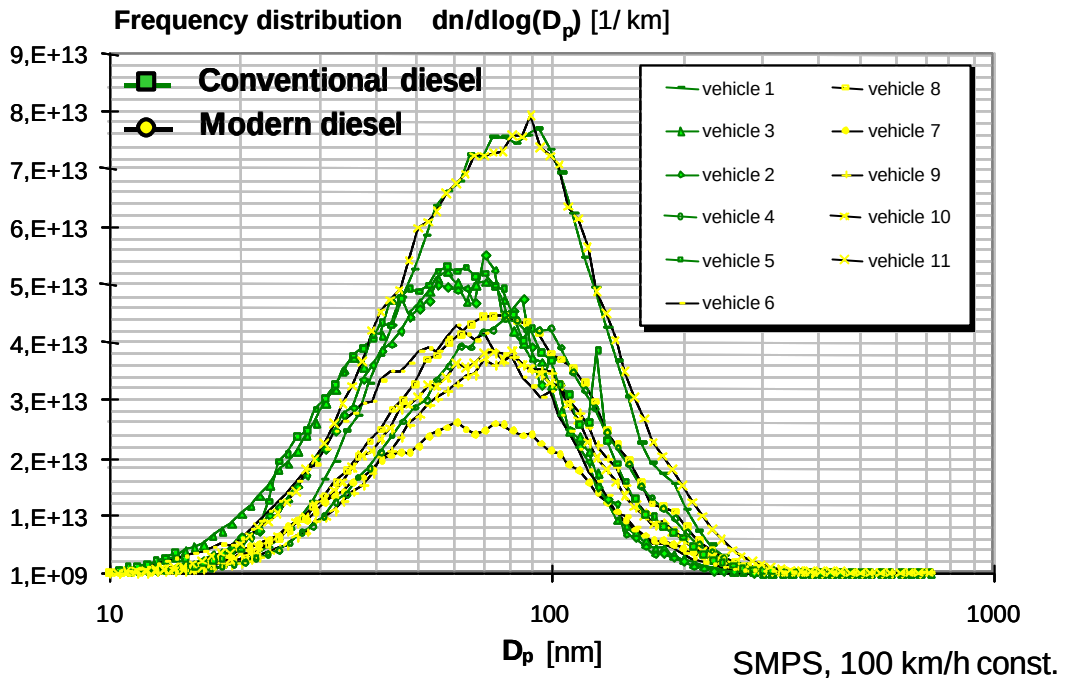


Abb. 7a: ACEA Meßprogramm: Größenverteilung der Dieselpartikel von 11 PKW [11]

Fig. 7a: ACEA measurement programme: size distribution of particulate emissions from 11 diesel cars [11]

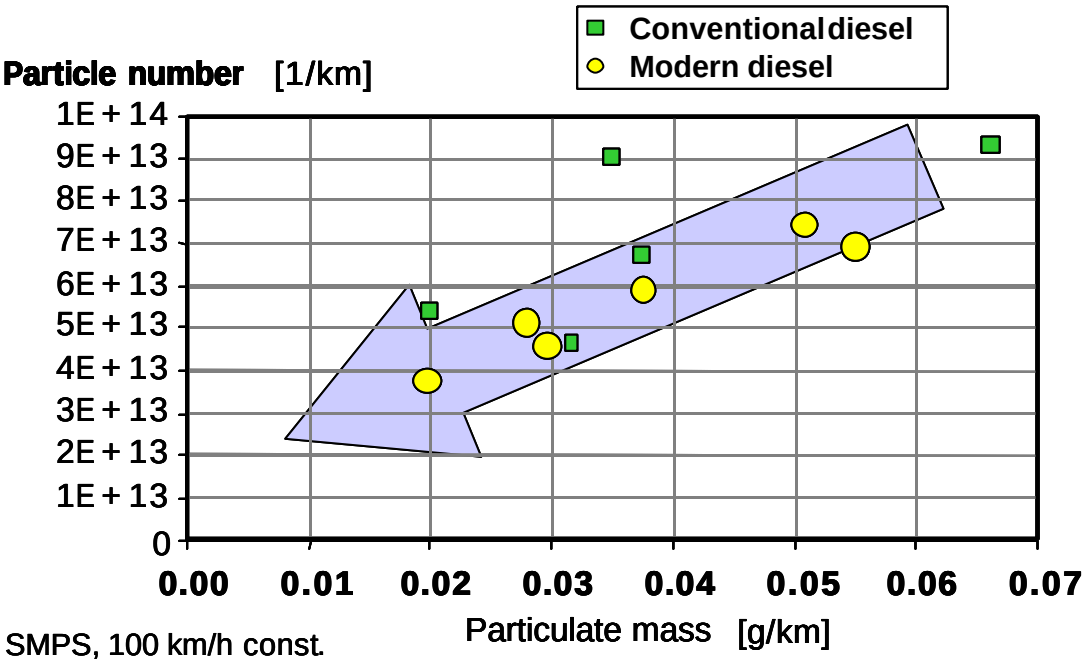


Abb. 7b: ACEA Meßprogramm: Partikelanzahl als Funktion der Partikelmasse [11]

Fig. 7b: Volkswagen measurement programme: particulate number as a function of particulate mass [11]

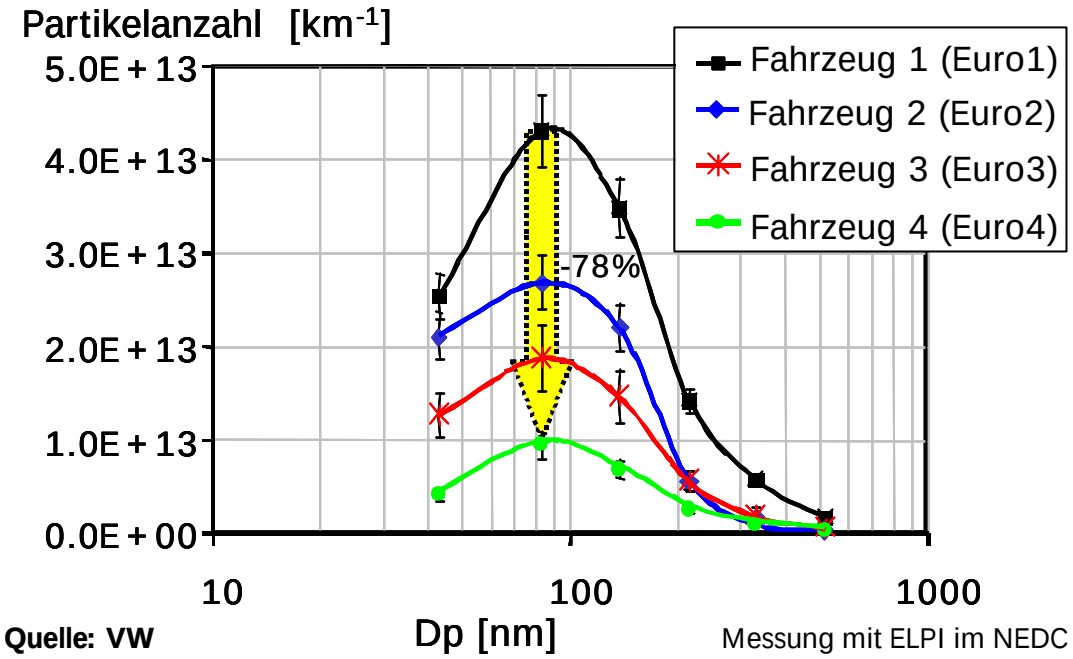


Abb. 8a: Volkswagen Meßprogramm: Größenverteilung der Dieselpartikel von 4 PKW

Fig. 8a: Volkswagen measurement: size distribution of particulate emissions from 4 diesel cars

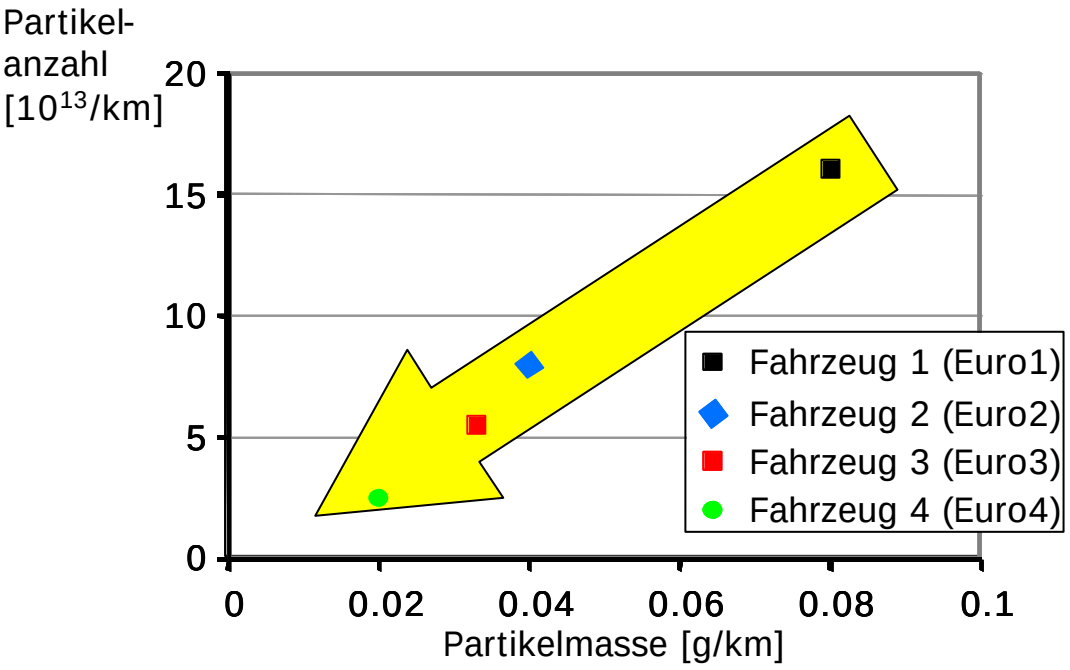


Abb. 8b: ACEA Meßprogramm: Partikelanzahl als Funktion der Partikelmasse

Fig. 8b: Volkswagen measurement programme: particulate number as a function of particulate mass

3. Wie werden Partikel gemessen?

Das Abgas des Fahrzeuges wird in einen Verdünnungstunnel mit festlegten Abmessungen geleitet und dort mit Umgebungsluft derart vermischt, dass ein konstanter Gesamtvolumenstrom entsteht. Der Verdünnungstunnel ermöglicht eine homogene Probenahme. Dem Verdünnungstunnel werden die Gas- und die Partikelproben entnommen. Die Partikel werden auf einem Primär- und Sekundärfilter gesammelt. Der Sekundärfilter soll die Partikel, die im Primärfilter nicht abgeschieden werden, aufnehmen.

3.1. Anforderungen an die Meßtechnik

Um Messtechniken diskutieren zu können, müssen die Anforderungen an das Messgerät und die Probenahme definiert und quantifiziert werden. Die Mindestanforderungen für die aus unserer Sicht wichtigsten Parameter - Bestimmungsgrenze[6], Reproduzierbarkeit[7], Wiederholbarkeit[8], Zeitauflösung und Kalibrierbarkeit - sind in Tabelle 1 dargestellt.

	Masse	Anzahl	Oberfläche
Bestimmungsgrenze	10% vom Grenzwert	Ab Durchmesser 30 nm	Nicht bekannt
Kalibrierung vor Ort überprüfbar	ja		
Wiederholbarkeit	5 % vom Grenzwert		
Reproduzierbarkeit	10 % vom Grenzwert		
Zeitauflösung	Integral Einzelphasen des Testzyklus		

Tabelle 1: Mindestanforderungen für das Gerät einschl. Probenahme zur Messung von Partikelmasse, -anzahl und –oberfläche

Table 1: Minimum requirements for the instrument incl. sampling system for measurement of particulate mass, number and surface area

[6] Bestimmungsgrenze: Nachweisgrenze + 3 Standardabweichungen
Nachweisgrenze: minimales Signal über den Untergrund

[7] Reproduzierbarkeit: Streuung bei Messung mit verschiedenen Geräten aber gleichem Meßaufbau unter gleichen Meßbedingungen

[8] Wiederholbarkeit: Streuung bei Messung mit einem Meßaufbau unter gleichen Meßbedingungen

Die Anforderungen wurden an die Partikelgrenzwerte gekoppelt. So liegt die Bestimmungsgrenze für die Messung der Partikelmasse von Euro4-Fahrzeugen bei 0,0025 g/km. Die Bestimmungsgrenze allein ist aber für die Eignung einer Messmethodik nicht ausschlaggebend. Das Zurückführen der Messwerte auf absolute, geeichte Größen ist erforderlich. Die Kalibrierung muß auch am Prüfstand handhabbar und mehrmals täglich realisierbar sein. Nur so können Resultate für die Typprüfung ermittelt werden.

Ebenso sind die Wiederholbarkeit und die Reproduzierbarkeit, also die Stabilität der Messtechnik von entscheidender Bedeutung. Beide Kriterien müssen zuverlässig genug erfüllt werden, damit die Messungen im eigenen Labor wie auch mit denen aus anderen Testlaboratorien verglichen werden können. Die Anforderungen müssen mindestens so streng sein, wie die der Gravimetrie. Aus der Praxis heraus wird für alle Systeme eine Wiederholbarkeit von 5% und eine Reproduzierbarkeit von 10% gefordert.

Die Zulassung erfordert eine integrale Messung über den Testzyklus. Für die Anwendung in der Entwicklung wäre eine Auflösung in die zwei Phasen des Testzyklus' oder besser noch eine ‚real time'-Messung wünschenswert.

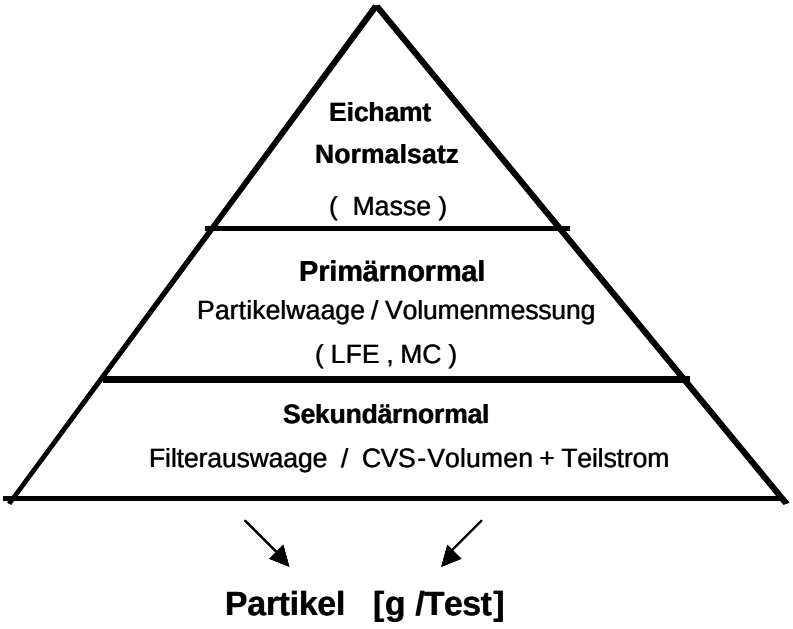


Abb. 9: Kalibrierkette der Partikelbestimmung

Fig. 9: Calibration sequence for particle measurement

3.2. Heutiges Messverfahren: Gravimetrie

Die quantitative Bestimmung der zulassungsrelevanten Abgaskomponenten setzt eine Ableitung zu eichfähigen Grundgrößen voraus. Abb. 9 zeigt die Kalibrierkette. Die Massennormale sind ein Gewichtssatz der im Eichamt geeicht wird. Damit wird die Partikelwaage kalibriert. Zur

Eichung des Volumenflusses wird von einem eichfähigen Messgerät (z.B. Laminar Flow Element oder Massendurchflussmesser) im Eichamt eine Kalibrierkurve aufgenommen. Dieser geeichte Volumenfluss wird dann auf die CVS–Anlage (Constant Volume Sampler) und andere Volumenmessgeräte übertragen.

Das Herzstück dieser Kalibrierkette ist die Partikelwaage mit einer Genauigkeit von $\pm$ 0,001 mg. Eine größere Unsicherheitsquelle liegt in dem mit der Partikelmasse beladenen Filter selbst. Das Filtermaterial ist vorgeschrieben: Glasfaserfilter mit PTFE-Beschichtung. Das Glasfasermaterial gewährleistet hohes Rückhaltevermögen bei gleichzeitig geringem Durchflusswiderstand. Der Nachteil, dass Glasfaserfilter eine nur begrenzte mechanische Stabilität aufweisen und im Filterinnern relativ grosse Mengen gasförmiger organischer Stoffe adsorbieren, kann durch die PTFE–Beschichtung in gewissem Masse kompensiert werden. Die tägliche Wägung eines leeren Referenzfilters (Blank-Filter) ergibt in der Praxis Streuungen von $\pm$ 0,005 mg, also das 5-fache der Genauigkeit der Waage. Dieses sind die kalibrierfähigen Messgrößen, die die Grundlage der Partikelmassenbestimmung darstellen.

Das Hauptproblem der Partikelmesstechnik stellt das eigentliche Messgut dar. Die Partikelbildung, d.h. die Agglomeratbildung, ist am Ende der Abgasanlage noch nicht abgeschlossen. Neben der Bestimmung der kalibrierfähigen Größen ist die Menge der Partikel deshalb abhängig von dem Verdünnungsverhältnis und dem Probenahmesystem, die in Abb. 10 dargestellt sind. Die Anordnung besteht aus den Einzelkomponenten Umgebungsluftfilter, Verdünnungstunnel, Partikelentnahme und Rotationskolbengebläse. Der Umgebungsluftfilter setzt sich aus mehreren Filterstufen zusammen und dient zur Reinigung der Umgebungsluft. Im Verdünnungstunnel erfolgt die Vermischung von Luft und Abgas, wobei zusätzlich eine Mischdüse eingesetzt wird. Am Ende des Tunnels befindet sich eine Absaugeinheit (Rotationsgebläse). Das verdünnte Abgas wird zur Bestimmung der Partikelmasse dem Tunnel definiert entnommen und über einen Filterhalter geleitet, in dem sich Primär- und Zusatzfilter (= Sekundärfilter) befinden. Die Gasuhr dient zur Bestimmung des Teilstromes.

Die EU-Vorschrift (Richtlinie 70/220/EG) sieht vor, dass die Auswaage des Sekundärfilters zur Auswaage des Primärfilters addiert wird, wenn sie größer als 5 % der gesamten Partikelmasse ist. Während der Zulassungsmessung kann die Probe auf einem Filter gesammelt werden. Für Entwicklungstests wird üblicherweise die Partikelprobe auf zwei Filtern (Teil 1 bzw. Teil 2 der EU-Fahrkurve) gesammelt, um den Einfluss der Fahrkurve auf die Partikelemissionen beurteilen zu können.

Die Partikelmasse wird aus der Filterbelegung unter Berücksichtigung des Teilstromes berechnet. Auf dem Filter scheiden sich auch höhersiedende Kohlenwasserstoffen und Schwefelverbindungen ab. In Verbindung mit der Absenkung des Kohlenwasserstoff-grenzwertes und durch den Einsatz schwefelarmer Kraftstoffe wird der Anteil der Komponenten, die die Messung der motorischen Partikeln beeinflussen können, reduziert.

Die Absenkung der Partikelgrenzwerte stellt eine hohe Anforderung an die Messgenauigkeit und erfordert im Detail Änderungen der Gesetzgebung. So ist heute vorgeschrieben, dass die

Filterbeladung während des Abgastestes zwischen 1 und 5 mg betragen soll. 1mg wird als Nachweisgrenze der Bestimmung der Filterbeladung angesehen, während die obere Grenze verhindern soll, den Messwert "Partikel" zu verfälschen. Auf Filtern mit hoher Partikelmasse kann es vermehrt, zur Adsorption von Wasser und von leichtflüchtigen Kohlenwasserstoffen sowie chemischen Reaktionen kommen, die beim Ausströmen des Abgases in die Umgebungsluft nicht auftreten würden.

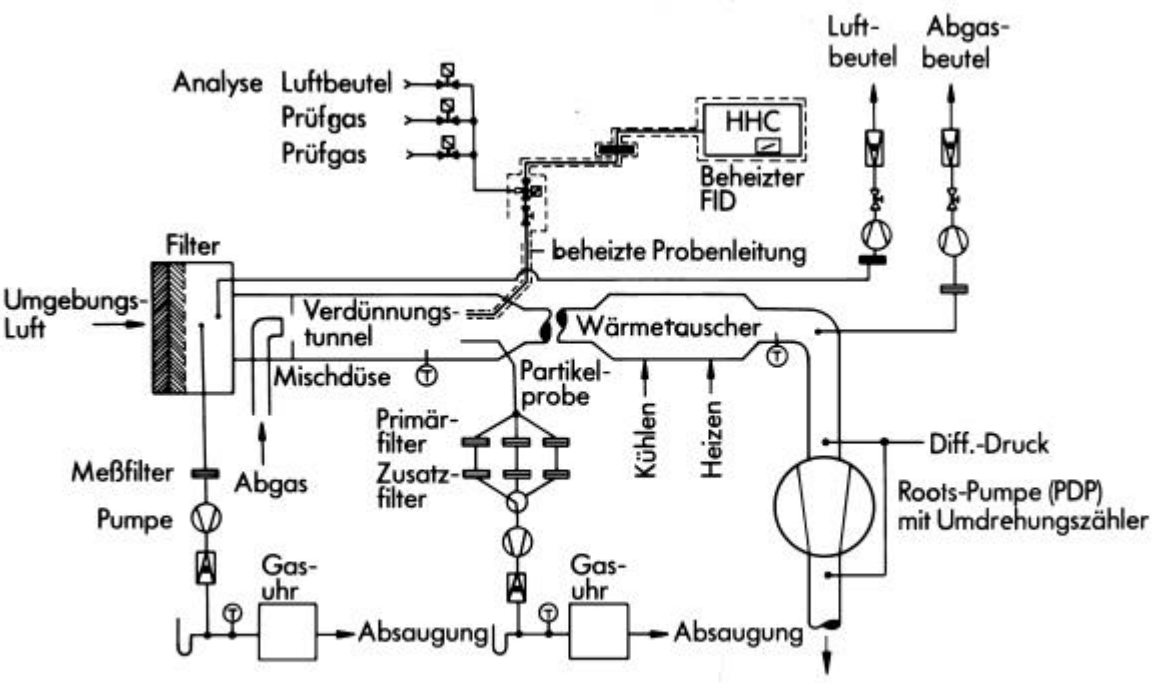


Abb. 10: Verdünnungstunnel und Probenahmesystem

Fig. 10: Dilution tunnel and sampling system

Die Abb. 11 zeigt die untere Nachweisgrenze des Partikelverfahrens anhand von Messungen mit Fahrzeugen, deren Partikelemissionen unter 0,010 g/km liegen. Zur Bestimmung der "Nachweisgrenze" der gesamten Messkette wurden im ersten Schritt die Partikelemissionen der Probenahme (= Untergrund) bestimmt. Hierzu wurde ein Test ohne Fahrzeug durchgeführt und nur die Umgebungsluft durch die Messanlage geleitet. Im Idealfall müsste hierbei unter Berücksichtigung des Untergrundes 0.00 g/km als Ergebnis erzielt werden. In der europäischen Gesetzgebung ist es jedoch nicht vorgesehen, die Partikelanteile der Umgebungsluft zu bestimmen und vom Abgaswert zu subtrahieren. In unserem Messprogramm lag der „Untergrund"-Wert zwischen 0,00011 und 0,00094 g/km. Die mittlere Filterbeladung bei der Bestimmung der Untergrundemission betrug 0,02 mg. Damit ist die Wägung mit $\pm$ 0,005 mg hinreichend exakt.

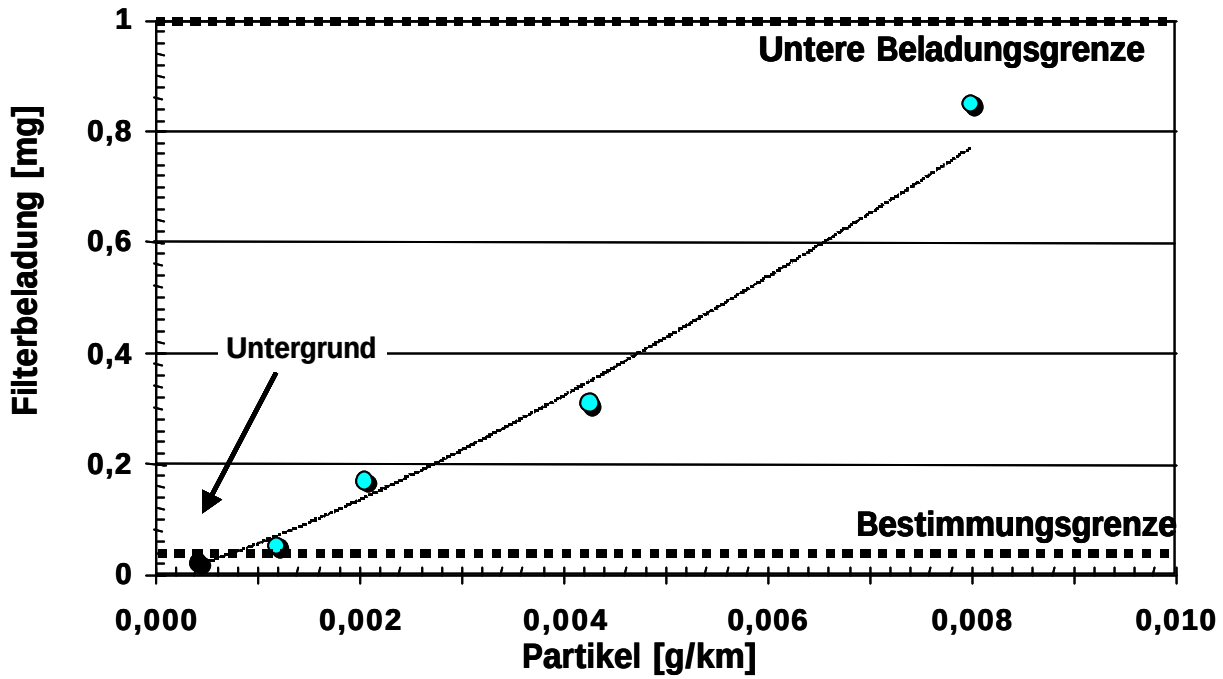


Abb. 11: Untere Bestimmungsgrenze des Verfahrens

Fig. 11: Lower practical limit of the gravimetric measurement procedure

Die anderen Messpunkte in Abb. 11 zeigen die mittlere Filterbeladung der Fahrzeuge im neuen europäischen Fahrzyklus (NEFZ). Jeder Messpunkt stellt einen Mittelwert von 3 - 25 Messungen dar. Bei allen Tests betrug die Filterbeladung weniger als 1 mg. Die gravimetrische Erfassung des Sekundärfilters gewinnt bei der Messung von Fahrzeugen mit minimalen Partikelemissionen an Bedeutung. Die Auswaage des Sekundärfilters ist allerdings unabhängig von der Beladung des Primärfilters. Im wesentlichen sind dort aus der Gasphase adsorbierte Kohlenwasserstoffe und Wasserdampfanteile zu finden. Die Berücksichtigung der Beladung des Sekundärfilters sollte für die zukünftige Gesetzgebung auf ihre Zweckmäßigkeit geprüft werden.

Abb. 12 zeigt die Ergebnisse einer Messreihe von Fahrzeugen mit niedrigen Partikelemissionen. Dargestellt sind die Mittelwerte der Partikelemission in g/km und die Standardabweichung von vier Fahrzeugen und der Untergrundmessung. Die Messreihen zeigen sehr deutlich, daß die Genauigkeit der Partikelmesstechnik viel besser ist, als die Richtlinien vermuten lassen. Die Untergrundemissionen von 0,0004 g/km (= 0,02 mg Filterbeladung) konnte mit einer Standardabweichung von 0,0003 g/km gemessen werden. Dieses entspricht einer relativen Standardabweichung von ca. 75%. Bezogen auf den Grenzwert von 0,025 g/km entspricht dies jedoch einer Messwertstreuung von kleiner als 2% für das Probenahmemesssystem einschließlich der Volumenbestimmung und der Wägung der Filter. Damit ist die in Tabelle 1 geforderte Wiederholbarkeit von 5% weit unterschritten.

Die Messreihe mit den vier Fahrzeugen demonstriert ebenfalls eine geringe Streuung der Messwerte. Ihre absolute Standardabweichung ist vergleichbar mit der Standardabweichung des Untergrundes, obwohl die Messkette hierbei um die Einflussgrößen Prüfstand, Fahrzeug und Fahrer erweitert wurde. Die relative Standardabweichung der Fahrzeuge liegt zwischen 4,7 und 8,8%; die Größen Prüfstand, Fahrzeug und Fahrer führen also zu einer Streuung von etwa 3-7%.

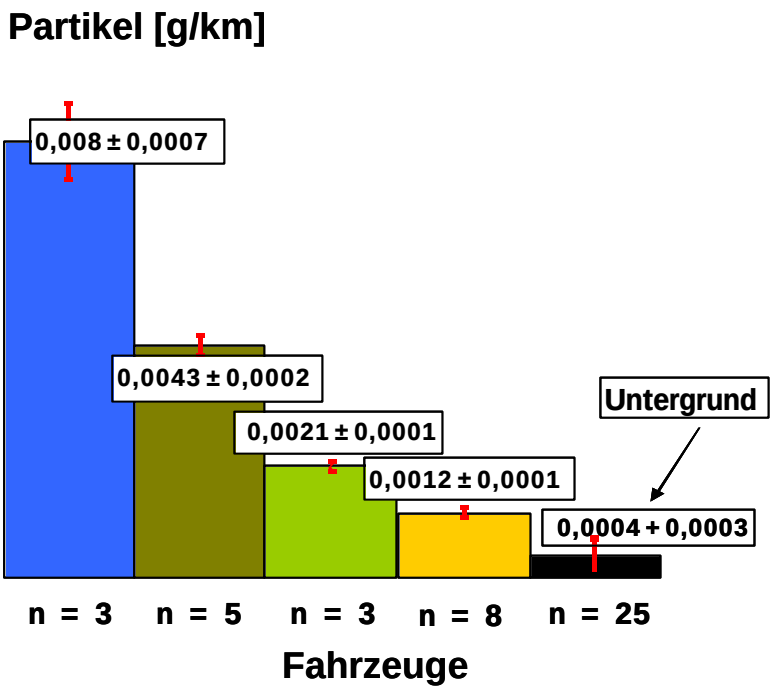


Abb. 12: Mittelwert und Standardabweichung von Untergrund und Fahrzeugen mit niedrigen Partikelemissionen

Fig. 12: Average particulate emissions and standard deviation of background and low particulate emissions vehicles

Zusammenfassend kann gesagt werden, daß die gravimetrische Partikelmessung eine kalibrierfähige Partikelmesstechnik darstellt. Die Grenzen des Partikelmessverfahrens sind noch nicht erreicht sind und lassen eine weitere Optimierung zu. Deutlich verbessert werden kann das Verfahren, wenn der gesamte Verdünnungstunnel, das Probenahmesystem, die Handhabung des Filters und der Waage anhand der neuen messtechnischen Möglichkeiten und unter Berücksichtigung des künftigen Abgasniveaus den zukünftigen Grenzwerten angepasst wird, z.B. Festlegung engerer Toleranzen, Herabsetzung der minimalen Filterbeladung, Aufbereitung der Verdünnungsluft (synthetisch), ...

3.3. Alternative Meßverfahren

Obwohl die Gravimetrie allen Anforderungen der heutigen Messtechnik genügt und weitere Potentiale bietet, werden neue Meßmethoden von der Politik gefordert. Andere Partikeleigenschaften wie Anzahl, Größe oder Oberfläche sollen zusätzlich zur Masse gemessen werden.

Die Partikel, die vom Dieselmotor abgegeben werden, liegen im Größenspektrum von 10-800 nm. In diesem Größenbereich sind die Trägheitseigenschaften und die Wechselwirkung mit Licht, die sonst zur Charakterisierung der Partikel eingesetzt werden, nicht besonders ausgeprägt. Es gibt verschiedene Ansätze, diese Partikel trotzdem zu messen. Einige Möglichkeiten sollen im folgenden beschrieben werden.

3.3.1. Prinzipien der alternativen Meßverfahren

Ausgelöst durch die neue Dieseldiskussion wurden oder werden alternative Prinzipien zur Partikelmessung des Diesels entwickelt [14]. Die Gravimetrie wurde in Kap. 3.2 diskutiert. Die genaueste Kohlenstoffbestimmung erreicht man durch Verbrennung der Partikel auf dem Filter im Sauerstoffstrom und Messung des dabei entstehenden Kohlendioxid mittels IR-Spektroskopie.

Eine andere Methode besteht in der Nutzung der trägen Masse der Partikel. Beim TEOM (Tapered Element Oscillation) und bei der QCM (Quartz Crystal Microbalance) wird die Verstimmung eines Quartzoszillators gemessen, die durch die zusätzliche Partikelmasse erzeugt wird. Eine weitere Möglichkeit besteht darin, den Gasstrom stark zu beschleunigen und so die geringen Trägheitskräfte zu verstärken. Niederdruckimpaktoren arbeiten nach diesem Prinzip. Dabei entsteht das Problem, die Partikel zu quantifizieren. In der Regel werden die Impaktorstufen gewogen. Damit kann die Partikelmassengrößenverteilung kumulativ über die Meßdauer bestimmt werden. Das Auswiegen der Impaktorstufen setzt bei den niedrigen Partikelemissionen, wie sie bei Euro4-Fahrzeugen auftreten, lange Meßzeiten voraus. Dieser Nachteil wird beim ELPI (Electrical Low Pressure Impactor) dadurch vermieden, indem die Partikel vor Eintritt in den Impaktor elektrisch aufgeladen und der auf der Impaktorstufe eintreffende Strom mit einem Elektrometer gemessen wird. Dies ermöglicht die Bestimmung der aerodynamischen Partikelanzahlgrößenverteilung mit Sekundenauflösung.

Andererseits bietet es sich an, Rußpartikel optisch nachzuweisen, da diese das Licht im sichtbaren Wellenlängenbereich nahezu vollständig absorbieren. Es gibt eine Reihe von Opazimetern und Extinktionsmeßgeräten, die zur Rußpartikelmessung verwendet werden. Ein großer Nachteil dieser Verfahren ist, daß die Empfindlichkeit der Lichtabsorption mit dem Partikeldurchmesser stark abnimmt. Daher werden Feinpartikel z.T. künstlich vergrößert, um diese dann optisch nachzuweisen. Dies ist das Prinzip der Kondensationskernzähler (CNC/CPC), die mit sehr guter Zeitauflösung Gesamtpartikelanzahlen messen. Um Informationen über die Größenverteilung zu gewinnen, existiert neben dem Impaktor das (SMPS = Scanning Mobility Particle Sizer), bei dem vor dem Kondensationskernzähler ein elektrischer Klassierer (DMA = Differential Mobility Analyser) geschaltet wird. Dabei werden die Partikel elektrisch geladen und dann scherungsfrei als Hüllstrom auf einen Reinluftstrom gegeben. Dieser Gasstrom wird durch ein elektrisches Feld geführt, in dem die Partikel gemäß ihrer Ladung und Größe abgelenkt werden. Liegt eine definierte Spannung an, können nur Partikel einer bestimmten Größenklasse den DMA verlassen. Dieser Ausschnitt aus dem Partikelgrößenspektrum wird dann im Kondensationskernzähler quantifiziert. Eine Variante besteht darin, die ohnehin geladenen Partikel mit

einem Elektrometer zu messen. Im Gegensatz zum Impaktor wird mit diesem Meßprinzip die elektrodynamische Anzahlgrößenverteilung ermittelt. Ein anderes System kombiniert Klassierer und Detektor in einem Gerät. Das DMA ist hierbei abschnittsweise aufgeteilt, wobei die einzelnen Abschnitte gegeneinander elektrisch isoliert und mit einem Elektrometer verbunden sind. Für jeden Abschnitt, der dann einer Größenklasse entspricht, wird der auftreffende elektrische Strom gemessen, der proportional zur Partikelanzahl ist.

Beim MasMo (Mass Monitor) wird aus der aero- und elektrodynamischen Mobilität die mittlere Partikeldichte bestimmt und dann aus der aerodynamischen Anzahlgrößenverteilung die Partikelgesamtmasse berechnet.

Eine andere Methode, Partikel zu messen, besteht darin, die unterschiedlich schnelle Diffusion der Partikel aufgrund der Brown'schen Molekularbewegung auszunutzen. Dabei diffundieren kleinere Partikel schneller als große. In den sog. Diffusionsbatterien werden Netze oder Blenden hintereinander geschaltet. In jeder Stufe der Diffusionsbatterie werden die kleineren Partikel anteilig am stärksten zurückgehalten, da diese durch Diffusion mit dem Netz oder der Blende kollidieren und so dem Meßgas entzogen werden. Aus der Partikelabnahme von einer Stufe zur nächsten lässt sich dann die Größenverteilung bestimmen. Die Partikel werden i.d.R. wieder mit Kondensationskernzählern nachgewiesen.

Eine neue Entwicklung bei lasergestützten Verfahren stellt das ad hoc Aufheizen der Partikel dar. Im Fall der Incandeszenz (LII-SA) wird das Abklingen des Glühlichtes gemessen, dessen Intensität von der Partikelanzahl und deren Abklingrate von der Primärpartikelgröße abhängen. Beim photoakustischen Partikelsensor wird ein gepulster Laserstrahl eingesetzt und die durch das Ausdehnen und Zusammenziehen der Partikel erzeugte Schallschwingung gemessen.

Daneben existieren oberflächenbasierende Meßverfahren, in denen die Partikeloberfläche geladen wird. Die Ladungen werden gemessen und liefern so das Meßsignal. Erhältlich sind Geräte, in denen das Laden der Partikel durch Diffusion von Gasionen (DC) oder durch Licht (PAS) geschieht.

Um den Fehler der gesamten Messkette für die Prüfung eines Dieselfahrzeuges (Euro4) abschätzen zu können, wurden basierend auf Literaturstudien und eigener Erfahrung folgende Annahmen vorgenommen:

- *Kraftstoff*: Referenzdieselkraftstoff kann unter anderem praktisch beliebig bezüglich des Tri^{+}aromatengehaltes (0-6%), in der Dichte um 10 g/l sowie demnächst von 0 – 50 ppm Schwefelgehalt schwanken. Hieraus ergibt sich in der Praxis ein Fehler in Masse und Anzahl von bis zu 30%.
- *Schmierstoff*: Art und Belastungsgrad des Öles können einen Fehler bei Partikelmasse und Partikelanzahl von ca. 3-5 % bewirken. Hinzu kommen Schwankungen beim Ölfüll-

stand. Da es sich hier z.T. um Blaurauch handelt, ist es plausibel, einen etwas höheren Fehler bei der Anzahl als bei der Partikelmasse anzunehmen.

?? *Konditionierung des Fahrzeugs*: Vor jedem Test wird ein Prekonditierungstest gefahren und das Fahrzeug temperaturangepaßt. Bestimmte Kondensate (Wasser, Kohlenwasserstoffe) können dennoch in der Abgasanlage verbleiben. Werden sie während des Tests ausgeheizt, so ist es möglich, daß eine größere Anzahl von Tropfen direkt vor dem Meßgerät kondensiert; eine geheizte Probennahme bzw. das Freifahren vor Test im Vollastbetrieb würden diesen auf 30% geschätzten Fehler auf etwa 5% reduzieren.

?? *Prüfstand/Fahrer*: Die Reproduzierbarkeit liegt nach unseren Erfahrungen bei 10% bzgl. Partikelmasse und Partikelanzahl.

?? *Verdünnungssystem*: Bei der Verdünnung kann es ggfs. zur Spontankondensation kommen. Deshalb liegt der Fehler ca. 10% über dem Fehler bei der Massenmessung.

?? *Probenahme*: Der Probenahmefehler wird bei der Partikelanzahlmessung mit 10% und damit deutlich höher als bei der Massenbestimmung abgeschätzt, da sich Effekte wie Koagulation, Diffusion und Thermophorese deutlich auf die Anzahl auswirken – aber nicht auf die Masse.

?? *Meßgerät*: Hier ist für die Gravimetrie (Konditionierung und Wägung) der maximale Fehler sicherlich bei unter fünf Prozent zu sehen. Die Reproduzierbarkeit der Partikelanzahlmessung kann nur abgeschätzt werden, indem das Meßergebnis diverser, vom Hersteller gewarteter Geräte an derselben Probennahmestelle verglichen wird. In Tabelle 2 ist die Abweichung angegeben, welche im Rahmen von Vergleichsstudien an 5 SMPS–Systemen beobachtet wurde.

	Partikelanzahl (SMPS)		Gravimetrie	
	derzeit	optimiert	derzeit	optimiert
Referenzkraftstoff	30%*	8%	30%*	8%
Schmierstoff	5 %*	1%	3%*	1%
Konditionierung	30%*	2%	5%	2%
Prüfstand/Fahrer	10%	10%	10%	10%
CVS – Tunnel, Probennahme	15%	5%	2%	2%
Verdünnung	10%	5%	-	-
Meßgerät	40%	15%	3%	2%
	140%	**46%**	**53%**	**25%**

Tabelle 2: Fehlerabschätzung der Messkette bzgl. Euro4 (Bezug ist der Meßwert)

Table 2: Error estimate of the measurement procedure with reference to Euro4 standards

Die angeführten Fehler sind nicht zufällig, d. h. durch Gestaltung des konkreten Meßaufbaus werden im Prinzip systematische Abweichungen erzeugt. Deshalb wird ein linearer Zusammenhang für die Fehleranalyse angenommen. Damit wird offensichtlich, daß sich die Gravimetrie als die Meßmethode mit dem geringerem Fehlerband aus der Analyse abhebt.

3.3.2. Einfluß der Probenahmebedingungen

Die Untersuchungen zum Einfluss der Probenahmebedingungen auf die Messung von Partikelanzahlemissionen wurden mit dem im Laborbereich verwendeten partikelzählenden Meßsystem SMPS durchgeführt [12, 13]. Als Versuchsträger standen ein Pkw (Passat) mit 85 kW TDI Dieselmotor auf einem Rollenprüfstand und der gleiche Motor auf einem Motorenprüfstand zur Verfügung. Fahrzeug und Motor wurden bei verschiedenen korrespondierenden Lastpunkten mit unterschiedlich schwefelhaltigen Dieselkraftstoffen (300 und 25 ppm S) vermessen.

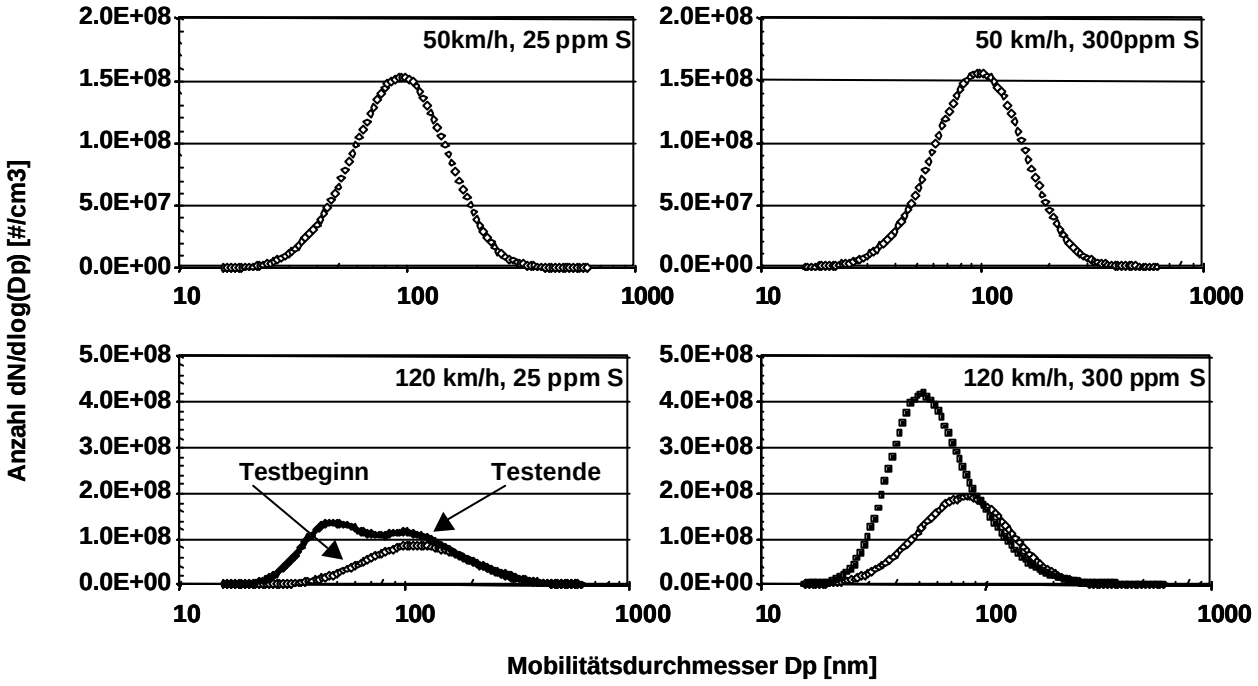


Abb. 13: Vergleich von SMPS-Größenverteilung bei 50 km/h (oben) und 120 km/h (unten) für 25 (links) und 300 ppm (rechts) Kraftstoffschwefelgehalt

Fig: 13: Comparison of SMPS particulate size distribution at 50km/h (upper diagrams) and 120km/h (lower diagrams) using diesel fuels containing 25 and 300ppm sulphur

Abb. 13 oben zeigt die SMPS-Partikelanzahlgrößenverteilungen bei 50 km/h des Fahrzeuges auf dem Rollenprüfstand für 25 ppm und 300 ppm Kraftstoffschwefelgehalt. Die Größenverteilungen sind monomodal mit einem Maximum bei etwa 90 nm Partikelgröße. Es ist kein signifikanter Kraftstoffschwefeleinflusses ersichtlich. Die Ergebnisse bei 120 km/h (Abb. 13 unten) zeigen einen deutlichen Unterschied bei Verwendung eines Kraftstoffes mit anderem Schwefelanteil. Insbesondere beim höheren Schwefelgehalt ist ein Kondensationspartikel-modus zu beobachten, der von Messung zu Messung immer stärker in Erscheinung tritt und letztendlich die Größenverteilung dominiert.

Parallel zu den Anzahlmessungen (Abb. 13) wurde die Partikelmasse ermittelt und die Partikelzusammensetzung bestimmt. Abb. 14a zeigt neben der Gesamtanzahlkonzentration die Resultate der Partikelanalysen für Ruß, die löslichen organischen Anteile, die wasserlöslichen Anteile und Sulfat (hauptsächlich wässrige Schwefelsäure). Partikelmasse und –anzahl nehmen mit der wachsender Fahrzeuggeschwindigkeit und steigendem Schwefelgehalt zu. Der Zuwachs ist hauptsächlich auf den höheren Schwefelsäureanteil zurückzuführen. Gesamtmasse und Gesamtpartikelanzahl zeigen eine gute Korrelation (Abb. 14b), wenn die Messungen, bei denen ein Kondensationspartikelmodus aufgetreten ist, nicht berücksichtigt werden.

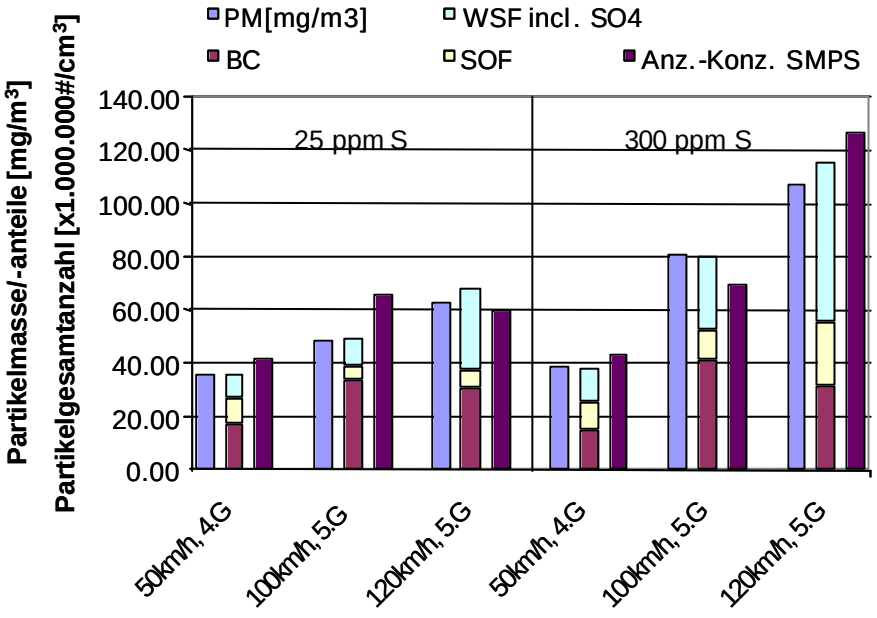


Abb. 14a: Vergleich von Partikelmassenemission analysiert hinsichtlich Zusammensetzung bei und Partikelanzahl bei verschiedenen Geschwindigkeiten für 25 und 300 ppm Kraftstoffschwefelgehalt

Fig. 14a: Comparison of composition of particulate mass emissions and particulate number at different speeds with 25 and 300ppm sulphur-containing diesel fuel

Um den Einfluss des Verdünnungsverhältnisses, der Verdünnungsluftfeuchte und -temperatur auf Partikelanzahlgrößenmessungen zu untersuchen, wurden weitere Messungen mit dem gleichen Motor auf einem mit einem Teilstromverdünnungstunnel ausgerüsteten Motorenprüfstand

durchgeführt. Mit diesem Aufbau können die relevanten Parameter unabhängig voneinander und in einem weiteren Bereich als beim Standard-Vollstromtunnel (CVS) eingestellt werden.

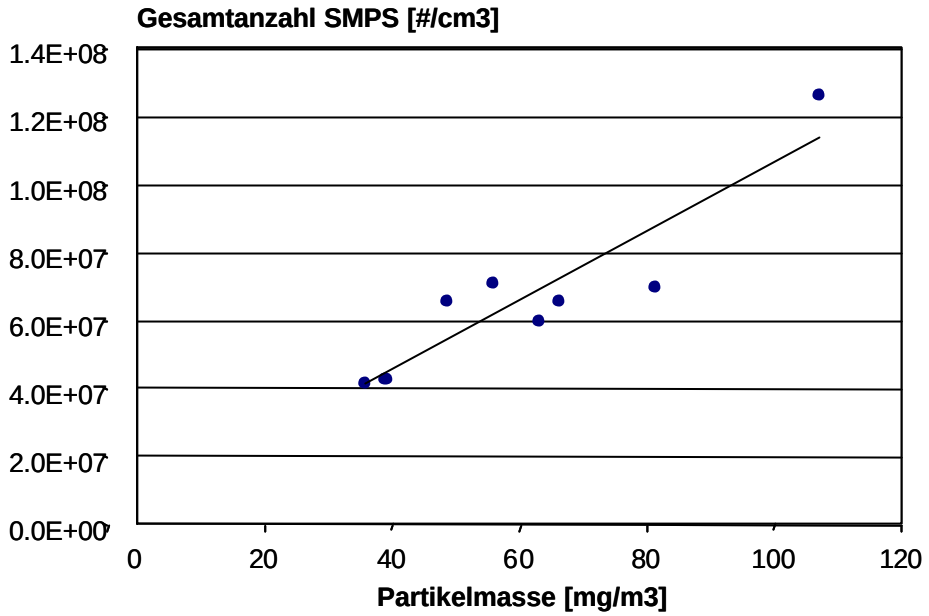


Abb. 14b: Korrelation zwischen Partikelgesamtmasse und –anzahl

Fig. 14b: Correlation between particulate total mass and number

Abb.15 zeigt den Einfluß der Variation des Verdünnungsverhältnisses von 1:7 bis 1:50, der Verdünnungsluftfeuchte und –temperatur auf die Anzahlgrößenverteilung der Partikel. Das Fahrzeug wurde im Lastpunkt 64 Nm und 2140 min^{-1} (entspricht 100km/h beim Pkw) mit 300 ppm Schwefel im Dieselkraftstoff betrieben. Bei einem Verdünnungsverhältnis von 1:7 treten Kondensatpartikel auf, die die Gesamtpartikelanzahl um eine ganze Größenordnung ansteigen lassen. Eine Erhöhung der Verdünnungsverhältnisses auf 1:20, d.h. maximaler Bereich des CVS-Tunnels, führt dazu, dass der Kondensationspartikelmodus – aber nicht der Akkumulationsmodus - sich zu kleineren und damit zu mehr Partikeln verschiebt. Getrocknete Verdünnungsluft mit 10% relative Feuchte führt zu einer Verstärkung dieses Effektes. Eine Verdünnung von 1:50 dagegen läßt die Kondensation (Nukleationsmodus) verschwinden. Den gleichen Effekt hat eine Aufheizung der Verdünnungsluft auf 80°C, was noch mal verdeutlicht, dass es sich hier um Probenahmeartefakte handelt.

Die Ergebnisse der Untersuchung zeigen, dass die Probenahmebedingungen in Kombination mit dem Kraftstoffschwefelgehalt einen extremen Einfluss auf die Partikelanzahl und Größenverteilung haben können und insbesondere bei der standardisierten Probenahme aus dem CVS-Verdünnungstunnel bei Partikelanzahlmessungen mit Artefakten, d.h. Verfälschungen der Meßergebnisse gerechnet werden muss.

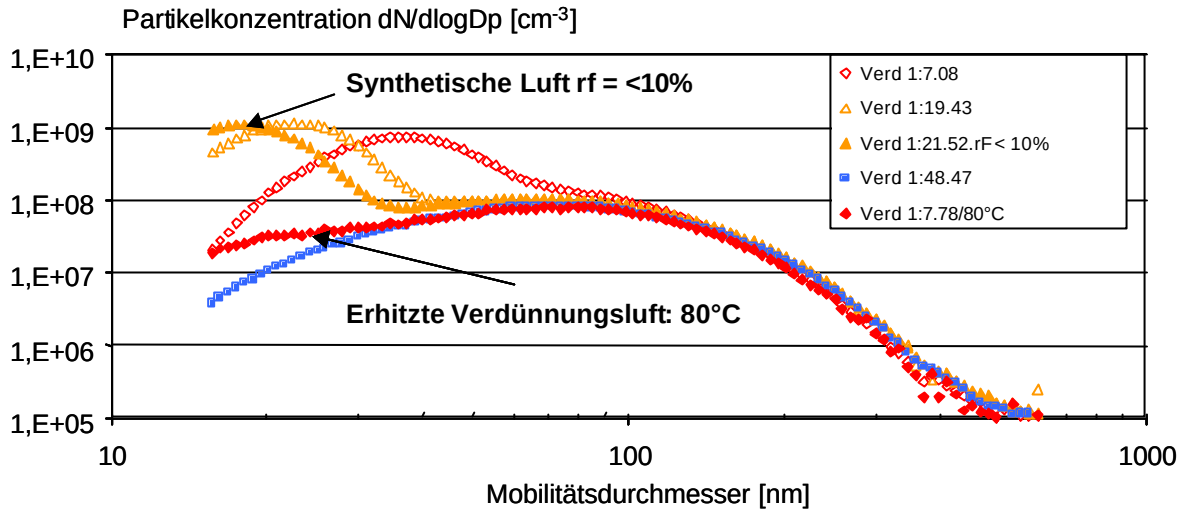


Abb. 15: Einfluß von Verdünnungsverhältnis, Verdünnungsluftfeucht und –temperatur auf die Partikelanzahlgrößenverteilung

Fig. 15: Effect of dilution ratio, humidity and temperature on particulate number size distribution

3.3.3. Vergleich von SMPS und ELPI

Neben dem SMPS wird im Laborbereich der ELPI eingesetzt. Die Prinzipien wurden in Kap. 3.3.1 beschrieben. Vergleichsmessungen zwischen beiden Geräten (Abb. 16) zeigen, daß die Art der Klassierung der Partikel, nämlich der aerodynamische Durchmesser beim ELPI und der elektrische Mobilitätsdurchmesser beim SMPS, entgegen anders lautender Aussagen [13] einen großen Einfluss auf die gemessene Partikelanzahl und Größenverteilung hat. Mit zunehmender Last und ansteigendem Kraftstoffschwefelgehalt zeigt der ELPI eine Abnahme der Partikelanzahl und eine Verschiebung des Verteilungsmaximums hin zu größeren Partikeldurchmessern, während beim SMPS das Verteilungsmaximum gleich bleibt und nur die Anzahl zunimmt. Ursache dafür könnten durch Laständerungen und Kraftstoffqualität verursachte Morphologieänderungen der Partikel sein (Abb. 3).

Im Rahmen der Untersuchung ist auch mit drei verschiedenen SMPS gemessen worden. Zu Beginn stand ein SMPS1 (Model 3071/3025) und ein weiteres Gerät SMPS2 (Model 3080/3010) zur Verfügung. Das frisch vom Hersteller kalibrierte Gerät SMPS2 wurde als Referenz eingesetzt und mit dem SMPS1 verglichen.

Bei drei Messungen stimmen die Geräte im Maximalwert der Größenverteilung (Abb. 17a) in etwa (7% Differenz) überein. SMPS1 zeigte jedoch einen 14 nm größeren medianen Anzahldurchmesser (15% Unterschied) und eine um 22% höhere Gesamtzahl.

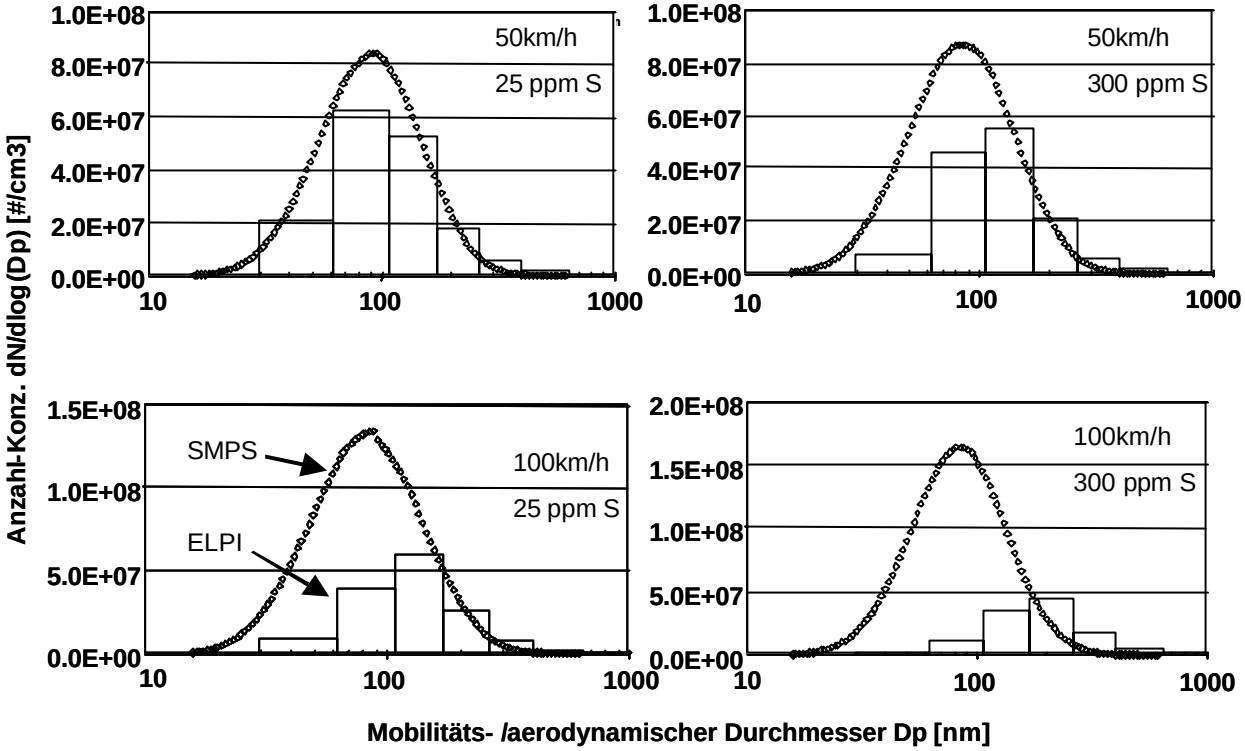


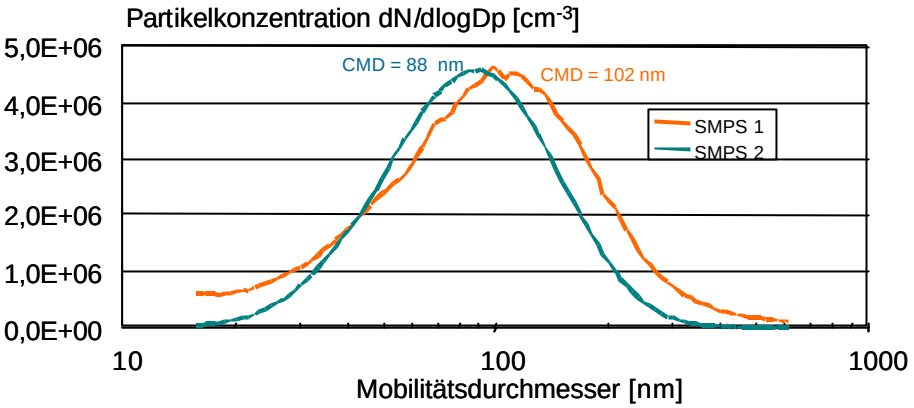
Abb. 16: Vergleich von SMPS- und ELPI-Messungen bei unterschiedlicher Last und Kraftstoffschwefelgehalt

Fig. 16: Comparison of SMPS and ELPI measurements under different loads and fuel sulphur content

Beim Vergleich mit einem anderen vom Hersteller neu kalibrierten Gerät (SMPS3 (Model 3080/3010)) stellte sich heraus, dass die Diskrepanz zwischen diesem Gerät und SMPS1 in der Gesamtpartikelanzahl deutlich höher war und der mediane Anzahldurchmesser sogar in die andere Richtung abwich als zum SMPS3 (Abb. 17b).

Diese Resultate zeigen, dass die Anforderungen bzgl. Kalibrierbarkeit und Reproduzierbarkeit (siehe Tabelle1 in Kap. 3.1) nicht erfüllt werden.

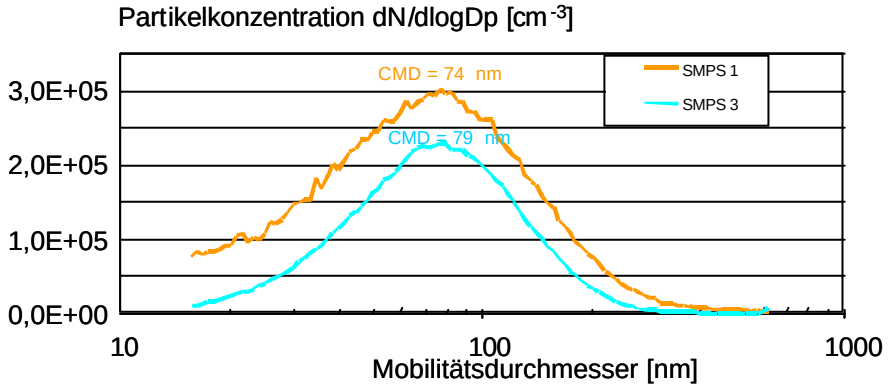
Zusammenfassend zeigt sich: Die derzeit eingesetzte Partikelanzahlmesstechnik mit Geräten, wie z.B. SMPS und ELPI, ist nur zur Gewinnung von qualitativen Aussagen zu Partikelanzahl und Größenverteilung geeignet, jedoch von der Möglichkeit der quantitativen, also absoluten Messung dieser Eigenschaften, weit entfernt. Darüber hinaus muß man feststellen, daß durch geeignete Wahl der Testbedingungen die Partikelanzahl praktisch beliebig manipuliert werden kann (s.a. Kap. 3.3.2).



	Anzahl-K. [#/cm3]			Peak-Höhe [#/cm3]		
	SMPS 1	SMPS 2	Verh. 1 : 2	SMPS 1	SMPS 2	Verh. 1 : 2
Scan 1	3,30E+06	2,77E+06	1,19	4,92E+06	4,87E+06	1,01
Scan 2	3,13E+06	2,59E+06	1,21	4,48E+06	4,69E+06	0,96
Scan 3	3,06E+06	2,44E+06	1,25	4,60E+06	4,23E+06	1,09
Mittel	**3,16E+06**	**2,60E+06**	**1,22**	**4,67E+06**	**4,60E+06**	**1,02**

Abb. 17a: Vergleich der SMPS-Meßgeräte 1 und 2

Fig. 17a: Comparison of SMPS measurement instruments 1 and 2



	Anzahl-K. [#/cm3]			Peak-Höhe [#/cm3]		
	SMPS 1	SMPS 3	Verh. 1 : 3	SMPS 1	SMPS 3	Verh. 1 : 3
Scan 1	2,099E+05	1,394E+05	1,51	3,108E+05	2,405E+05	1,29
Scan 2	2,166E+05	1,326E+05	1,63	3,083E+05	2,317E+05	1,33
Scan 3	2,181E+05	1,293E+05	1,69	3,157E+05	2,236E+05	1,41
Scan 4	2,165E+05	1,288E+05	1,68	3,060E+05	2,239E+05	1,37
Mittel	**2,153E+05**	**1,325E+05**	**1,62**	**3,102E+05**	**2,299E+05**	**1,35**

Abb. 17b: Vergleich der SMPS-Meßgeräte 1 und 3

Fig. 17b: Comparison of SMPS measurement instruments 1 and 3

3.4. Bewertung der Meßverfahren

Bereits heute wird eine große Anzahl von Partikelmessinstrumenten in unterschiedlichsten Entwicklungsstadien angeboten. Um die öffentliche Diskussion besser bewerten und verfolgen zu können, wurde eine Matrix mit einer technischen Beschreibung aller uns bekannten Messinstrumente erstellt. Durch Vergleich mit den Anforderungen (s. Kap. 3.1) ließ sich eine Auswahl der Messgeräte mit dem höchsten Potential für den Einsatz in der Zulassung treffen.

Die Probenahme der Partikel spielt - wie oben gezeigt - eine wesentliche Rolle. Die Bedingungen müssen für alle Messverfahren festgelegt werden. Die folgende Bewertung der Messinstrumente wurde ohne Einbeziehung der Probenahmen durchgeführt.

Die Anfangsliste der Messinstrumente beinhaltete die technischen Angaben von 22 Instrumenten (Gravimetrie, Horiba I, FID Horiba II, TEOM, ß-Staubmeter, Berner Impaktor, LI^{2}SA, Streulicht, photoakustischer Aerosolsensor, Opazimetrie, Aethalometer, DC Sensor, photoelektrischer Aerosolsensor, elektrische Diffusionsbatterie, ELPI, SMPS, Kondensationskernzähler, Photometrie, Elektrometer mit Vorimpaktor, Cambustion, QCM, MasMo). Daten wurden für folgende Kategorien zusammengestellt: Gemessene Partikeleigenschaft, abzuleitende Meßgröße, Messbereich, Auflösung der gemessenen Größe, Zeitauflösung, Wiederholbarkeit, Reproduzierbarkeit, Veränderung der Partikel vor der Messung (Konditionierung), weitere Untersuchungsmöglichkeit der Partikel nach der Messung, Verfahren der Probenahme und Verdünnung, Grad der Verbreitung und Zusammensetzung.

Die technischen Informationen waren leider nicht für alle Instrumente vollständig verfügbar. Instrumente, die sich noch im Forschungsstadium befinden, wurden nicht in die weitere Analyse einbezogen. In den folgenden Tabellen sind die Ergebnisse der Analyse dargestellt

Instrument	Bestimmungs-grenze	Wiederholbar-keit	Reprodu-zier-barkeit	Zeitauflösung	Kalibrierung vor Ort überprüfbar?
QCM	Ja	Ja	Ja	Ja	Schwierig
Li^{2}SA	Ja aber nur EC	Nicht bekannt	Nicht be-kannt	Ja	Ja, indirekt
MassMo	Ja	Ja	Nicht be-kannt	Ja	Ja, indirekt
Gravimetrie	Ja	Ja	Ja	Ja	Ja

Tabelle 3: Ergebnis für Massemessungen

Table 3: Results for mass measurement

Instrument	Bestimmungs-grenze	Wiederholbar-keit	Reproduzier-barkeit	Zeitauflösung	Kalibrierung vor Ort überprüfbar?
CPC	Ja	Ja	Nicht bekannt	Ja	Nein
ELPI	Nein	Ja	Nein	Ja	Nein
SMPS	Ja	Ja	Nein	Nein	Nein
MassMo	Ja	Ja	Nicht bekannt	Ja	Nein
FAS Cam-bustion	Nein	Ja	Ja	Ja	Nicht bekannt
Streulicht	Nein	Ja	Nicht bekannt	Ja	Ja

Tabelle 4: Ergebnis für Anzahlmessungen

Table 4: Results for particulate number measurement

Instrument	Bestimmungs-grenze	Wiederholbar-keit	Reproduzier-barkeit	Zeitauflösung	Kalibrierung vor Ort überprüfbar?
DC Sensor	Ja	Nicht bekannt	Nicht bekannt	Nein	Nein

Tabelle 5: Ergebnis für Oberflächenmessungen

Table 5: Results for particulate surface area measurement

Von den ausgewählten Instrumenten für die Messung der Masse ist nur die Gravimetrie direkt kalibrierbar. Streulicht-, MassMo-, Li^2SA- (EC) und QCM-Verfahren sind indirekt über die Gravimetrie oder Coulometrie kalibrierbar.

Eine Kalibrierung zur Messung der Partikelanzahl ist heute nicht möglich, da ein Normaerosol nicht reproduzierbar und robust herstellbar ist, ohne wiederum auf die vorhandene Partikelmeßtechnik zur Verifikation zurückgreifen zu müssen. Die zur Zeit verwendeten Verfahren benutzen Sprays aus Salz- oder Latexlösungen, die für die Messung der sehr komplexen Rußpartikel nicht repräsentativ sind. Eine Partikelerzeugung durch Präzisionsbrenner oder elektrische Entladungsstrecken sind gegenwärtig nicht robust genug, um als „Eichnormal“ dienen zu können.

Die Analyse zeigt, dass nur die Gravimetrie die anfangs formulierten Anforderungen (s. Kap. 3.1) vollständig erfüllt. Potential zur Erfüllung der Vorgaben der Tabelle 1 haben außerdem die auf der massebezogenen Verfahren, wie z.B. die Streulicht-, MassMo-, Li^2SA- (EC) und QCM-Methoden.

4. Zusammenfassung und Ausblick

Da der Diesel der effektivste Antrieb ist, liefert er einen erheblichen Beitrag zur Erfüllung der Verbrauchszusage des VDA und der CO_2-Zusage von ACEA. Trotz der bisher enormen Reduktionen der Abgasemissionen bei den Dieselmotoren wird von Teilen der Politik eine weitergehende Minderung besonders bei NO_x und den Partikeln gefordert. Dabei bezieht man sich auf angeblich belastbare medizinische Experimente.

Toxikologische Untersuchungen zeigen, daß Tierexperimente nicht auf den Menschen übertragbar sind. Die Ergebnisse der epidemiologischen Untersuchungen sind nicht eindeutig genug, um sichere Aussagen geben zu können. Gesundheitliche Befürchtungen sind mehr durch das Argument der Vorsorge denn durch eindeutige wissenschaftliche Resultate begründet.

Über Veränderungen der Partikel in der Atmosphäre ist bis heute wenig bekannt. Deshalb wissen wir nicht exakt, von welcher Struktur und Zusammensetzung diejenigen Partikel sind, die in die tiefen Bereiche der Lunge gelangen können und welcher der für ein mögliche Gesundheitsgefährdung wichtige Parameter ist. Somit ist der - vorausgesetzt es gibt ihn - Wirkungsparameter nicht klar belegt und damit stellt sich immer noch die Frage: **Was soll gemessen werden?**

Die während der Verbrennung entstehenden Partikel werden in molekularen Prozessen in der Gasphase gebildet. Unterschiedliche Motorentechnologien haben daher keinen Einfluß auf die Größenverteilung der Partikel, denn das Gas hat keine Kenntnis darüber, wie groß der ursprüngliche Kraftstofftropfen vor der Verdampfung war. Teilweise gebildete Nanopartikel sind im wesentlichen aus der Gasphase kondensierte Tröpfchen und hängen stark von den Meßbedingungen ab.

Gegenwärtig werden Partikel bei der Fahrzeugzulassung mit der Gravimetrie bestimmt. Obwohl die Gravimetrie allen Anforderungen der heutigen Messtechnik genügt und weitere Potentiale bietet, werden neue Meßmethoden von der Politik gefordert. Andere Partikeleigenschaften wie Anzahl, Größe oder Oberfläche sollen zusätzlich zur Masse gemessen werden. Eigene Untersuchungen bei Volkswagen zeigen, dass die Gravimetrie Fahrzeuge mit Partikelemissionen deutlich unter 0,01g/km sehr zuverlässig messen kann. Eine Messreihe mit einigen der neuen, alternativen Messinstrumente ergab weder reproduzierbare noch kalibrierbare Resultate.

Neben der heute verwendeten Gravimetrie wurden 21 alternative Messverfahren, die in der Lage sein sollen, Masse, Anzahl oder Oberfläche der Partikel messen zu können, analysiert und bewertet. Dabei zeigte sich, daß für die Messung der Masse nur die Gravimetrie direkt kalibrierbar ist. MassMo-, Li^2SA-(EC), Streulicht- und QCM-Verfahren sind indirekt über die Gravimetrie oder Coulometrie kalibrierbar. Eine Kalibrierung zur Messung der Partikelanzahl ist zur Zeit nicht möglich. Weiterhin bestehen Zweifel bezüglich der Reproduzierbarkeit, die für Zulassungsmessungen von entscheidender Bedeutung ist. Hier ist für die meisten Geräte noch der Nachweis einer hinreichenden Übereinstimung mit den Anforderungen zu führen.

Damit hat der derzeitige Stand der neuen Messtechnik nur den Status der Gewinnung von qualitativen Aussagen zu Partikelanzahl und Größenverteilung erreicht, ist jedoch von der Möglichkeit der quantitativen absoluten Messung dieser Eigenschaften weit entfernt. Durch geeignete Wahl der Testbedingungen kann die Partikelanzahl praktisch beliebig manipuliert werden. Grundsätzlich sollte eine zukünftige Methode aber die Qualitätsanforderungen des derzeitigen Verfahrens zur Bewertung der Partikelemission erfüllen können. Deshalb liegt in der Weiterentwicklung der Gravimetrie das höchste Potential.

So ist die Notwendigkeit einer Partikelanzahlmessung derzeit nicht nachvollziehbar, da eine Korrelation zur Masse gefunden wurde und die neuen Verfahren nicht absolut adjustierbar sind. Sie würden nur zu einem unnötigem Aufwand in der Entwicklung und bei der Zertifizierung führen.

5. Danksagung

Die Autoren bedanken sich an dieser Stelle recht herzlich bei den Herren Dr. von Borstel, Dippel, Dr. Lörch, Dr. Schriever, Dr. Spallek, Stendel, Wessels und Dr. Wiebrecht für ihre Beiträge zur Bewertung der Partikelmesstechnik.

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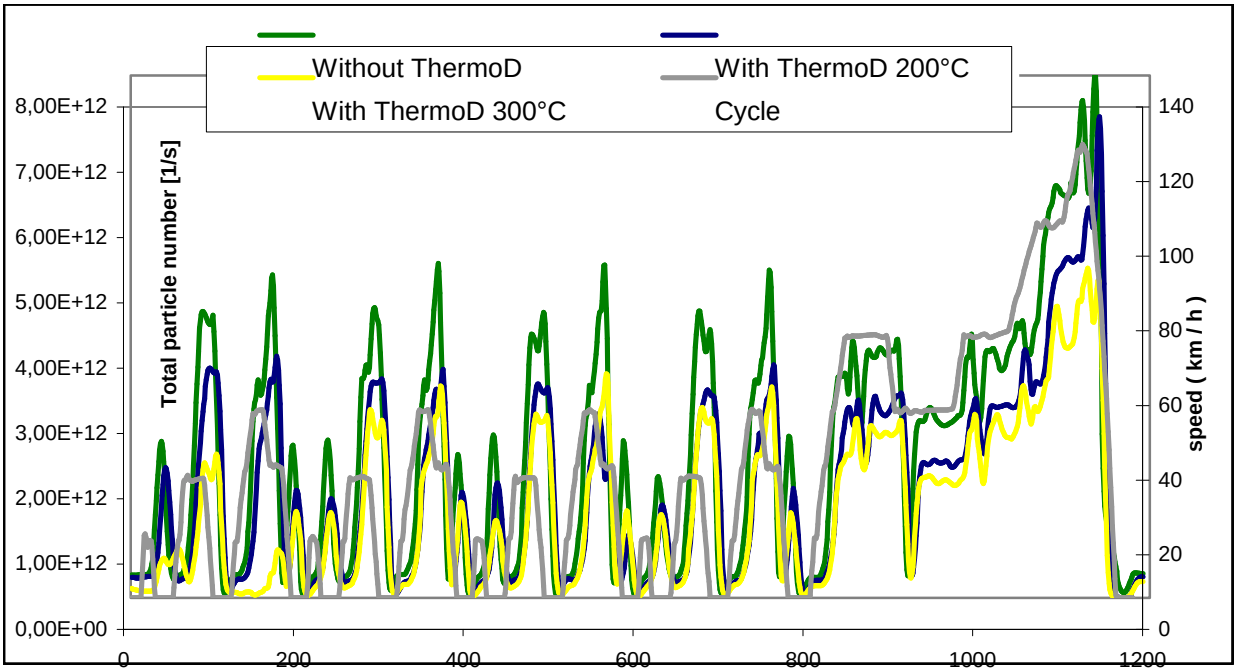
DIESEL CAR (Euro 3) - 1,9 Common Rail Turbo-Charged : Diesel Fuel with 270 ppm S

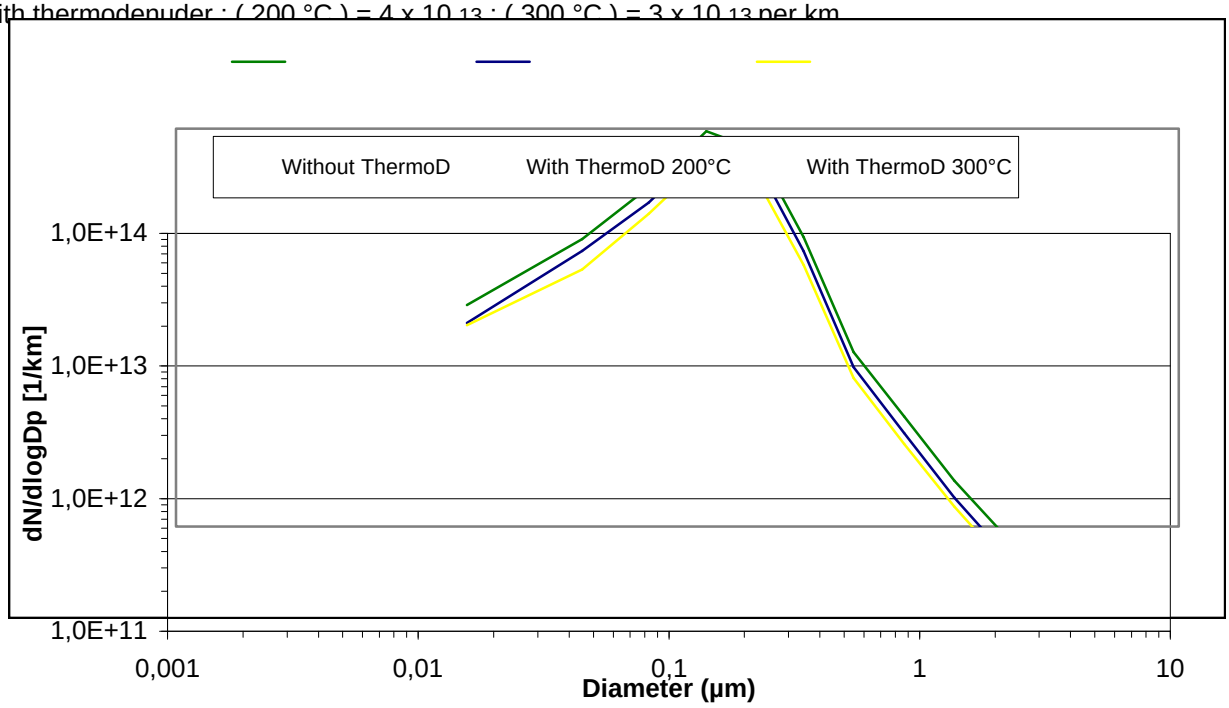
HOT European Driving Cycle

ELPI sampling from the CVS + secondary dil. (x 10) :
10 nm - 10 microns - 13 channels - 1 Hz greased sintered metal plates
thermodenuder : installed between the dilution stage (with N2) and the ELPI (10 dm3/mn)



PM number (as measured with the ELPI) :

w/out thermodenuder : 5 x 10 13 per km
with thermodenuder : (200 °C) = 4 x 10 13 ; (300 °C) = 3 x 10 13 per km



SIZE / Number distribution as a function of the thermodesorber settings

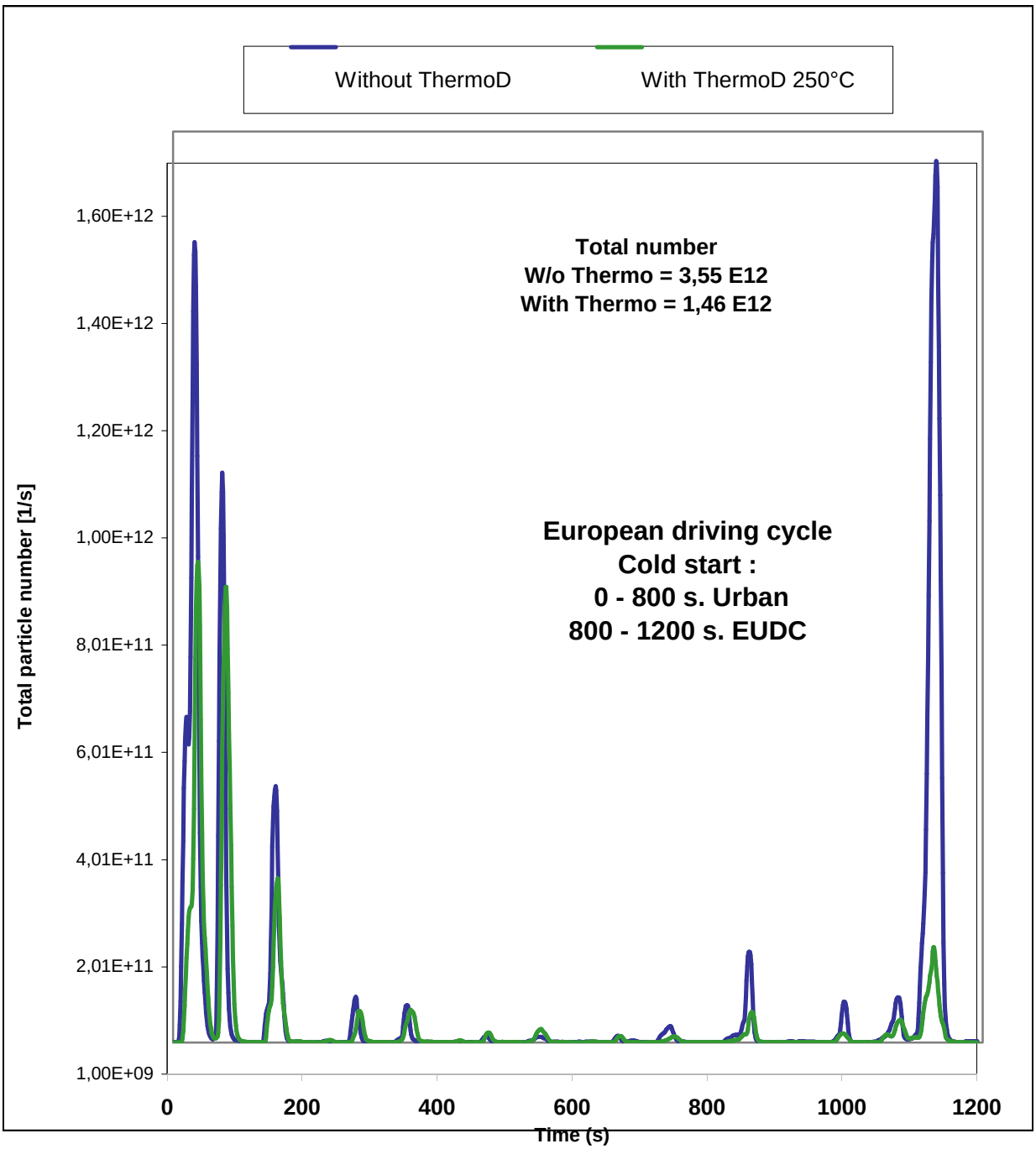
conclusion : the thermodesorber will reduce the PM number without affecting the distribution
no real need ! ; additional drawbacks : maintenance, response lag, desorption,... **RENAULT**

RENAULT

GASOLINE CAR (Euro 3) - 1,6 MPI - 16V : Gasoline Fuel with 127 ppm S

ELPI : 10 nm - 10 microns - 13 channels - 1 Hz - greased Aluminium plates
thermodenuder : installed between the dilution stage (with N2) and the ELPI (10 dm3 / mn)

Sampling from the CVS tunnel with additional N2 dilution (x 10)

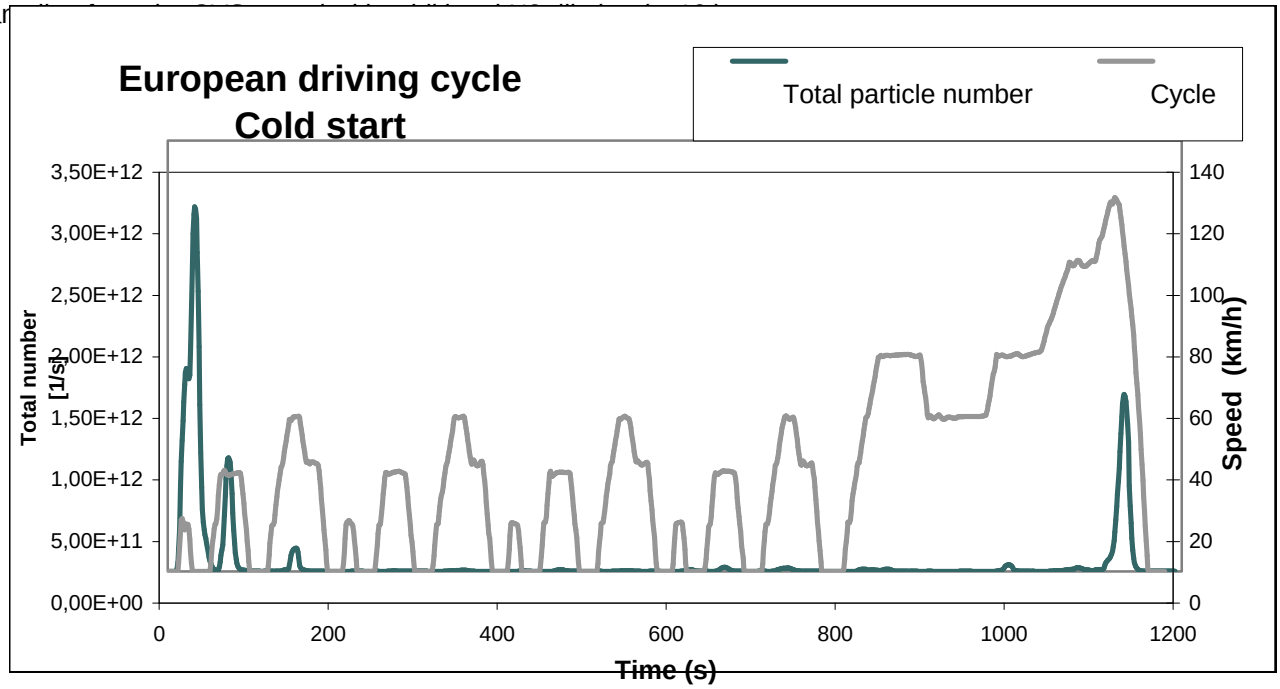


the presence of the thermodenuder drastically affect the PM measurements (number, composition) and will induced possible sudden desorption, some maintenance concerns and response time lag, ...

GASOLINE CAR (Euro 3) - 1,6 MPI - 16V : Gasoline Fuel with 127 ppm S **RENAULT**

ELPI : 10 nm - 10 microns - 13 channels - 1 Hz - greased Aluminium plates
WITHOUT the thermodenuder

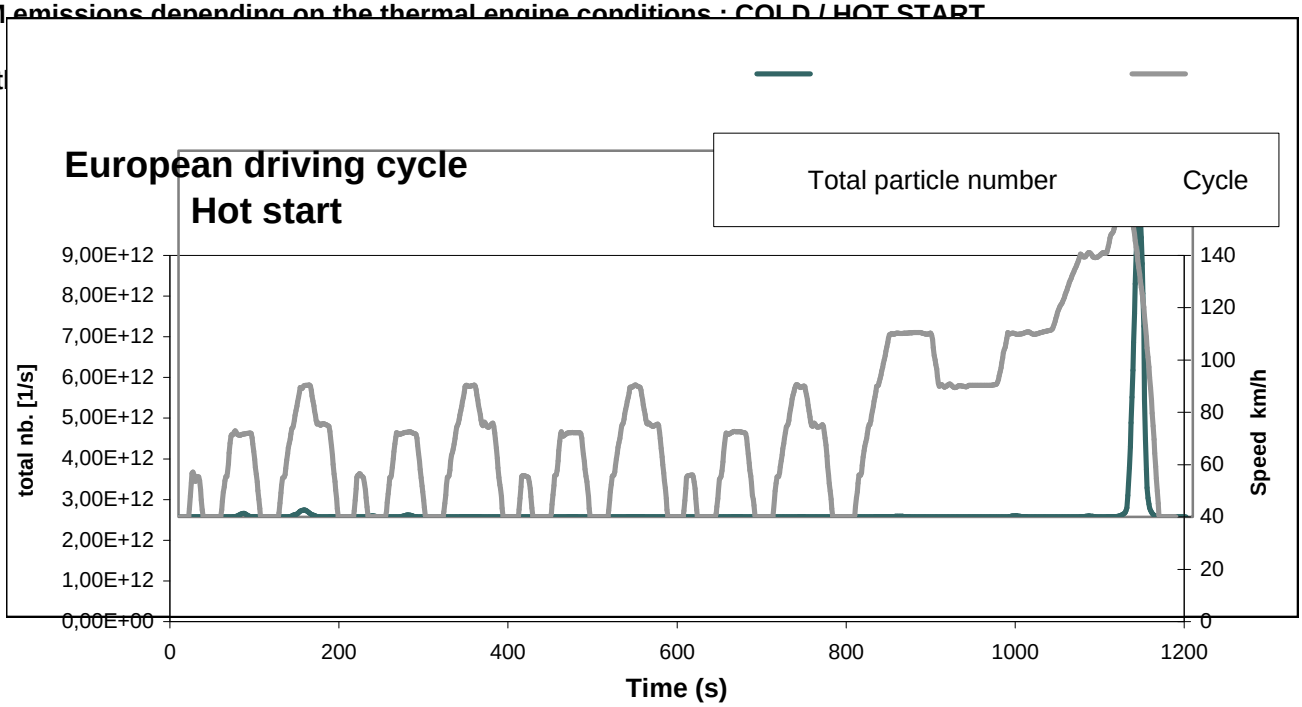
Sar



without thermodenuder

PM emissions depending on the thermal engine conditions : COLD / HOT START

wit

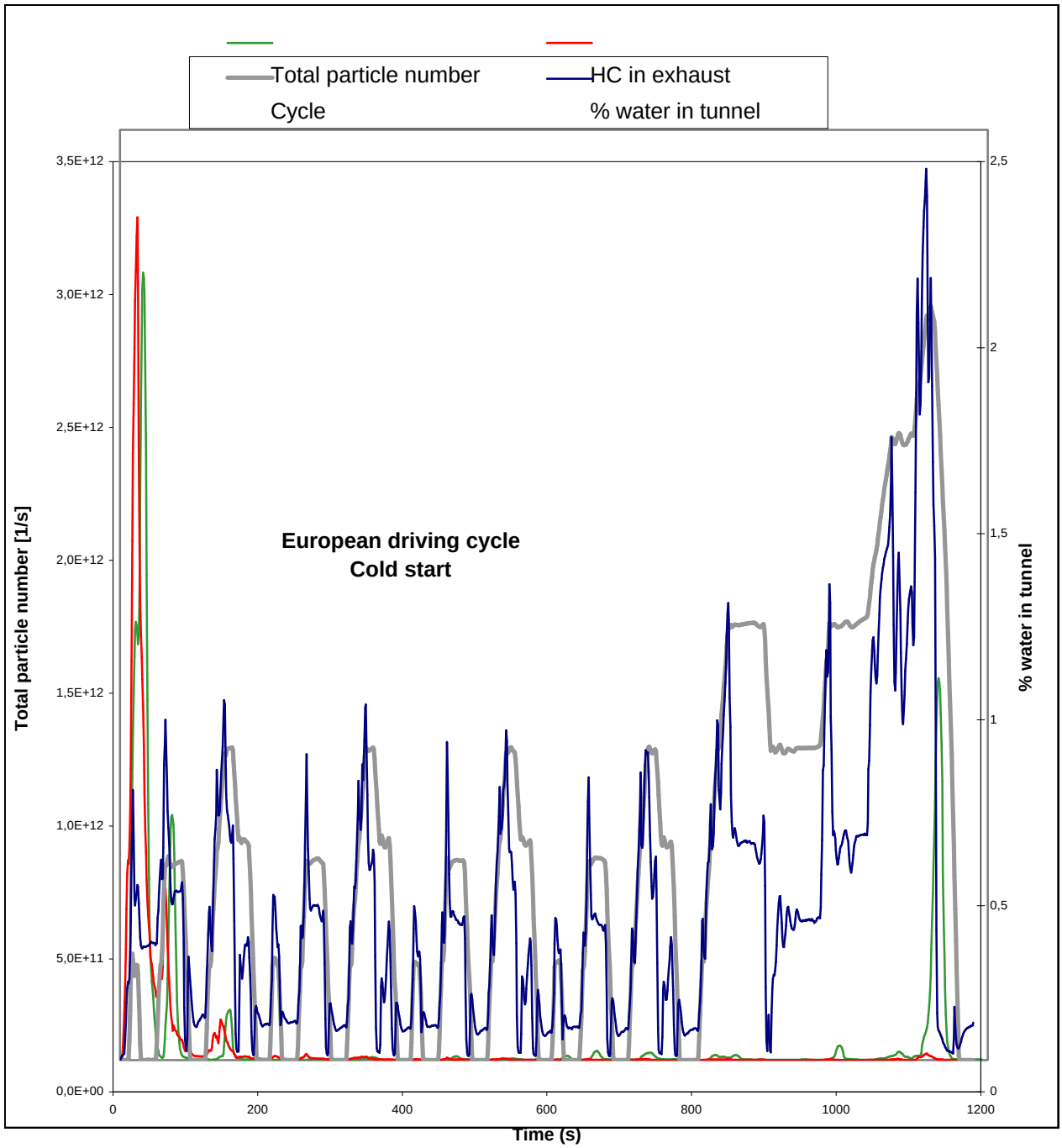


RENAULT

GASOLINE CAR (Euro 3) - 1,6 MPI - 16V : Gasoline Fuel with 127 ppm S

ELPI : 10 nm - 10 microns - 13 channels - 1 Hz - greased Aluminium plates
WITHOUT the thermodenuder

Sampling from the CVS tunnel with additional N2 dilution (x 10)



the effect of the thermodenuder is mainly on water , and not on Hydrocarbons
proposal / recommendations :
to avoid measurement interference with water , a dilution with warm N2 is recommended, and so :
*the thermodenuder is not any longer needed : no maintenance , no additional response lag, no sudden release, ...
nota : water concentrations in the exhaust are estimated from calculations (combustion products)

JAMA Comments on PMP

December 16th, 2002

Unregulated Emissions Group
Emissions & Fuel Efficiency Subcommittee
Japan Automobile Manufacturers Association,Inc.
(JAMA)

1. Summary

1.1 JAMA believes that the emission regulations using with number concentration method is premature and should be continued using with the current method (mass measurement method).

1) There are no findings on health effects of the PM number concentration.

2) The relation between PM number in automobile emission and in ambient air is not clarified..

3) The ongoing research on PM measuring method except for weight measurement is now in the stage of investigating current status of emissions.

1.2 To use the new measuring equipment as the tool for type approval, JAMA believes that it is important to guarantee the accuracy and to establish the calibrating method.

1) In the research conducted by JAMA, the tools (DMA+CPC, ELPI, DC, etc) are not accurate sufficiently.

2) CAST (combustion device to generate particles) shows the stable average diameter (median diameter), but shows the trends toward the decreasing number concentration with time.

2.Study on Calibration

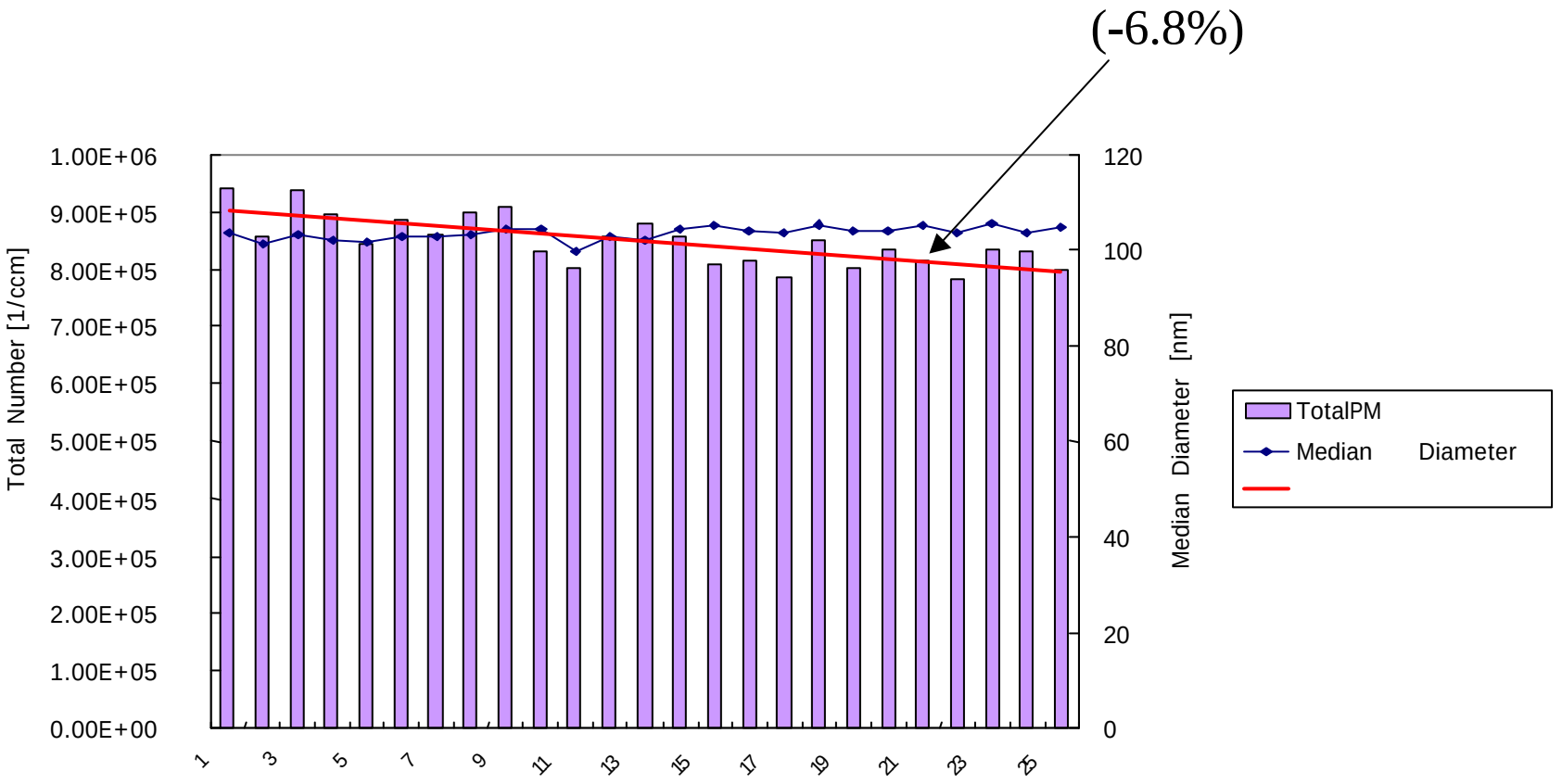
2.1 The reproducibility of a CAST

1) Concerning the reproducibility (shown in Figure 1, 2), although the average diameter (Median Diameter) of CAST is stable, the number concentration has a tendency to decrease with time.

2) The cause investigation and improvement need to be considered.

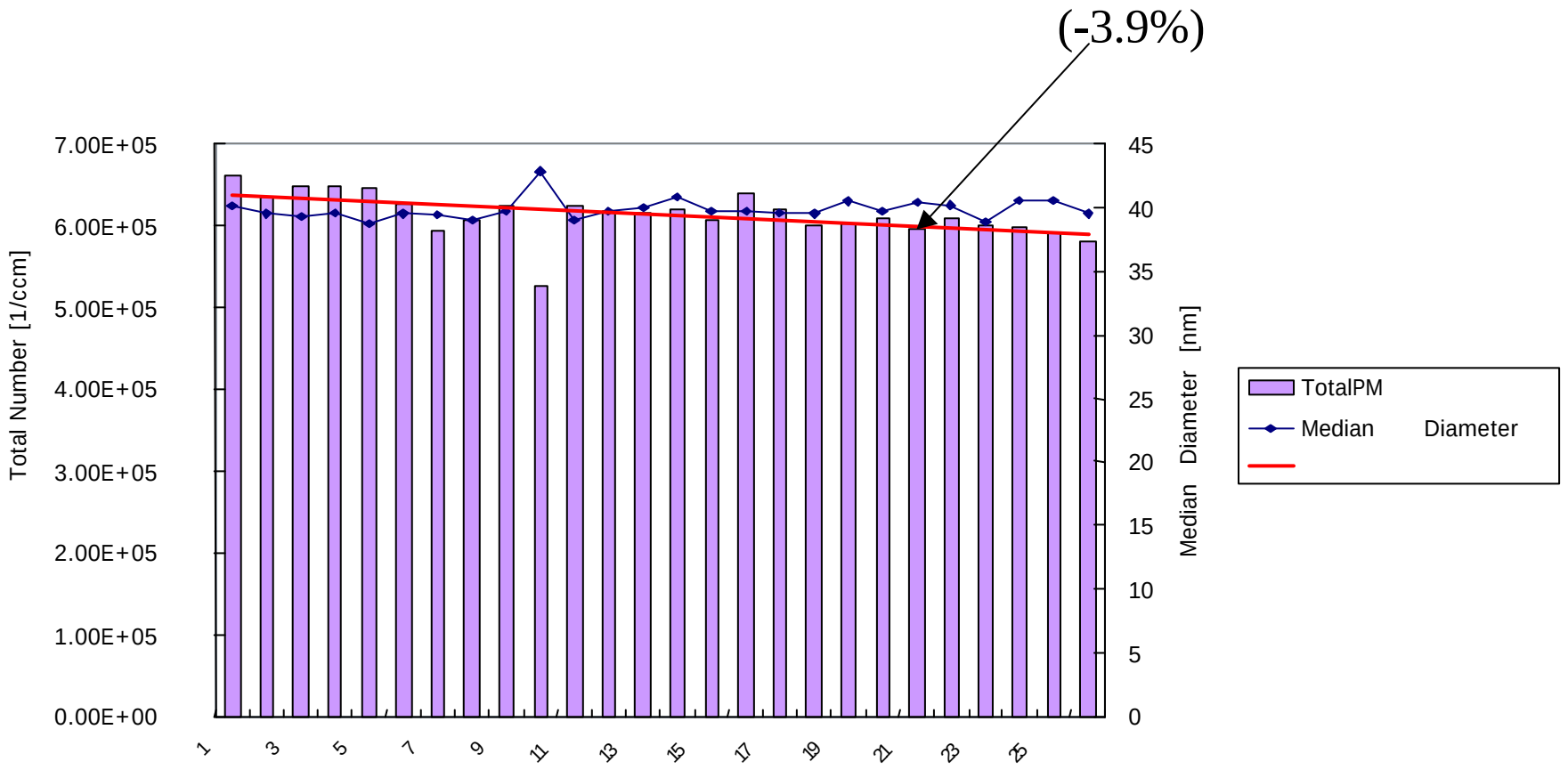
3) JAMA conducted a Round-Robin tests of simultaneous measurement.

Fig. 1 Repeatability of continuous scans with a CAST (100nm)



Notes) measurement after warming-up

Fig. 2 Repeatability of continuous scans with a CAST (30 nm)



Notes) measurement after warming-up

2.2. The Round-Robin Tests of DMA+CPCs, ELPIs, DCs

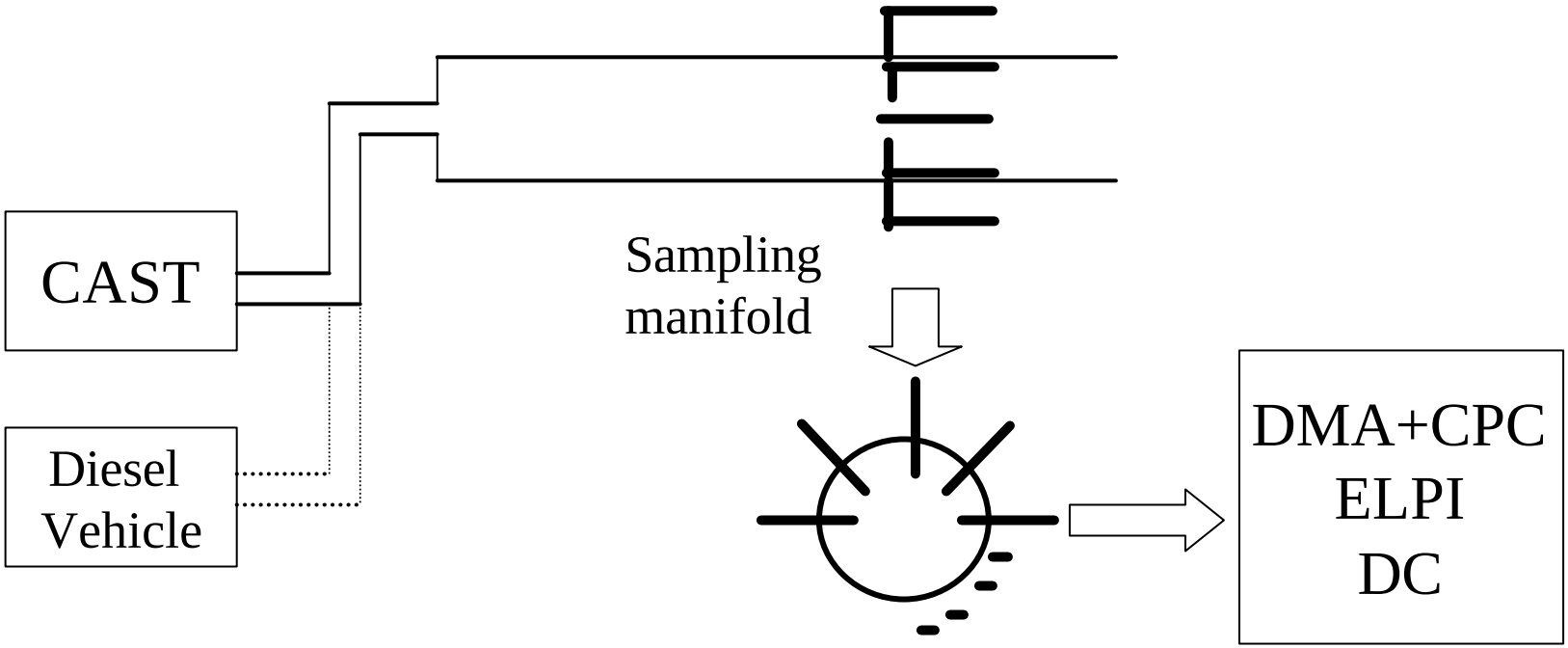
We carried out Round-Robin tests Round-Robin of simultaneous measurement with the various kinds of equipments using a CAST and a diesel exhaust.

As a result, the measured values of DMA+CPC, ELPI and DC have insufficient accuracy for the regulation in that the standard deviation is large yet (Figure 3 to Figure 5).

From now on the accuracy improvement and the development of calibration methods of the equipments need to be conducted.

Round-robin Test Setup

- Simultaneous sampling with the same kind of instruments



Summary of Round-Robin Tests

- COV values for DMA+CPC, ELPI, DC

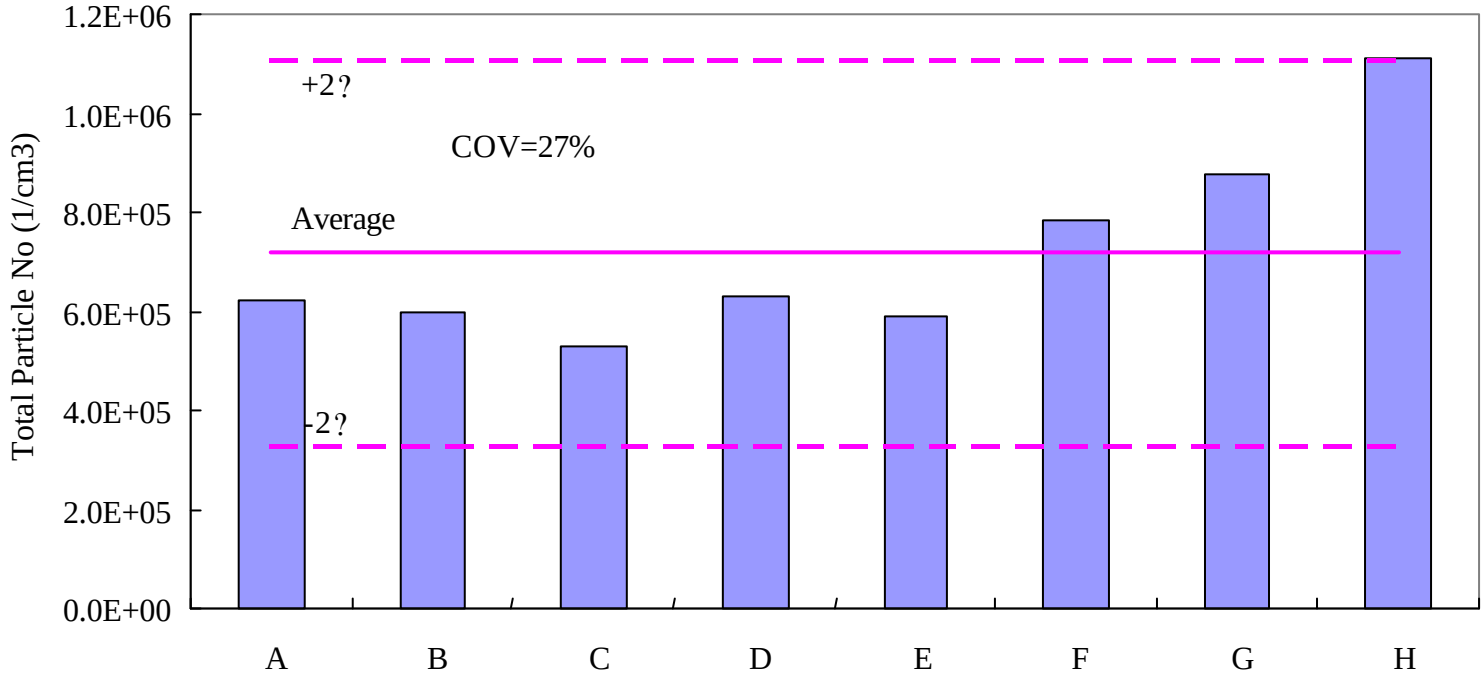
	CAST(1) MP3(100nm)	CAST(2) MP6(30nm)	Diesel Exhaust
ELPI Total Particle Number	27%	40%	23%
DMA+CPC Total Particle Number	28%	19%	27%
DC Total Surface Area	48%	48%	54%

Data from JCAP (Japan Clean Air Program)

Fig.3 ELPIs Total Particle Number with a CAST (100nm)

- Simultaneous measurements of total number of particles from CAST using different ELPIs

ELPI : 5min averaged value, A-G: with filter stage, H: without filter stage
CAST: MP3 (Dp = ca. 100nm)



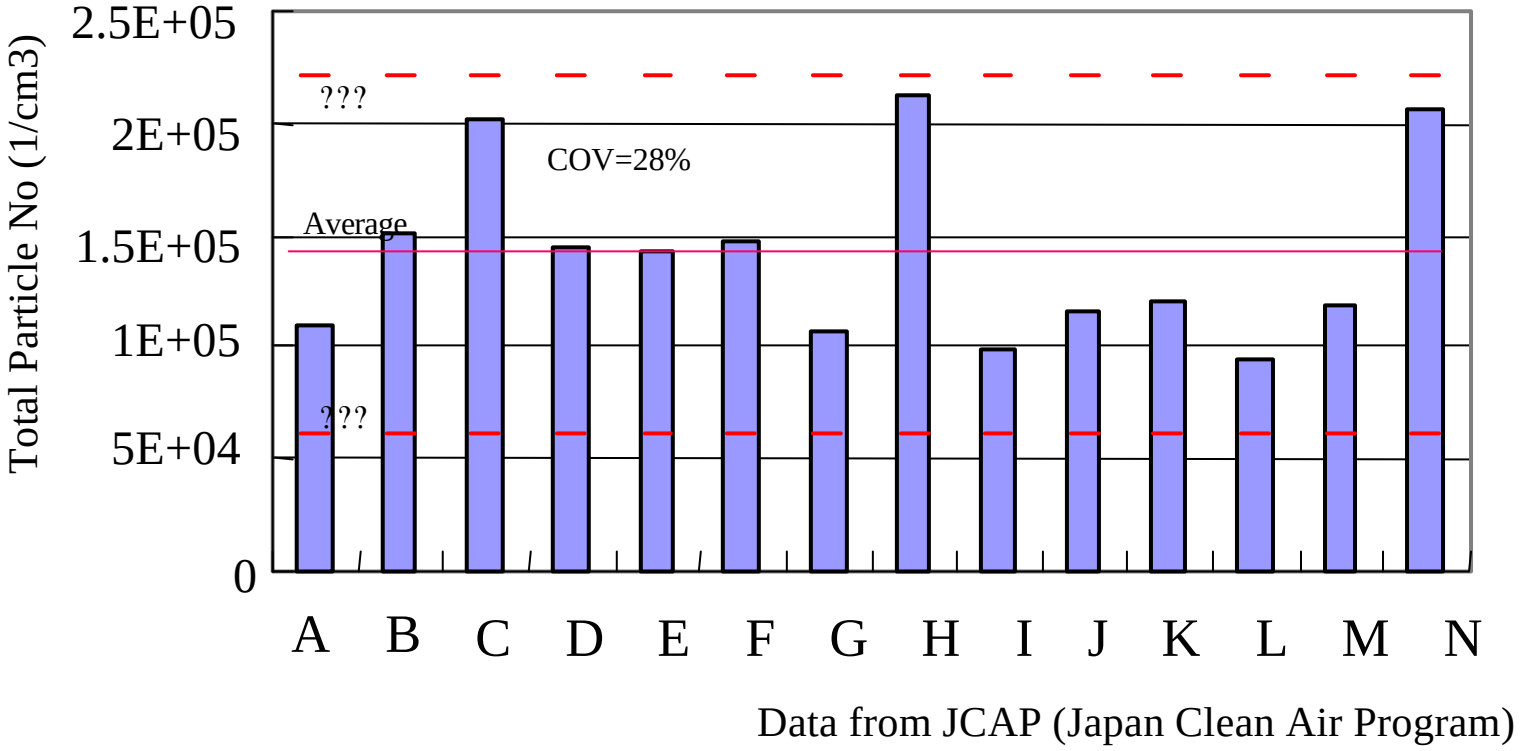
Data from JCAP (Japan Clean Air Program)

Fig.4 DMA+CPC Total Particle Number – CAST (100nm)

- Simultaneous measurements of total number of particles from CAST using different DMA+CPCs

DMA+CPC : 5scan averaged value,

CAST: MP3 (Dp = ca. 100nm)



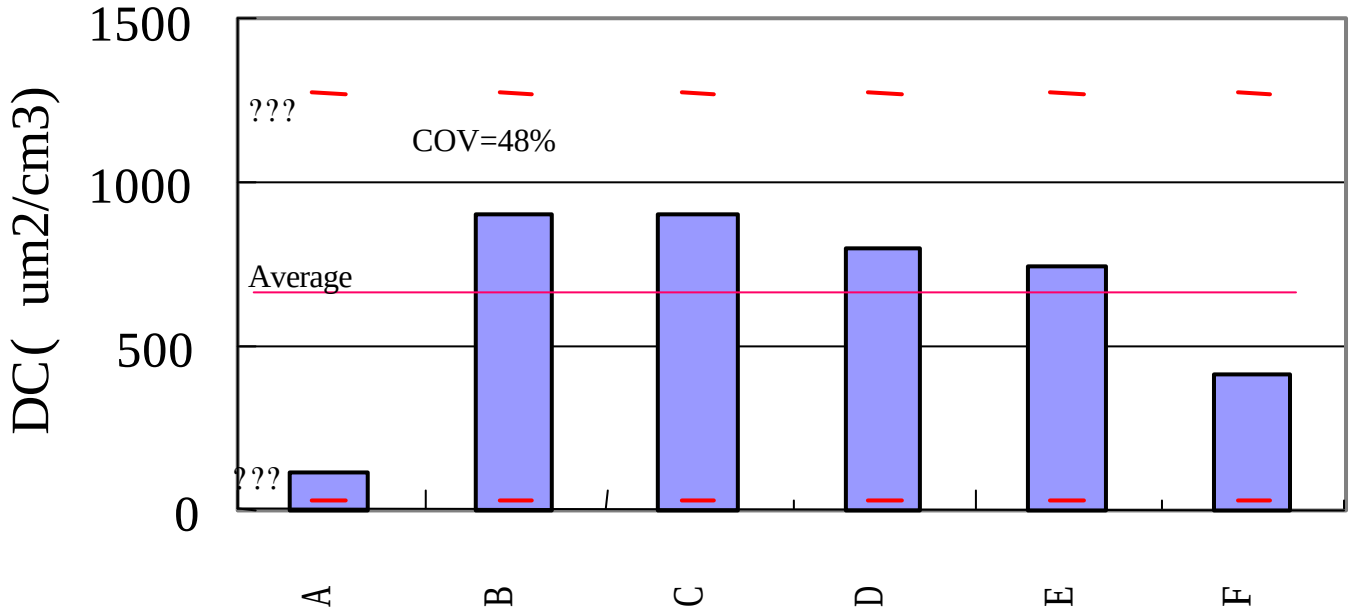
Data from JCAP (Japan Clean Air Program)

Fig.5 DC Total Particle Surface Area (100nm)

- Simultaneous measurements of total particle surface area from CAST using different DCs

  DC : 5scan averaged value,

  CAST: MP3 (Dp = ca. 100nm)



Data from JCAP (Japan Clean Air Program)