Literature Study

on

Tailpipe Particulate Emission Measurement for Diesel Engines

Heinz Burtscher

Fachhochschule Aargau, University of Applied Science
CH 5210 Windisch, Switzerland[*]

March 2001

done for the Particle Measurement Programme (PMP)
for BUWAL/GRPE

---

[*] e-mail: h.burtscher@fh-aargau.ch

Content

1. Introduction

Today diesel particulate emissions are limited on a mass basis. The mass is determined by gravimetric analysis of samples, taken at a temperature < 52°C. For a number of reasons this method is no longer adequate:

Modern low emission engines, in particular engines equipped with traps, have such low emissions that the gravimetric analysis is at its detection limit. The volatile fraction, mainly sulphur compounds in the emissions of these engines dominates the mass which makes the measurement unstable and inadequate.

From the point of view of health effects it is evident that solid and solvable fraction should be treated separately, because they behave completely different after deposition in the respiratory tract. Health effect studies indicate that mainly ultrafine solid particles are of importance. This topic is treated in detail in the section 4 by L. Hofer.

Modern trap technology allows a very efficient removal of solid particles, also of the nanometer sized fraction (see section 6 by J. Czerwinski).

Application of this technology requires adequate limits and means to measure emissions of the limited quantity after a trap with sufficient accuracy.

In this study requirements, posed on such a quantity, and possibilities to measure it are discussed.

2. General remarks

Diesel particles and particles from other combustion sources are a complex mixture of elemental carbon, a variety of hydrocarbons, sulphur compounds and other species. Fig. 1 shows the composition of particles from heavy duty diesel engines, measured in a transient cycle (Kittelson, 1998). Many of these species are volatile and may be in the gas- or the particulate phase, depending on temperature, dilution, and other parameters. This makes the quantification of particulate emissions and the definition of a limit so difficult. Depending on how samples are taken (location of sampling, temperature, dilution) different amounts of the species mentioned above will be measured as particle emissions. The sample contains not only particles, formed in the combustion process, but also during cooling in the sampling line. Particles differ in size, composition, solvability and therefore also in their toxic properties. Therefore different fractions should be treated differently.

Other air quality standards are based on one clearly defined species.

Regarding the particle size, three modes exist:

Nucleation mode (< 30nm): This mode mainly comprises volatile organic material and sulphur compounds (sulphate, sulphuric acid). Particles in this mode may be solid or droplets. This mode is very delicate in that small changes, for example in temperature, may have significant consequences on size and number concentration of particles in this mode. In many cases particles in the nucleation mode can be removed by heating. The nucleation mode contains only 1-20% of the particle mass, but may contain more than 90% of their number (Kittelson and Watts, 2000).

Accumulation mode, often also named **soot mode** (50-300nm): This mode mainly contains solid agglomerated material (elemental carbon, ash) and usually is stable and reproducible.

Coarse mode (1-10µm): This mode mainly contains re-entrained material (material from the accumulation mode, previously deposited in the exhaust system). As the re-entrainment is a stochastic process, this mode is not very reproducible and depends on 'history' (how much material has already been deposited). The contribution of the coarse mode to number- and surface concentration is insignificant, however, for the mass concentration it may be of importance. According to Bell et al. (1999) particles >300nm contribute less than 30% of the total mass.

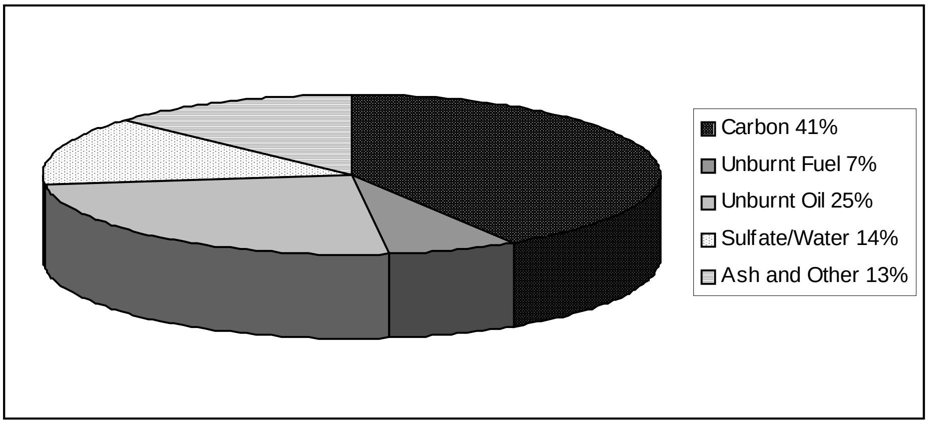

Fig. 1: Composition of particles from a heavy duty diesel engine, tested in a transient cycle (Kittelson, 1998). Depending on engine design and operating conditions the composition may vary widely.

Particulate emissions from vehicles are not only produced by combustion, but also due to tyre-, brake- and roadway wear and resuspension of road dust (Fauser, 1999). The influence of these species to the nucleation and accumulation mode is small. According to Fauser (1999) tyre and bitumen are responsible for about 5% of the weight of urban aerosol. Particles from other combustion systems (spark ignition engines, boilers etc. may be very different from diesel particles. Solid fuels yield a much higher fraction of 'non-combustible material' (ash), spark ignition engines have a high organic fraction and only little elemental carbon. A brief comparison of particles from different combustion sources is given in Burtscher (2000).

When volatile material condenses or nucleates, it may be in the solid or liquid phase, depending on temperature and melting point. This has great influence on the particle structure. Liquid particles will coalesce after agglomeration and form spherical particles, solid material forms chain- or grapelike agglomerates.

The state of the art of laboratory emission measurements is well developed. A number of tools exist for the quantitative characterisation of particles. However, some of these tools

- are very expensive
- are sensitive to environmental conditions (e.g. temperature) and not suited for field use
- yield a composition or size distribution, which is at least not directly the kind of information required for regulatory testing (preferably one single value). Some kind of mean value has to be calculated from the size distribution, which is limited.

A number of studies to compare different systems to measure particulate emissions have already been performed, see for example: Bell et al. (1999), Cartus et al. (1999), Dickens et al. (1997), Kittelson et al. (1998), McAughey (2000).

Some of these studies assume state of the art engines. Problems with nucleation of volatile material will be much more significant with modern low emission engines or especially those equipped with aftertreatment devices. These problems are reduced if low sulphur fuels are used.

3. Requirements

Important basic criteria for any method must be:

- Accuracy
- Repeatability
- Traceability
- Robustness
- Costs

As no real particle standard exists traceability is an especially difficult task. Usually round robin tests are used to test repeatability and comparability of results between laboratories and between methods without knowing the absolute accuracy.

More details to the requirements from the point of view of metrology can be found in the appendix by J. Schlatter.

So far limit values for particles are based on particle mass, in the case of combustion emissions without any size limits. However, it is known that ultrafine particles penetrate more deeply into the lung (for the deposition characteristic of the human respiratory system see for example Hinds, 1999). There is also strong evidence that ultrafine particles and especially solid particles are of greater importance as far as health effects are concerned. Solid nanoparticles constitute a separate class of pollutants whose effects are only weekly or not at all correlated to those of larger particles and which should therefore be treated separately (Wichmann and Peters, 2000).

Health studies indicate that mainly the particle surface is of importance (see for example Oberdörster, 1996 and 1998). To consider this, future emission and ambient air quality legislation should incorporate size criteria, or limits should be based on particle number or surface area concentration.

Fig. 2 shows a typical size distribution of diesel exhaust particles. It is a measurement of emissions from a heavy duty engine equipped with a particle trap. Without trap most particles are in the size range 30nm - 300 nm (accumulation mode). As shown by Cartus(1999) and in ACEA (1999) the size distribution is similar for passenger car diesel under very different operating conditions. After the trap the accumulation mode particles are reduced by about two orders of magnitude. However, a large number of particles occur in the nucleation mode. Particles belonging to this mode consist of volatile material (condensates). Under certain operation and dilution conditions condensates occur also without trap.

After a particle trap, the mass, determined by the present regulatory test, is dominated by condensates (see Fig. 3) and therefore becomes extremely dependent on temperature and dilution. This effect may be much more pronounced than shown in Fig. 3. Table 1 shows another example. For some cases the apparent filter efficiency in terms of mass is close to zero, whereas 99% of the particles in terms of number count integrated over the accumulation mode are removed. These effects are treated in more detail in the section on aftertreatment of this report by J Czerwinski.

This dependence and the very low mass hardly allow a reproducible measurement. Beside the questionable relevance of volatile material in terms of health effects, a mass measurement therefore seems inadequate for vehicles equipped with particle traps.

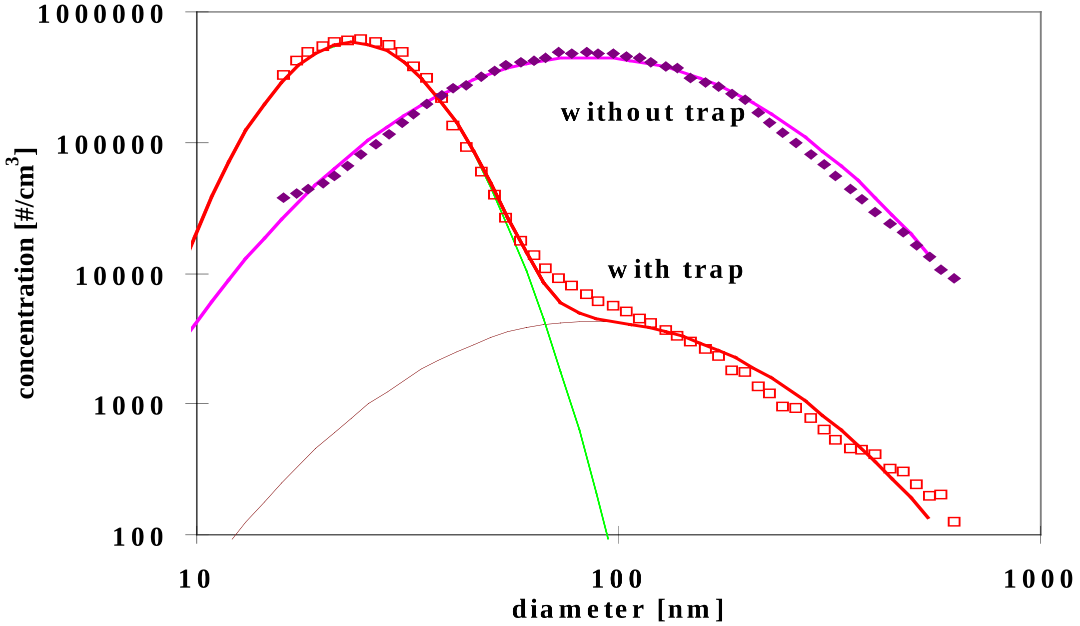

***Fig. 2**: Typical size distributions of diesel exhaust particles with and without particle trap. When the solid fraction is removed by the trap, volatile material, which condenses on the solid particles without trap, nucleates homogeneously. This means that even if the concentration of ultrafine particles is higher after the trap, no new material is created, it just occurs at a smaller size. Experiments show that most of the newly formed nucleation particles do not have a solid core. They can be completely evaporated or dissolved. This will also happen after precipitation in the respiratory tract. The effect of these particles therefore is completely different from solid particles.*

	mass	Number count
A	76.52	95.38
B	70.46	86.65
C	77.54	97.79
D	64.20	91.03
E	54.76	98.98
F	3.2	96.3
G	12.4	99.9

Table 1 Filter efficiency of different filters in % according to mass and number count. Average at four points ISO8178 for the trap in states as delivered using standard diesel. Taken from Mayer et al., 1999. For more details see section by J. Czerwinski of this report.

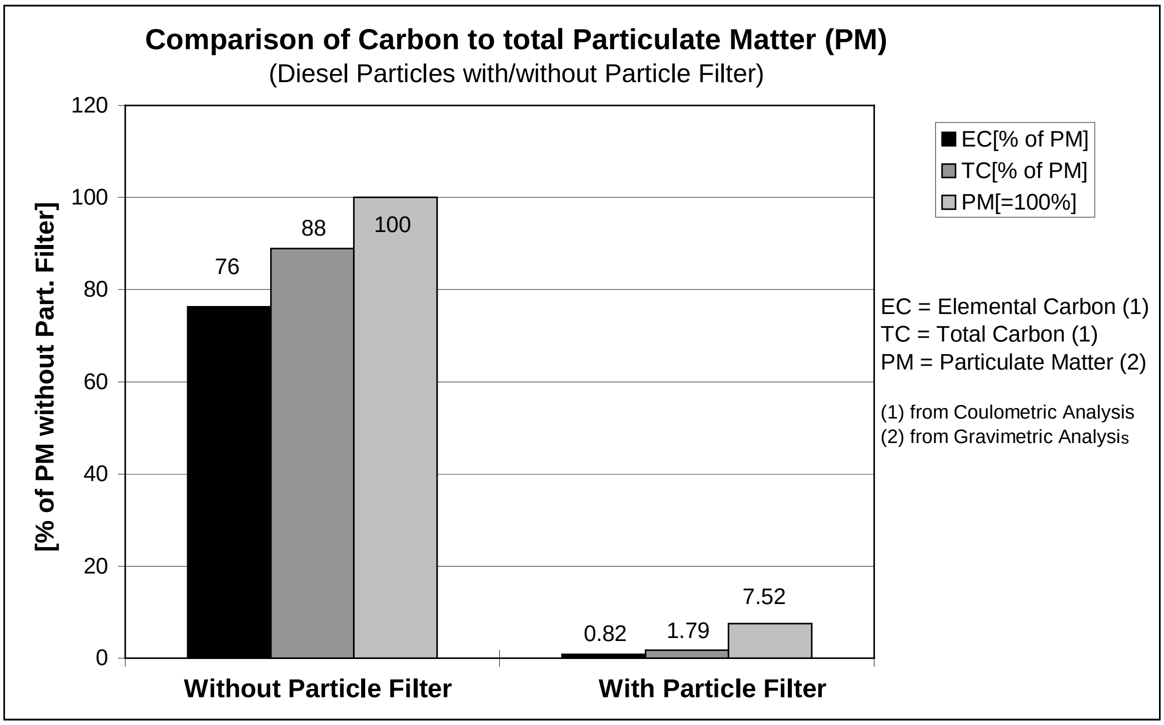

Fig. 3*: Total mass, Total carbon and elemental carbon mass before and after a trap: The much higher filter efficiency for elemental carbon can be ascribed to volatile material, passing the trap in the gas phase and condensing during cooling of the exhaust gas (From Matter et al., 1999).*

The following characteristics are important for a measurement:

- Two completely different types of particles coexist: Soot particles, belonging to the accumulation mode around 80 nm, and condensates, belonging to the nucleation mode. The health effects of these two species also will be very different. The condensates can be dissolved after inhalation, and it will be mainly the mass of the dissolved material which determines their effect. The solid fraction (mainly elemental carbon EC) remains as particle. Other properties than mass, eventually the surface, may then be of importance. Therefore these types should be distinguishable and have to be treated differently. Limits for the sum of both hardly make sense.
- The resolution of a size classification should be sufficient to distinguish between the two modes. However, due to the smooth shape of the size distribution no high resolution size measurement is required. The size distribution can well be approximated by a uni- or bimodal log-normal distribution (indicated by the solid lines in Fig. 2).
- The diameter definition used should be consistent with the one determining deposition in the airways. Smaller particles (<300nm) are deposited by diffusion. This means that the diameter definition should be based on the diffusion equivalent diameter, which is identical to the mobility diameter. The measurement technique used should be based on this definition. Larger particles are deposited by impaction. In this case the aerodynamic diameter is relevant, however, when looking at the size distribution it is obvious that particles <300nm are dominant.
- The condensate peak is very sensitive to the way the exhaust is cooled and diluted. Depending on the exhaust gas pre-treatment (dilution, temperature) it may vanish

completely or exceed the soot concentration at least in number. This has to be considered carefully to obtain reproducible results (Ricardo, 2001).

- After a particle trap the concentrations are too low for many measurement techniques
- To obtain representative results, transient operation conditions should be included in a test. Transient processes occur with time constants in the order of seconds. A good method should therefore have a time resolution in this order or better.
- It is desirable to have the same values measured for emission, occupational exposure, and ambient air limits. The concentration of elemental or total carbon concentration, presently measured in occupational health in Germany and Switzerland cannot easily be compared with total mass, measured for emissions and in ambient air. As shown above, this inconsistency becomes even more important for low emission engines and engines equipped with traps. Ash particles from the lubricant also gain importance, as the engine emissions of carbonaceous material are decreased.
- The measured (and limited) quantity must be relevant with respect to health effects, on the other hand a stable and reproducible measurement must be possible. Bringing these two requirements together will need a compromise. In occupational health in many countries elemental carbon is already used as tracer (TRGS 554 in Germany, SUVA MAK 2000 in Switzerland, NIOSH in USA). It could make sense to use the same for emissions too. Besides being of toxicological relevance this would allow a much easier comparison of emission and working place concentrations.

4. Sampling System/Pre-Treatment/Dilution

To obtain a representative measurement, this step is very important and also very difficult. The high particle concentration in the undiluted exhaust leads to rapid coagulation, as the coagulation rate depends on the square of the number concentration N.

$$\frac{dN}{dt} = K \cdot N^2 \Rightarrow N(t) = \frac{N_0}{1 + N_0 K t},$$

where K is the coagulation coefficient and N_0 the initial concentration. Fig. 4 shows the resulting concentration as function of time. It is evident that at high N_0 the initial concentration is no longer important for the concentration after short time.

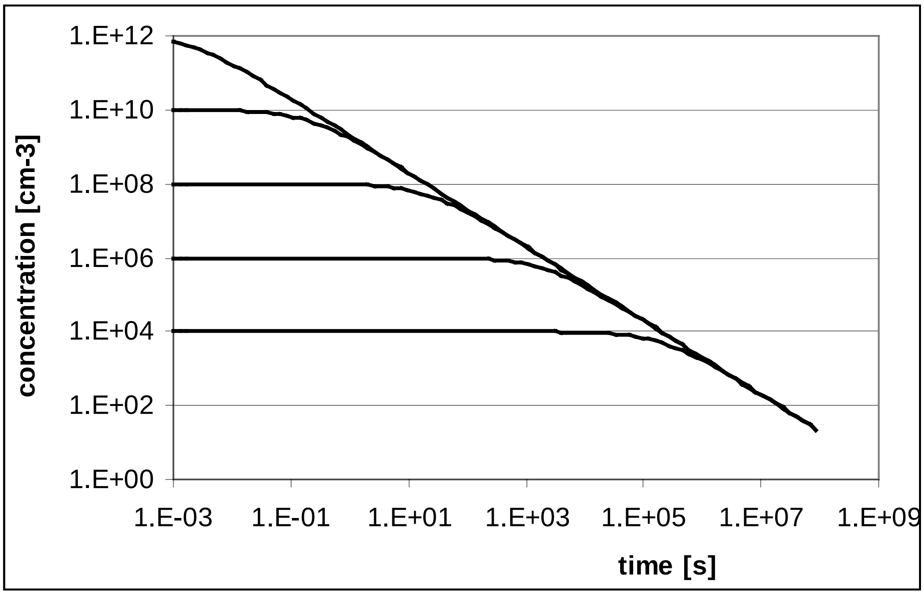

Fig. 4: Number concentration versus time for different initial concentrations, assuming a coagulation coefficient $K = 5\ 10^{-10}\ cm^3 s^{-1}$.

Coagulation can be reduced by rapid dilution. An example for the influence of coagulation on the size distribution is given by Cartus et al. (1999).
Changes in temperature may induce condensation and nucleation of volatile material. Condensation of liquids on agglomerates may also change their structure by capillary forces, leading to more compact structures (Weingartner et al., 1997). Nucleation becomes especially strong if the concentration of solid particles is reduced by traps and by oxidation of SO_2 to SO_3 (by catalytic traps, fuel additives, or catalysts), favouring formation of sulphuric acid droplets.
All these processes are highly non-linear, which means that small changes in the sampling parameters may have dramatic effects.

4.1. Particle Losses

Several processes lead to losses in the sampling system. Losses occur by inertial impaction, diffusion, thermophoresis, electrostatic deposition (McAughey, 2000, Dickens et al., 1997). They have to be minimised by an adequate design of sampling system. Losses by diffusion and thermophoresis have been analysed by Stratmann and Fissan (1988).

According to Ahlvik et al. (1998) losses in the sampling line of a typical light duty chassis dynamometer are less than 5%. A summary of losses is given in table 1 (see also Kittelson et al., 1999).

Table 1: Summary of Particle losses

Loss mechanism	effect	Counter measure
Inertial and gravitational deposition	Mainly important for larger particles, small effect for particles <1µm in diameter	Avoid sharp bending (impaction) and long horizontal tubing (gravitational settling)
Diffusional deposition	Efficient for small particles, which contribute significantly to the number concentration, usually negligible, if mass is considered	Short residence time
Thermophoretic deposition	If the sampling line is much colder than the exhaust, particles are driven towards the wall	Heat sampling line, avoid high temperature gradients
Electrostatic deposition	A significant fraction of particles is charged after emission. These particles are attracted by electrostatically charged walls	Use electrically conductive tubing material (no Teflon!), no nonconducting surfaces

4.2. Reentrainment

Another process, which may lead to measurement artefacts is reentrainment of material, deposited in the exhaust gas system. This material may be reentrained as larger agglomerates, (Kittelson, 1990), and can lead to irreproducible results, because this process occurs accidentally. Due to adhesive Van der Waals forces the probability of reentrainment of particles in the accumulation mode is very small.

Whereas the effect of non-isokinetic sampling is small for particles in the size range of main interest (below some hundred nanometers), it may be significant for reentrained agglomerates. To eliminate artefacts by reentrainment large particles could be removed by an impactor or cyclone before the measurement.

4.3. Condensation/Nucleation

As mentioned earlier, condensation or nucleation of volatile material can have a great influence on the number concentration. When the exhaust gas cools down, the saturation ratio of volatile material increases. Approximately when the dew point is reached (saturation ratio 1) condensation starts (for a more precise consideration the particle diameter and material also have to be taken into account). To initiate nucleation a supersaturation is required.

These processes occur in the exhaust system and mainly in the sampling lines and can be influenced by the way the exhaust is diluted and cooled (see Kittelson et al., 1999, Kittelson and Watts, 2000, Maricq et al, 1999, Mohr et al, 2000). If dilution is done with preheated air at high enough dilution ratio the saturation ratio can be kept low enough at any time to avoid condensation and nucleation. Only solid particles are measured in this case (mainly EC).

Kittelson et al. (1999, Figure 7 in this reference) show the range of temperatures and dilution ratios where supersaturation occurs, leading to nucleation/condensation. Dilution ratios >50 usually are sufficient to prevent supersaturation. The influence of residence time before dilution or in the primary dilution stage on the formation of nucleation particles is discussed by Kittelson and Watts (2000). A dramatic influence of residence time in the primary dilution tunnel was found by Abdul-Khalek, et al., (1998). When changing the residence time from 40ms to 6 s, the number concentration of nanoparticles increased by four orders of magnitude. As already mentioned earlier, the highly non-linear nature of these processes is responsible for the sudden strong effects, depending on the saturation ratio and on the time required by the gas diffusion processes involved.

Another critical parameter is the particle surface available for condensation. Older engines emit higher concentrations of carbonaceous material, having a large surface area available for adsorption of volatile material. This adsorption reduces the saturation ratio and prevents nucleation. At modern low emission engines much higher nucleation is observed, because the surface is small, the supersaturation correspondingly high (Bagley et al., 1996, Kittelson et al., 1999). This effect is even stronger when particle traps are used. The high efficiency of the traps (>99%) removes most of the solid particles. Only a very small particle surface is available after the trap. On the other hand all condensable material passes the trap in the gas phase. Nucleation of particles is enhanced by catalytic oxidation reactions in the trap, by which for example SO_3 may be formed from SO_2, which will lead to sulphuric acid droplets and sulphates (Matter et al., 1999b).

A similar effect (which is not related to sampling) is also observed for additive restituants, if fuel additives are applied. If enough soot is available, this material is incorporated in soot particles, otherwise it nucleates homogeneously and forms new particles (Skillas et al., 2000).

Volatile material can also be removed by a thermodesorber (TD, see Fig. 5). In the thermodesorber the sample is first heated to a well defined temperature and then passed through a cooled section containing activated charcoal, where all volatile material is removed. As not only material previously desorbed from particles but also vapours entering the thermodesorber in the gas phase are removed, the TD also allows to avoid later nucleation problems. Scanning the temperature in the thermodesorber allows to measure 'thermograms', yielding information on the volatility. They may give valuable information on the nature of the volatile material. A detailed description of the TD and several applications is given in Burtscher et al. (2001). Matter et al. (1999) show its application to diesel exhaust. There thermograms are used to investigate nucleation particles.

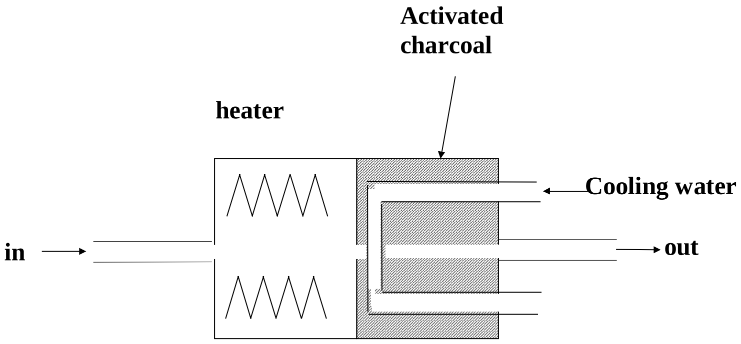

Fig. 5: Thermodesorber

Adequate dilution techniques or removal of volatile material by a thermodesorber allow to avoid problems with condensation/nucleation. However, this does not reflect the 'real-life' situation. Road experiments show that there condensation occurs (Kittelson and Watts, 2000). As long as particle mass is measured and conventional engines without aftertreatment devices are used, this is not a big problem, because the contribution of the volatile particles to the mass is not very significant. As soon as the weight of small particles is increased, for example by measuring the number concentration, this question becomes important. If no good way is found to deal with condensable material, no reproducible measurement is possible. In 'real life' situations usually a part of the condensable material will nucleate, another part will not, the fraction may vary drastically by small changes in the environmental conditions. A reproducible measurement under these conditions seems quite impossible. To obtain reproducible conditions, one can a) make a 'dry measurement'. This means avoid condensation/nucleation and measure only the solid fraction. As there is a certain evidence that it is the solid soot fraction which is mainly related to observed health effects this would be a way to get defined and relevant results.

On the other hand one can b) try to make a 'wet measurement' i.e. condense all condensable material by rapid dilution with cold air and thus measure all condensable material as suggested by D. Kittelson. Even then the number concentration will hardly be reproducible. A mass measurement, for example of particles <300nm could then be used to judge the small particle fraction.

The second suggestion would be 'on the safe side', because all potential material is measured, but is the more complicated solution. In combination with particle traps, where sulphur compounds play an important role in determining the mass – but probably not for health effects – a limit based on a 'wet measurement' will be questionable. The great importance of sulphur for the nucleation particles also means that only measurements using exactly the same fuel and lubricating oil quality can be compared. When aftertreatment systems are used, sulphur compounds may dominate the particle mass. The EURO IV limit can be exceeded by sulphur compounds (and the corresponding water) alone at a fuel sulphur content of 50ppm as shown in ACEA (1999b).

Based on these considerations a 'dry measurement' seems be a useful compromise, which allows a simple and stable measurement and yields relevant information.

If the condensates are considered, it would make sense to look at both, solid fraction (for example in terms of EC concentration) and the volatile fraction (in terms of mass). As already mentioned, this mass measurement would require an exact definition of parameters like dilution or temperature to obtain reliable results. The final answer has to come from health effect considerations.

4.4. Dilution Systems

The most frequently used dilution systems are **full flow** (constant volume sampling, CVS) and **partial flow dilution tunnels**. These systems are very expensive, mainly the CVS-technique, and do not allow to control dilution and temperature independently. On the other hand it is not required to know the exact exhaust gas flow and the flow rates are high enough to obtain sufficient mass on a filter for gravimetric analysis within a reasonable time. A comparison oft the two techniques and a discussion of their applicability for low concentrations is given by Schindler and Silvis (2000). Both techniques can be used for transient tests too, as shown by Stein (2001). Conditions in a CVS dilution tunnel favour the formation of particles by nucleation because the temperature drops to low values at moderate dilution ratios.

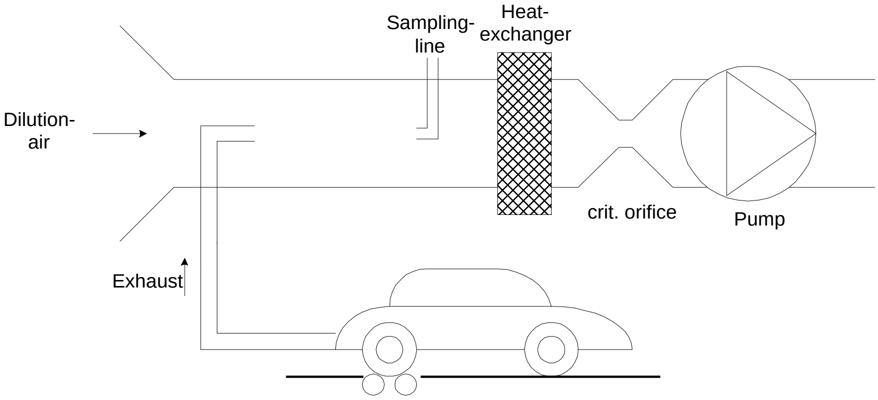

Fig. 6 System with CVS Dilution tunnel

Another system is the ejector dilutor. Dilutor and dilution air can be heated, which gives more possibilities to control the process. The dilution factor is typically in the order of ten, by varying the dilution air pressure it can be varied in a relatively narrow range. For higher dilution ratios several dilutors can easily be cascaded. The dilution ratio depends on the inlet pressure. This pressure has to be considered when calculating the dilution ratio, for example when measuring upstream a trap. Ejector dilutor can be used for the entire size range from nanometer particles up to several µm.

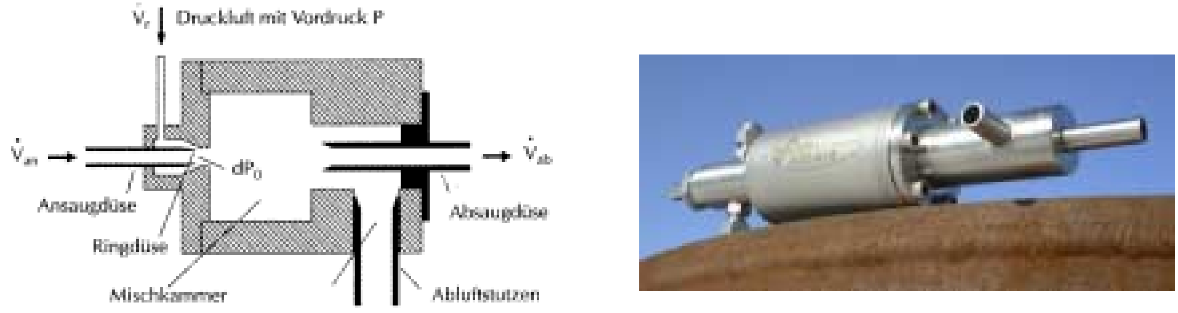

Fig. 7 Ejector dilutor (left side: drawing of the Palas-system, right side: picture of the system, manufacured by Dekati)

The rotating disk dilution system, described by Hüglin et al. (1997) allows a high and adjustable dilution ratio(1:30 to 1:1000) and an adjustable temperature of dilution system and dilution air. This enables one to prevent condensation or to study the process by systematically varying temperature and dilution ratio in a very easy way. This dilution system is integrated in the NanoMet system (Kasper et al., 2000). It works well for particles below 1 µm. The flow rate of the diluted gas is restricted to a few litres per minute.

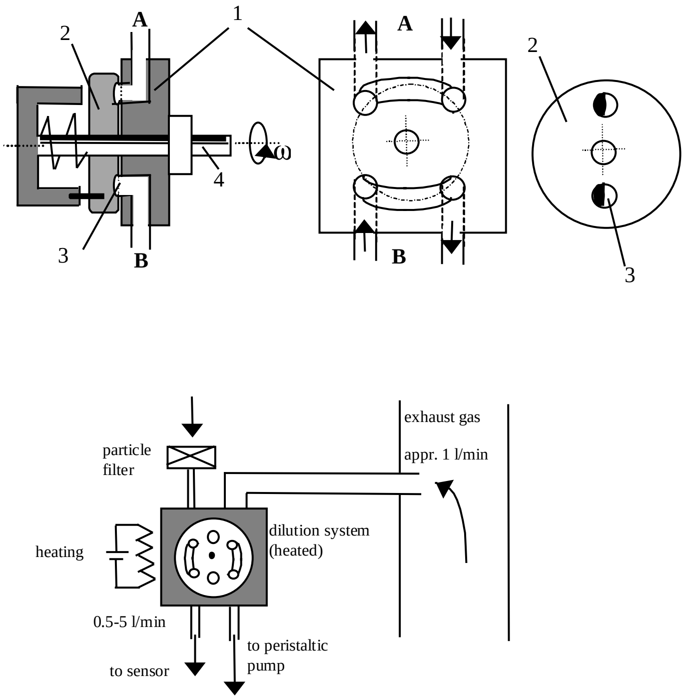

Fig. 8 Rotating disk dilution system A: undiluted gas channel, B: diluted gas channel, 1: body, 2: rotating disc, 3: disc cavity, 4: axis of rotation

A basic difference between CVS systems and diluters like ejector or rotating disk diluter is that for the first system the dilution factor is variable. It depends on the exhaust flow rate, which varies with engine load and speed. On the other hand, the total volume flow is constant. The other system operates at a constant dilution ratio, which therefore is well defined, but does not directly consider the exhaust volume flow. This means that the direct reading with the second kind is a concentration (value per unit volume), with the first a mass flow (value per unit time). The two results can be related via the exhaust flow rate.

5. Brief description of existing measuring techniques

Two main classes of techniques can be distinguished: Collecting techniques, where particles are first deposited in or on a filter and then analysed, and techniques doing the analysis or at least the important steps in the aerosol phase (in situ techniques).
During depositing as well as during analysis particles may be considerably changed, their properties may then be very different from the airborne properties. Phase transitions may lead to condensation of initially gaseous material, or material may evaporate from the filter (see *Fig. 9*). In addition, no detailed information on transient behaviour is obtained. On the other hand, a large number of analysis methods is available.

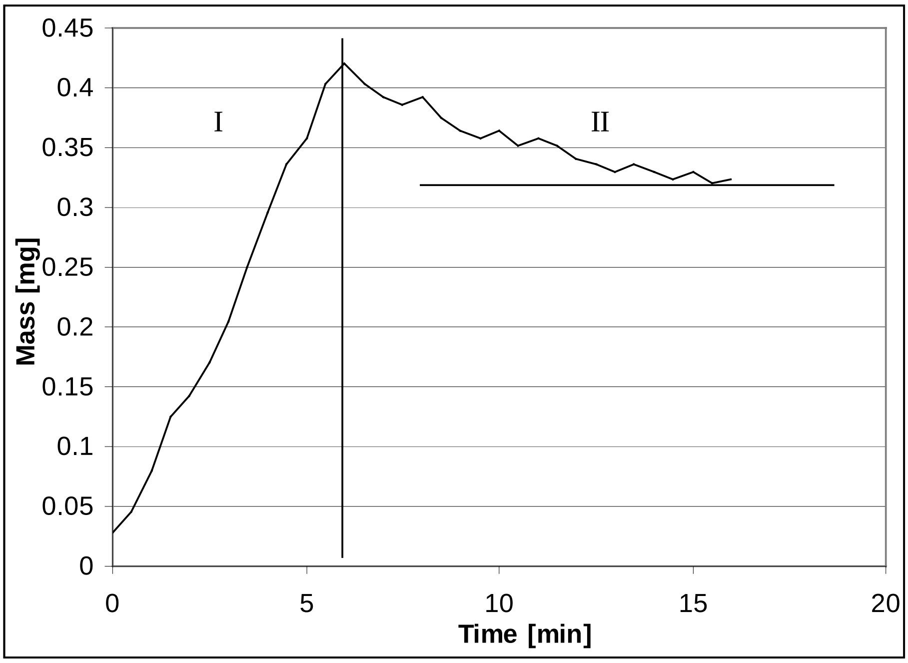

Fig. 9: Diesel particle mass on a filter, measured by beta-absorption. First exhaust gas is sampled from the engine, running at constant operating condition, which leads to a linear increase in mass on the filter (phase I). Then (phase II) particle free air is drawn through the filter. A significant reduction in mass (20%) is observed, which is ascribed to volatilisation of material collected before (from Burtscher, 1992).

Techniques working in the aerosol phase (in-situ techniques) avoid many artefacts and often allow a continuous measurement, however, often they yield only indirect results. For example opacity is measured and then transformed into a mass concentration.
Many techniques are somewhere in between. Conventional impactors, for example, classify particles in the gas phase, but then collect them for mass analysis or chemical analysis. Instruments as TEOM, beta absorption meter or Aethalometer collect the particles on a filter, but allow a continuous or quasi-continuous measurement.
The wide application of in-situ aerosol techniques to characterise diesel particles is relatively new. However, most of the techniques are known for a long time already and have been used intensively in other fields. For example, the first commercial mobility analyser was available in 1967, the principle of the condensation particle counter was already used by Aitken in the 19th century.

5.1. Collecting techniques

5.1.1. Gravimetry

This is the commonly used technique on which present legal limits are based. The procedure for the legal measurement including temperatures and dilution is well described. Dilution is done in a CVS dilution tunnel, the temperature of the diluted exhaust gas must not exceed 51.7 °C. Anything being condensed at this temperature is measured as particle.

If traps or an Oxicat are used, SO_2 may be converted to SO_3, which leads to formation of additional particles. The sulphate fraction of the particles may then be very high (>50%, Cartus et al., 1999, Stein 2001), slight changes of the temperature in the trap or catalytic converter may lead to significant changes in this conversion rate, making reproducibility difficult.

Gravimetry cannot be used for transient cycles such as free acceleration. As the mass emission of modern engines is very low, the sensitivity of gravimetry is becoming too low, causing significant errors (see Fig. 10 and Gifhorn et al., 2000). Schindler and Silvis (2000) discuss possibilities to minimise errors.

Current PM-measurement can only be applied for virtually sulphur free fuel with many aftertreatment systems (Stein, 2001).

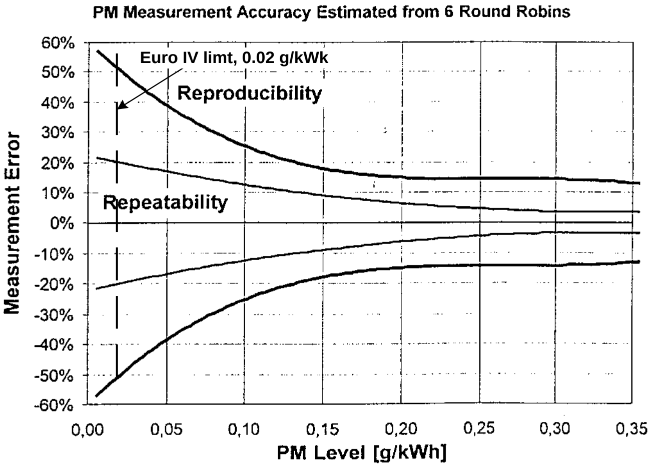

Fig. 10: Accuracy of the standard gravimetric measurement as function of the mass emission (from ACEA, 1999b). Repeatability is test-to-test variation of one single laboratory, the reproducibility the lab-to-lab variation.

5.1.2. SOF/INSOF-analysis

An extension of the gravimetric analysis is to analyse samples for their content of soluble and insoluble material. After the normal gravimetric analysis first the organic material is extracted (Soxhlet with CH_2Cl_2). The sample is again conditioned and weighted. The difference in weight corresponds to the solvable organic fraction. The next step is second extraction with an Isopropanol/water mixture to extract the water solvable fraction, which is then analysed for sulphates.

The fraction remaining on the filter is the non solvable fraction (mainly elemental carbon, also may contain ash, minerals, metal compounds)

5.1.3. Filter Smoke Number (Bosch, Bacharach Test)

A certain volume of exhaust is drawn through a filter, then the blackness of the filter is determined by an optical measurement. If the particles consist mainly of soot, this simple technique yields results which correspond to the total elemental carbon concentration (Christian et al., 1993)

As gravimetry, or even more, this technique is not sensitive enough for modern engines, especially if traps are used. Singer et al. (2000) discuss the application of this method to measure low concentrations.

5.1.4. Coulometry, carbon analysis

Coulometry is the reference method to determine elemental and organic carbon (VDI, 1996). A filter sample is heated in an oxygen flow to a temperature, where all carbon is burnt to CO_2. The CO_2 concentration is then measured by a coulometric technique. To measure elemental carbon only, the organic fraction is first extracted and thermally desorbed in a N_2 flow. This allows a reliable determination of carbon, however, it is a very time consuming and therefore expensive procedure.

Different methods for the analysis of filter samples for total-, elemental- and organic carbon are compared in a round robin test (Schmid et al., 2001). These test showed a relatively small variance (relative standard. deviation < 9%) for the total carbon analysis, but up to 46% for elemental carbon between different laboratories. Up to 18% were found within the same laboratory. Obviously the distinction between elemental and organic carbon causes problems. Another interlaboratory comparison test, organised by the VDI/DIN working group 'measurement of soot' (Neuroth et al., 1999) focused on the determination of elemental carbon. In these test 85% of the analysed samples were within ± 30% of the mean value.

5.1.5. Microscopy

Transmission electron microscopy (TEM) or scanning electron microscopy (SEM) are very powerful tools to study shape and morphology of particles. Equipped with energy dispersive X-ray (EDX) or electron energy loss (ELL) spectroscopy they also give information on the elemental composition. Whereas microscopy is an extremely useful instrument for basic studies, it can hardly be used for regulatory testing.

5.1.6. BET-Method

As already mentioned above, there is some evidence that health effects are best related to the particle surface (Oberdörster, 1998). Studies for example in the group of Heyder at FHG show that the surface, determined by the BET-method (Brunauer, Emmett, and Teller, see for example Shoemaker and Garland, 1967) yields a good correlation. The BET method measures the amount of a gas like N_2, which can be adsorbed on the particle surface and uses this as a measure for the surface. However, this analysis is very time consuming and a large amount of material is needed.

5.1.7. Chemical analysis of filter samples

A large variety of methods developed in analytical chemistry exists which can also be used for particle analysis, for example to quantify trace elements as heavy metals. As these will hardly be applicable for type approval testing, they are not treated here.

5.2. In-situ techniques

5.2.1. Condensation particle counters, number concentration measurement

The most frequently used instrument to determine the number concentration is the condensation particle counter (CPC) or condensation nucleus counter (CNC). Particles are guided through a saturated vapour, usually butanol. By cooling the vapour becomes supersaturated and condenses on the particles (see Fig. 11). Thus they grow to a diameter of about 10μm and can easily be detected optically (Hinds, 1999, Willeke and Baron, 1993). The required supersaturation increases with decreasing diameter (Kelvin effect, Hinds, 1999), which leads to the detection limit in diameter. For modern CPC's this is in the order of 10nm or even less. This limit is no problem for particles in the accumulation mode (soot particles), however, it may be a problem for condensates.

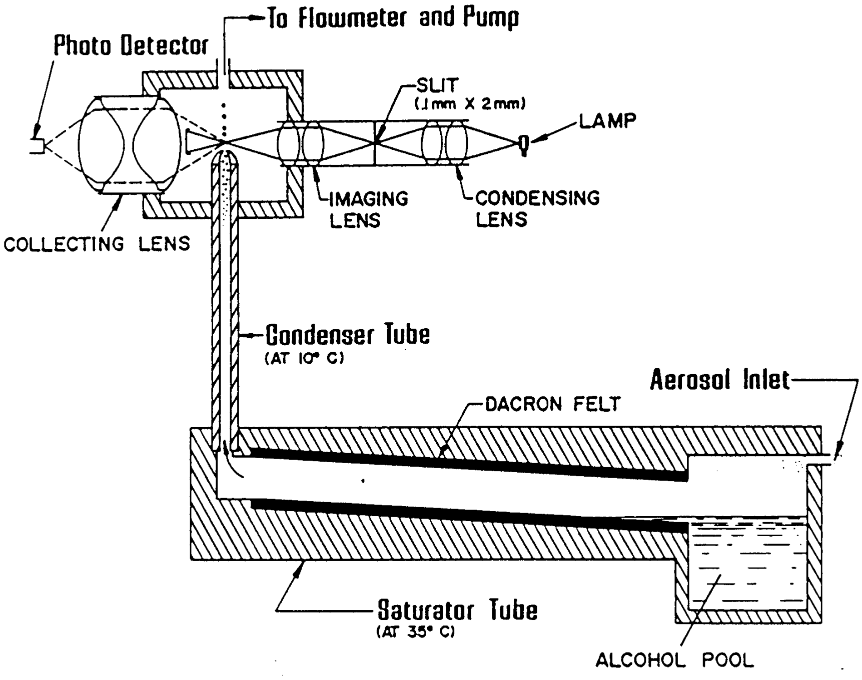

Fig. 11: Condensation particle counter

CPC's have two modes of operation: a counting mode, where pulses of scattered light from individual particles are counted. This mode allows a precise measurement, independently of the parameters of the optical system. However, only one particle is allowed in the detection volume at the same time, which is only possible if the concentration is low. In the second mode (sometimes called opacity-mode), used for high concentrations (typically >10^4 cm^{-3}),

the total scattering intensity is measured and used as a measure for the particle concentration. This requires that all particles grow to the same well defined diameter, and a well calibrated optical system. Generally, this mode is subject to greater errors than the counting mode and requires frequent and careful calibration.
A possible calibration procedure is for example described by Wiedensohler et al. (1997).
To have a well defined supersaturation, the temperature inside a CPC is very critical (tolerance in the order of tenth of K). The range of ambient temperature, where a CPC can be operated, is therefore limited. This may be a problem for field measurements. Beside that the instruments are sensitive to vibrations and horizontal positioning is of crucial importance.

5.2.2. Aerodynamic methods

The aerodynamic techniques make use of an accelerated particle motion, the measured quantity is the relaxation time constant

$$\tau = m\, b,$$

which is the product of particle mobility b and mass m (Hinds, 1999).
The corresponding equivalent diameter is the aerodynamic diameter d_{ae}. d_{ae} depends on the particle geometry (via mobility) and mass. It determines impaction and settling velocity, which are the dominant precipitation processes for larger particles, where inertial forces overcome drag forces (high Stokes number). When looking for example at deposition in the respiratory system, this concerns particles > ca. 300nm. Precipitation of smaller particles occurs by diffusion, which depends on the mobility diameter only.
There are mainly two classes of aerodynamic instruments: Impactors, obtaining the acceleration by deflecting the flow and 'aerodynamic particle sizers (APS 33, Aerosizer, Willeke and Baron, 1993), using a linear acceleration (Fig. 12).

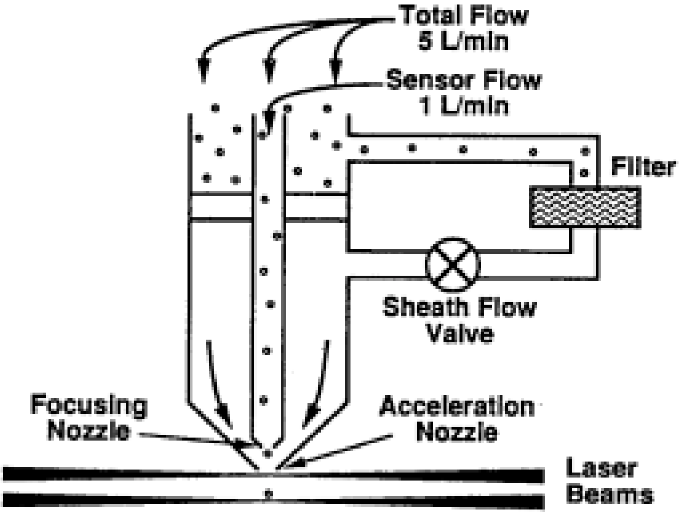

Fig. 12: Aerodynamic particle sizer (TSI APS 33)

Due to the optical particle detection, the lower limit of the second class is at about 0.5 µm. This makes them inadequate for diesel particles. Therefore they are not considered here. Impactors can be used down to nanometer particles, however, this requires low pressure stages, which may lead to evaporation of volatile materials. This problem increases with decreasing lower cut-off diameter (=lower pressure). For example, the lowest stage of the Electrical low pressure impactor (ELPI, see below) with a mean diameter of 30nm is operated at 8 kPa.

Usually cascade impactors (Fig. 13) with 6 to 12 stages are used (Hinds, 1999), which allow a parallel measurement in all size classes. Material, precipitated in the impactor stages is weighted or analysed chemically. This yields a mass distribution or a size fractionated distribution of a certain species. Often relatively long sampling times are required.

Frequently used types of cascade impactors:

- Andersen MarkIII Impactor: Conventional eight stage impactor, with a range from 0.4 - 10 µm, probably the most widely used impactor, well established technique, however lower limit too high, mass determined by weighing.
  Bell et al (1999) used an Anderson impactor to separate particles into two classes (<,> 300nm). They report significant loss of small particles in this impactor.
- Low pressure impactor (LPI)
  Low pressure impactors allow to measure also small particles. The Berner 10-stage LPI goes down to 16 nm (Hillamo and Kauppinen, 1991).
- Micro-Orifice Uniform Deposit Impactor (MOUDI, Marple et al., 1991) The MOUDI is a 10 stage impactor, the cutoff of the lowest stage is 60nm. A version with enhanced operation in the very small region is the Nano-MOUDI (Marple et al., 1994), which has 13 stages, reaching down to 10 nm.

A comparison of MOUDI-measurments and gravimetric analysis by Ricaro (2001) show differences up to a factor of 3, if much volatile material is present.

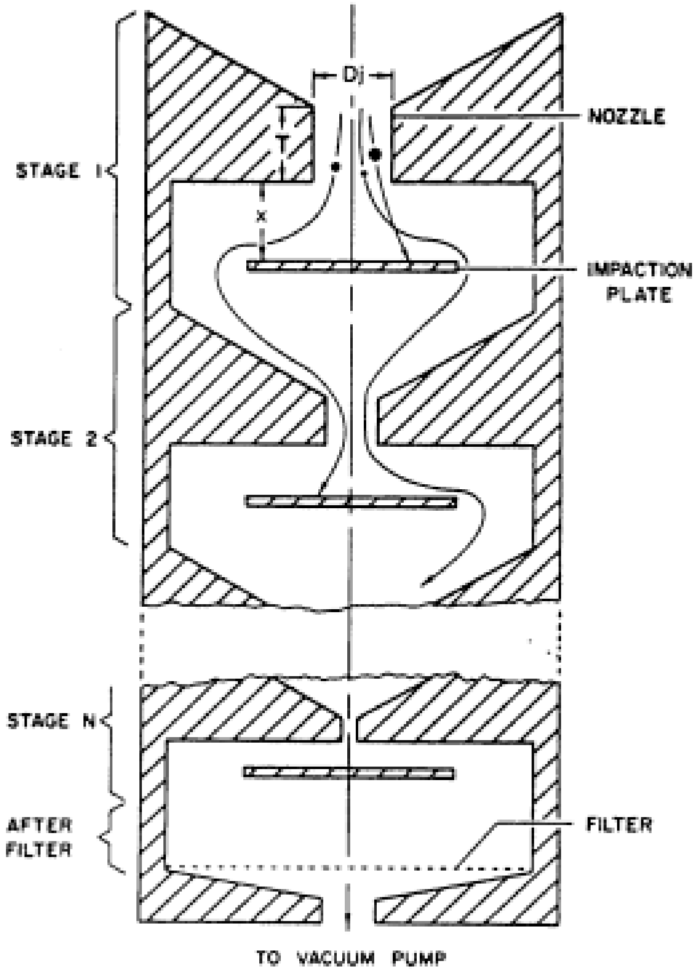

Fig. 13: Cascade impactor

Conventional impactors have a sensitivity problem, when reasonable sampling times are used and they do not allow transient measurements. Therefore impactors with other sensing techniques have been developed.

- One possibility is to use oscillating piezoelectric crystals as collection plates and use the change in the resonance frequency as measure for the mass, deposited on the plate (Fairchild and Wheat, 1984). This type of impactors showed severe bouncing problems. Especially for highly agglomerated particles another problem is the sometimes loose coupling of the particle to the substrate, leading to errors when calculating the mass from the frequency shift.

- Electrical Low Pressure Impactor (ELPI, Keskinen et al., 1992, see Fig. 14): Particles are charged by a corona discharge (unipolar diffusion charging, Hinds, 1999) prior to entering the impactor. In each impactor stage the current, produced by precipitated particles, is measured. Knowing the charging efficiency, the number concentration can be derived. This allows a real time measurement. The ELPI can be used for transient measurements, the time resolution being in the order of seconds. The sensitivity is high enough for ambient aerosol measurements. The present version has12 stages. The lowest stage has a cutoff diameter of 32 nm , the highest 10µm. 32 nm is a very low limit for an impactor, however, for diesel particles it is still not really sufficient. A new version of the ELPI with a cutoff diameter of 10nm for the last stage is announced.
  The charging efficiency is determined by the mobility diameter, the classification occurs according to aerodynamic diameter. If the particle density is not known, this leads to a calibration problem. For combustion particles the density often is a function of size, which makes the situation even more complicated (see discussion, chapter 6.4., Fig. 23 and Fig. 24).
  Problems with the calibration of the ELPI have been reported (see Kittelson et al., 1998, and references there). A recent comparison to SMPS data also shows significant differences between ELPI and SMPS results (Maricq et al., 2000).

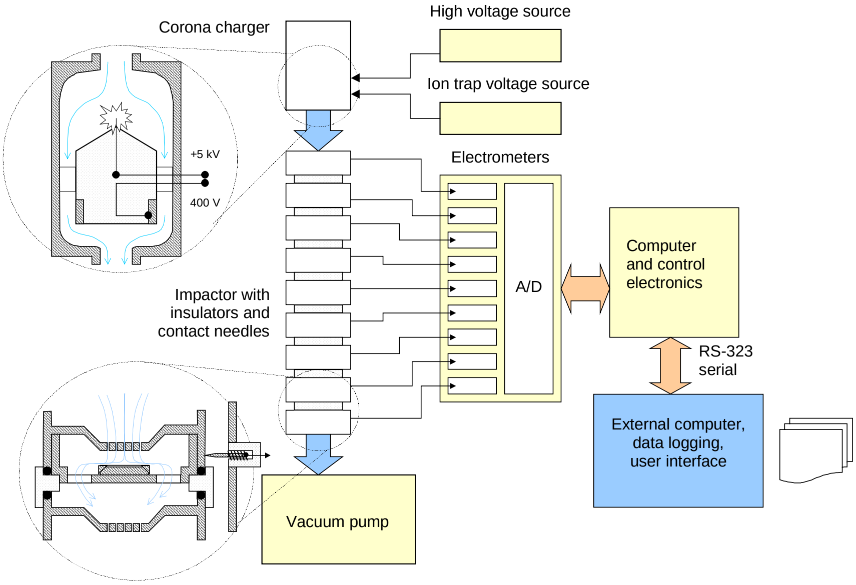

Fig. 14: Electrical low pressure impactor ELPI

- Charged particles down to nanometers can be detected by the impactor design described by Fernandez de la Mora et al. (1990). They use a single stage impactor, where the cutoff diameter is varied by varying the pressure. Applications of this type of impactor to study combustion particles are given by Schleicher et al. (1995) and Burtscher et al. (1998). A combination of impactor and differential mobility analyser allows to determine the particle mass as function of the diameter. This yields information on the structure of the particles, which may for example be expressed in terms of a fractal like dimension d_f for the relation between particle diameter and mass (Schleicher, 1995)

$$m \propto d^{df} .$$

$d_f = 3$ means compact, densely packed particles; the smaller d_f, the looser the agglomerates.

5.2.3. Methods based on Mobility and Diffusion

Particle mechanical mobility b and diffusion coefficient D are related by the Einstein relation

$$D = kT \cdot b \,.$$

This means that mobility analysis and diffusion analysis yield the same information, the 'mobility diameter'.

Mobility analysis

For mobility analysis particles are first charged, the mobility is then measured by their drift in an electrical field. In this case the electrical mobility z

$$z = b \cdot q \,,$$

where q is the particle charge is measured. To calculate the size from z, the charge has to be known, preferably the particles should carry one elemental charge. This can easily obtained for nanometer particles, but if the size approaches a µm correction for multiple charging becomes necessary.

Systems to classify particles according to their mobility are the electrical aerosol analyser (EAA) and the differential mobility analyser (DMA, Fig. 15). The EAA (Liu and Pui, 1974) used to be very popular, however, it is hardly used any more because of significant advantages of the differential mobility analyser.

Bipolar diffusion charging is used with differential mobility analysis. Particles are charged to their equilibrium charge (Boltzman equilibrium), which is well defined. Particle detection is usually done with a CPC. As alternative a Faraday cup (Wiklmayr et al., 1991) can be used, if the concentration is high enough for the measurement of the electric current.

For correct consideration of multiple charging no particles larger than the measured range must enter, there is a need for the removal of larger particles which is usually done by an impactor.

Two modes of operation are used: In the operation as differential mobility particle sizer (DMPS) the analyser voltage is increased stepwise to measure a size distribution. This takes about 20 min for a complete run. As scanning mobility particle sizer (SMPS, Wang and Flagan, 1990) the analyser voltage is scanned in a continuous ramp instead of steps. This reduces the time required to about one minute (depending on concentration and precision required). This significant reduction in time is accompanied by a slightly reduced accuracy. Due to the much faster scan, the SMPS is extensively used. Care has to be taken to choose the correct scanning time. If it is too fast, the size spectrum is distorted. The scanning time can be shortened by reducing the size interval investigated. It is important that during the scan the size distribution is constant.

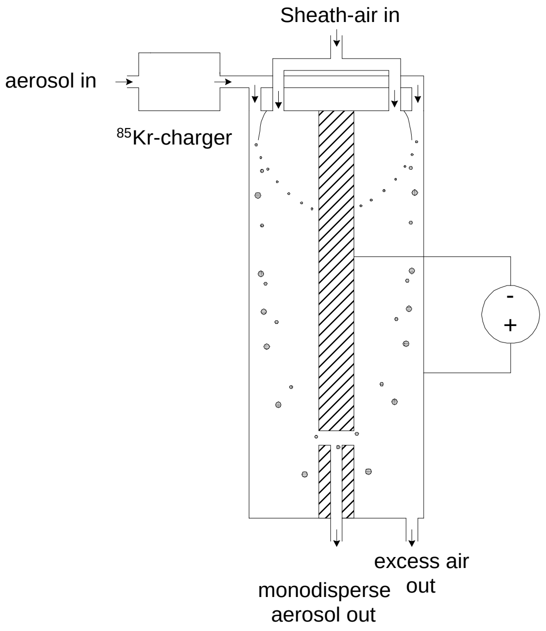

Fig. 15: Differential mobility analyser

Mobility analysis allows a very good size resolution, one scan covers about two orders of magnitude in size. The size range is some nm to about 700nm. The lower limit is due to diffusion, the upper one to multiple charging for larger particles.

The time resolution of one minute allows a quasi transient measurement, which, however, is still insufficient for transient test cycles or free acceleration tests. The speed can be increased by using two instruments in parallel (DDMPS, Double Differential Mobility Spectrometer). Of course this also means double cost of a technique, which is already expensive when using only one system.

Information on the calibration of mobility analysers is given by Stratmann et al., 1997.

A DMA can also be operated at a fixed voltage, thus selecting one size. Then the response time is only a few seconds and the system can be used for transient cycles. However, only information on a small size range is obtained. About 5 sizes are required to obtain an approximation of the size distribution. This means as many runs or five instruments in parallel, both of which are costly solutions.

The time problem can be also be overcome by a bag sampler, which is filled quickly. Care with coagulation, losses, and condensation has to be taken.

To analyse very small particles, the Vienna DMA (Winklmayr et al., 1991) and the Nano-DMA (manufactured by TSI) have been developed.

Kinney et al. (1991) tested the size resolution which can be obtained with differential mobility analysis. A recent Round Robin Test of 11 SMPS systems (Schlatter, 2000) using diesel particles showed differences up to 10% in the particle size and 20% in their number between the different systems. A significant fraction of these differences is due to inaccurate flow controllers. Another comparison of SMPS-systems can be found in Ricardo (2001).

In summary it can be said that mobility analysis is a high performance, however complex and expensive laboratory technique.

Diffusion battery

A Diffusion battery (DB) classifies particles according to their diffusion coefficient. As diffusion is strong for very small particles, this method is especially useful to analyse particles < 300nm. Diffusion batteries have been used for a long time. Different types such as parallel plate or screen type DB's (Scheibl and Porstendörfer, 1984) are used (Fig. 16, Hinds, 1999). Often a CPC is used to determine the input and output concentration. Usually valves are applied to change the diffusion length (e.g. number of screens). In this case the measurement is stepwise, this means it takes some time. Another possibility is to use a or parallel flow setup (Cheng and Yeh 1984), which allows a fast measurement and real time response, but requires several CPC's.

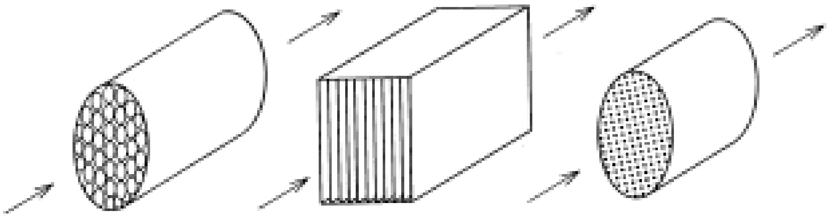

Fig. 16 Types of diffusion batteries: Tube package, parallel plate and screen type.

A new type, the 'Electrical diffusion battery' is introduced in Burtscher et al., 2001. There the particles are charged prior to entering into a 4 stage screen type diffusion battery (see Fig. 17).

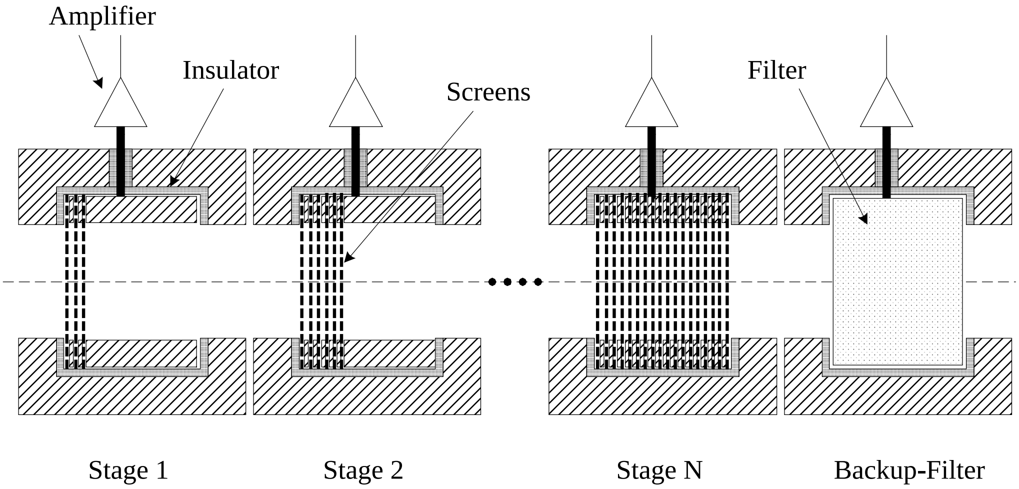

Fig. 17 Electrical diffusion battery. The smallest particles (of only a few nanometers in diamter) are precipitated in the first stage, containing only a few screens, larger ones in the second and so on. Particles penetrating all stages are collected in the backup filter.

Charged particles, deposited in each stage can then be measured by measuring the resulting electrical current. A backup filter, following the 4 stages collects all particles which have not been deposited before. This device allows a very simple and fast (seconds) measurement of the size distribution in the size range below about 300nm. Though using an electrical measurement, the sizing occurs by diffusion and therefore is not affected by multiple charging of particles. The pressure drop across the diffusion battery is very small, no problems with evaporation of volatile material occurs.

The electrical diffusion battery can be operated with a diffusion charger (material independent charging) and a photoelectric charger (selective charging of soot particles, see below). This allows to distinguish between soot and non-soot particles in every size class.

5.2.4. Optical methods

Optical methods have the great advantage that they allow a 'remote' measurement. It is not necessary that the exhaust gas is in touch with the measurement system. This makes for example in-cylinder diagnostics possible. Many of the optical methods allow a very fast measurement, which means that they can well be used for transient analysis.

As most of the diesel particles are smaller than the wavelength of the light, Rayleigh theory can be applied.

5.2.4.1. Opacimetry

The extinction of a light beam by scattering and absorption is measured. As sulphates, HC-fraction etc. may have a significant contribution, neither a clear correlation to total mass nor to EC-mass exists, except for cases where EC is dominant. No information on particle number- or surface concentration is obtained. For modern engines and definitely for those equipped with traps, opacity is out of the sensitivity range except for multilpe path systems, using mirrors (Zahoransky et al., 2001).

More information can be obtained by multi-wavelength techniques. This allows to obtain a mean size. However, for the agglomerate structure of combustion particles the mean primary particle size and no information on the agglomerate size is obtained. The setup described by Zahoransky et al. (2001) uses a multiple path system with an optical length up to 15 m to obtain a sufficient sensitivity.

The transient measurement of low concentrations is discussed by Thaller et al. (2000).

5.2.4.2. Light scattering

Light scattering can be determined by an integral measurement, the instruments used therefore are Nephelometer (wide angle measurement) and photometer (smaller angle). Another way is used in optical particle counters. There the intensity of light, scattered from a single particle is measured. The intensity is used to obtain information on the particle size, the count rate yields the concentration. The scattering intensity depends on diameter and index of refraction (material). Usually optical particle counters are calibrated with Latex-particles. The measurement yields an optical equivalent diameter. In the Rayleigh regime (particle << wavelength) the scattering intensity scales with d^6. This leads to a rapid decay when particles get smaller and limits the detectable size to about 100 nm. Therefore optical particle counters cannot be used for exhaust particles. An integrating measurement is possible if the concentration is high enough. However, again due to the d^6-relation, an interpretation in terms of mass or number requires a good knowledge of the size distribution. Small shifts in size have strong effects.

5.2.4.3. Light absorption

Light absorption of exhaust particles is dominated by elemental carbon. Absorption in the Rayleigh regime scales with d^3. This means that absorption is related to the particle volume and therefore to the mass. Absorption measurements can be used to determine the carbon mass.

Usually absorption cannot be measured by attenuation of a light beam, because this is dominated or at least strongly influenced by scattering. A number of techniques have been developed for absorption measurements. some of them are reviewed by Turpin et al. (1990) or Moosmüler et al. (1997).

Aethalometer:

The Aethalometer measures the attenuation of a white light beam through a transparent filter, on which the particles are collected (Hansen and Novakov, 1990). The chosen configuration allows to minimise the influence of scattering. Nevertheless, absorption coefficients found vary significantly. Liousse et al. (1993) find values ranging from 10 to 25 m^2g^{-1}, depending on the origin of the particles. If one calibrates the instrument for diesel particles, this variation will be much smaller, but still not negligible.

Photoacoustic Spectroscopy:

In photoacoustic spectroscopy particles are heated by absorption of light from a chopped laser beam (Adams, 1988, Petzold and Niessner, 1996, Arnott et al., 1999, Krämer et al., 2000). The resulting acoustic wave is then measured. This is a very direct in situ method. So far no commercial instruments are available. A problem are cross sensitivities by absorption of gaseous species (water vapour, NO_x). If these can be overcome, photoacoustics will be a relatively simple, direct, and fast method.

Time Resolved Laser induced incandescence (TIRE-LII):

In TIRE-LII the radiation of particles, heated by a short (some ns) laser pulse, is measured. The intensity of the radiation can be used to determine the elemental carbon mass, the time dependence of the cooling of the particles yields information on the primary particle size, based on a thermal model of the particle radiation. (Mewes and Seitzman, 1997, Schraml et al., 2000a, Schraml et al., 2000b, Bryce, 2000, Allouis at al., 2000, Dankers et al., 2000). LII was introduced as a tool for combustion research and recently has also been used for exhaust gas measurements. The advantages of TIRE-LII are that it is a very fast and sensitive method, having no problems with transient tests and modern low emission engines. It can be applied in the undiluted gas, for example directly at the end of the exhaust pipe (Fig. 18). The system is relatively compact, however, the frequency doubled pulsed laser system (Nd:YAG), the spectral filters required to suppress elastic scattering and reflections, and the nanosecond electronics have their price.

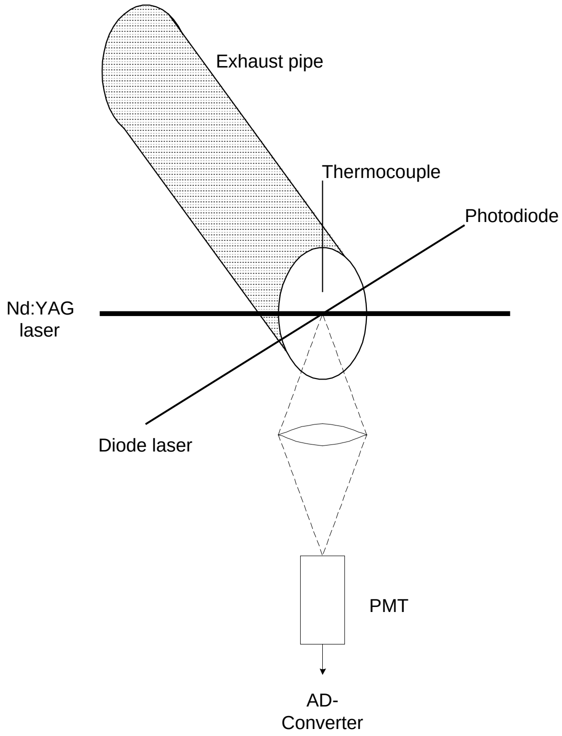

Fig. 18 Setup for a measurement with TIRE-LII at the end of the tailpipe. The additional laserdiode-extinction measurement is used for calibration (from Schraml et al., 2000b)

As already mentioned the data evaluation is based on a radiation model, which has to include also volatile material and requires the knowledge of a number of parameters. This may lead to errors. An important input parameter is the gas temperature which is measured by a thermocouple in the setup shown in Fig. 18. The mass determination requires calibration. From mass and primary particle size a number concentration can be calculated under assumption of a particle density and therefore there structure. However, this is the concentration of primary particles, not the concentration of emitted particles, as the particles form agglomerates. The same has to be said for the determined size, which is a kind of volume based diameter of the primary particles. As mentioned earlier, from the health effects point of view the mobility diameter of the agglomerates seems to be the most significant size-characteristic.

Polar Photometer

This is a recently suggested method (Kopp et al., 1999) which seems to have potential to determine the black carbon concentration of particles, deposited on a filter. It makes use of the observation that choosing an optimal scattering angle allows to significantly reduce the influence of material other than EC on the specific attenuation cross section.

Photoelectric aerosol sensor (PAS)

In the photoelectric aerosol sensor (Fig. 19, Burtscher and Siegmann, 1994) particles are illuminated by ultraviolet light, which leads to emission of electrons (photoelectric effect). The electrons are then quickly removed from the gas by an electric field (ion trap in *Fig. 19*). As photoemission involves absorption of a photon by the particle bulk material and emission of an electron through the particle surface, the resulting charge on the particles depends on surface properties and a material coefficient. This material coefficient is especially large for particles from incomplete combustion. A number of empirical studies show that the emission probability is closely related to the elemental carbon concentration in the case of diesel engines (Dahmann et al., 2000, Briska, 1999). In former ambient air studies the PAS signal was correlated with total concentration of particle bound polycyclic aromatic hydrocarbons(Hart et al., 1993).

Good correlation between PAS signal and EC concentration is obtained for specific sources. This means to measure EC from diesel exhaust by PAS, the PAS has to be calibrated for diesel exhaust.

The PAS allows a continuous measurement with a time resolution of about 1 s. The detection limit is in the order of 100ng/m^3 and is good enough for ambient air measurements in urban areas.

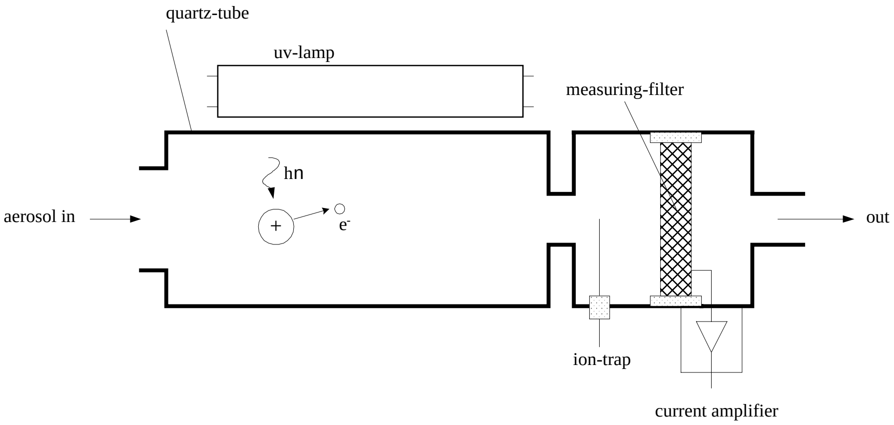

Fig. 19: Photoelectric aerosol sensor

5.2.5. Mass measurement

TEOM:

An instrument for the direct measurement of the total mass concentration is the tapered element oscillation microbalance (TEOM). The change in the resonance frequency of the tapered element, carrying the filter on top, is used to determine the mass of particles, collected in the filter (Patashnick and Rupprecht 1983). The TEOM is sensitive enough for ambient air measurements. The time resolution depends on the particle concentration, for diluted exhaust it will be some seconds. According to Cartus et al.(1999) no correlation within 10% to a gravimetric CVS measurement is obtained.

According to the manufacturer the detection limit of the instrument is less than 2 µg m^{-3} for a 24-hour integrated sample.

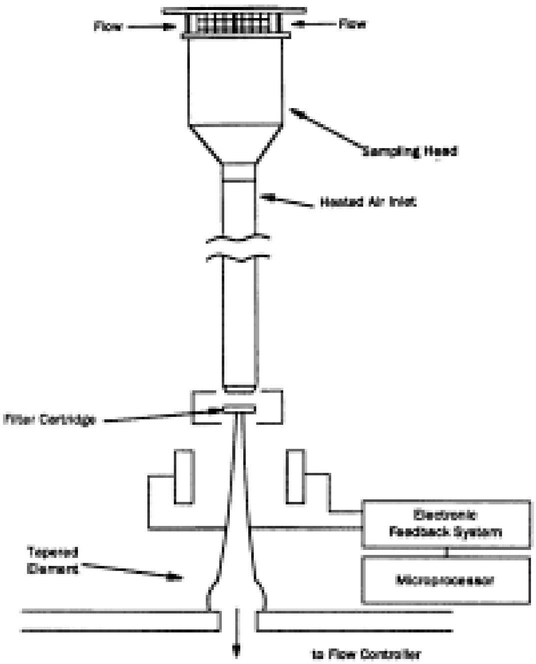

Fig. 20: TEOM, version with sampling head for ambient air sampling

Beta-Meter

The beta gauge method of mass determination depends upon the near exponential decrease in the number of beta particles transmitted through a thin sample as the deposit thickness is increased. The beta particles are emitted as a continuum energy distribution by a radioisotope source (often ^{85}Kr) and a suitable electron counter measures their intensity. The method has the advantages of instrumental simplicity and robustness. The dynamic range of sensitivity is sufficient, the response time may be a problem. A detailed understanding of the parameters which affect the measurements is necessary in order to ensure optimal instrumental implementation and correct interpretation of results (Jaklevic et al., 1981). A drawback may be that a radioactive source is required.

Quartz Crystal Microbalance (QCM)

The QCM has the some working principle as the TEOM. However, particles are deposited on a quartz crystal usually by electrostatic precipitation. The quartz oscillates at much higher frequencies than the TEOM (some MHz). The QCM was very popular in the 1970's. Then it disappeared due to problems with overloading, bouncing and calibration problems due to non-ideal coupling between substrate and particles. New developments in progress may lead to a new generation of the QCM which is fast enough for transient measurements (Booker, 2001).

5.2.6. Surface measurement

Both instruments described in the following measure the so called 'active surface', which is based on the integral collision cross section (Siegmann and Siegmann, 2000).

Epiphaniometer:

The Epiphaniometer (EPI) was developed at the Paul Scherrer Institute (PSI, Gäggeler et al. 1989). The EPI is based on the attachment of lead atoms (^{211}Pb), produced by the radioactive decay of a long-lived ^{227}Ac source. The number of attached ^{211}Pb lead atoms is then determined by counting the α-decay events of its daughter, ^{211}Bi. The Epiphaniometer measures the active surface of particles. It is a very sensitive, but slow instrument, for an integration time of 30 min, the detection limit is 0.003 $\mu m^2\ cm^{-3}$.

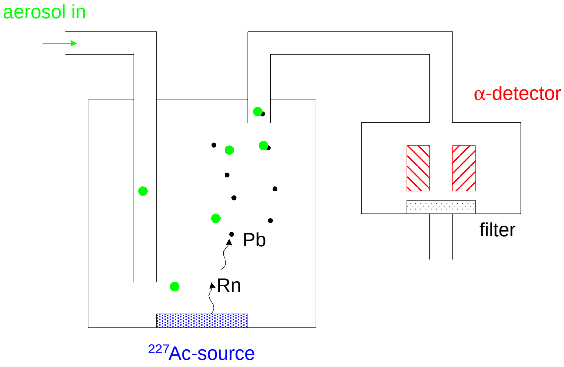

Fig. 21: Epiphaniometer

Diffusion Charging Sensor (DC):

In the diffusion charging sensor (referred to as DC) positive ions from a corona discharge diffuse onto the particles. The filter current is proportional to the active surface of the particle ensemble. The DC yields the same information as Epiphaniometer, but is much faster and simpler and, on the other hand, significantly less sensitive. The response time is short enough to allow transient measurements. To avoid artefacts by the repelling Coulomb potential high particle charges have to be avoided, which on the other hand reduces the detection limit. The detection limit of about 1$\mu m^2/cm^3$ is sufficient for emission- and ambient air measurement in urban areas.

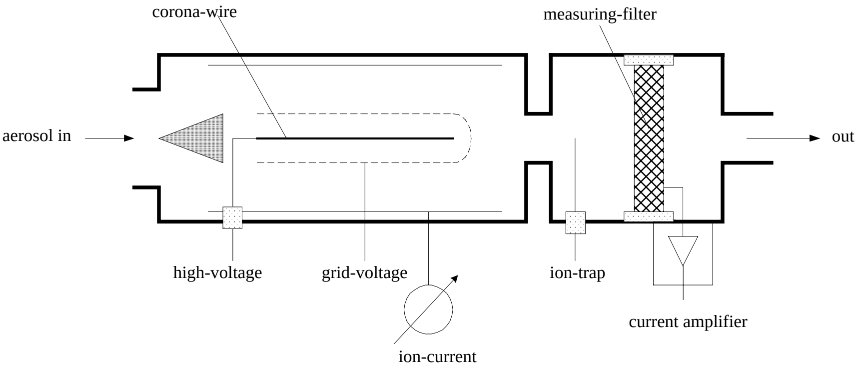

Fig. 22: Diffusion Charging Sensor

5.2.7. NanoMet

The NanoMet in its present version uses two sensors: a diffusion charging sensor (DC) and Photoelectric Aerosol Sensor (PAS), combined with a rotating disk dilution system (Kasper et al., 2000). Simultaneous operation of the two sensors yields both the active surface (DC sensor) and the active surface times material coefficient (PAS). Division of the readings provides the material coefficient which turns out to be characteristic of the particle source. Thanks to the diluter the measurable concentration range stretches from (vehicle) raw emissions to ambient air / occupational exposure measurements. As already mentioned in the sections of PAS and DC, these sensors are fast enough for transient measurements.

The combination of these two sensors was first used to study volcanic particles (Ammann et al., 1992) and applied at sites close to the crater rim. This hostile environment required a very robust construction, which helped in the development of NanoMet.

In the case of diesel particles the ratio of PAS and DC allows for example to determine whether nucleation of volatiles takes place or not.

5.2.8. Mass spectrometry

Mass spectrometry can be used to get information on particle composition. A strong laser pulse evaporates the particle (or a part of it). Evaporated material is then analysed my mass spectrometry. An instrument developed for aerosol particle analysis is the Aerosol Time-of-Flight Mass Spectrometer (ATOFMS, Silvia and Prather, 1997, Gard et al., 1997). This instrument, manufactured now by TSI, measures the aerodynamic diameter of entering particles by an APS (see chapter 4.2.2), so that in addition to the chemical information the particle size (aerodynamic diameter) is also known. This works down to a particle diameter of 0.3 µm. Two analysers allow a parallel measurement of positive and negative ions.

A direct measurement of particles and their precursors by a time of flight mass-spectrometer was performed by Siegmann and Siegmann (1997). They studied soot formation in a gas diffusion flame.

6. Discussion

6.1. Important factors

Here some important points are summarised which have to be considered

- Particles are agglomerates of primary particles, typically 20nm in diameter, which have a chain- or grapelike structure. Due to this structure, the volume does not scale with d^3. This means that no direct relation between number concentration and mass exists. The data from ACEA (1999) show for example that for the same number concentration the particle mass can vary by a factor of 6.
- Particles >500 nm have no significant influence on number concentration, but may significantly influence the mass. On the other hand, particles <20nm have almost no contribution to mass, but may dominate the number count.
  After a particle trap the mass is so low that condensable material which passes the trap in the gas phase and then nucleates and forms nanoparticles, may also be important for the mass (see Fig. 3 and table 1)
- Processes as dilution, coagulation, nucleation, and condensation during sample collection strongly influence the result of a measurement. Whereas many of these processes are known for a long time already and can well be modelled, some are still not well understood.
- The reading of the available monitors depends on the nature of the particles. Although many aspects as flow rate, temperature can be assessed there is no guarantee that an instruments respond to aerosols of different composition in the same way (Hall et al., 1998). Therefore it is important to do a proper calibration with particles which are at least similar to those which are to be measured.
- A stable accumulation mode containing mainly solid carbonaceous material is observed, whereas the nucleation mode may contain large numbers of volatile ultrafine particle in the range 10nm, whose concentration is hardly reproducible (Kittelson and Watts, 2000, Matter et al., 1999b)
- In occupational health elemental carbon is measured among other reasons because it allows a stable measurement and can unambiguously be attributed to engine emissions at working places, whereas other quantities may be influenced by other sources (for example evaporated solvents, dust...)
- Limits for passenger cars are in value per km, for heavy duty engines per kWh. Measured values usually are concentrations. To transform a concentration into a km or kWh-based value an accurate exhaust flow measurement and consideration of temperature is crucial.

6.2. Summary of sampling artefacts

The main reasons for sampling artefacts are:

- Agglomeration, which can be minimised by immediate strong dilution. Agglomeration has a strong effect on the number count, it is not important if a mass related quantity, e.g. EC, is measured.
- Nucleation/condensation may lead to a very high number of ultrafine particles. It can be avoided by adequate dilution (at elevated temperature). Condensation and nucleation occur also in 'real life' situations.
- Evaporation may occur from sampling filters and preferably from the small particle stages of low pressure impactors.

- Losses by deposition occur mainly by diffusion for the particle sizes of interest for diesel emissions. Can be reduced by reduced residence time in the sampling system.

6.3. Comparison of quantities without size classification

The following table gives a summery of the quantities that could be used for regulatory testing.

quantity	remarks
Total particle mass	lot of data and experience available, probably not the best indicator for health effects, problematic if traps are used because then semivolatile material dominates, reentrained particles may cause problems. Measures the sum of different species (solid fraction, sulphur compounds, volatile organic compounds), which should be treated separately as already done in occupational health.
Mass in size interval (PM10, PM2.5)	Current ambient air limits are based on this definition, allows to exclude large particles, problem with volatiles remains, unless 'dry mass' is measured
Total number concentration	If nucleation occurs, number may be dominated by nucleation particles. In this case it is hard to get reproducible results. Stable measurement possible if nucleation is prevented by adequate dilution/thermodesorption. At high concentrations coagulation is very rapid, only immediate dilution allows an accurate measurement in this case.
Number concentration in size interval	Allows to exclude condensation particles, Number concentration in accumulation mode may be a useful quantity, will be closely related to elemental carbon concentration.
Surface area concentration	Good correlation to health effects (Oberdörster, 1998), no applicable method to measure geometrical surface (BET surface), simple tools for active surface available, which also allow transient measurements. Surface calculated by integration of SMPS or ELPI spectra assuming spherical particles is unrealistic for combustion particles.
Elemental carbon concentration	Allows stable measurement, elemental carbon is the main component of the accumulation mode, direct measurement by coulometric analysis is expensive, no transient measurements. Several indirect methods available, which allow transient measurements. EC is the preferred quantity in occupational health regulations.

6.4. Size classification

The following considerations are important when using size classifying methods:

- Results from different techniques which are based on different physical/chemical particle properties are difficult to relate. In particular, different sizing instruments yield different 'sizes'. The really measured property (mobility, scattering intensity....) is related to an equivalent diameter (mobility diameter, aerodynamic diameter, optical diameter).

- No method covers the entire size range, no diameter definition can be used for the entire size range.
- Often a volume equivalent diameter is calculated from the measured quantity (often the mobility diameter) by using a dynamic shape factor. As the particle shape is not really known and different for every particle, the shape factor is not known either and based on assumptions. As the mobility diameter is more relevant anyway, because it is related to diffusion and deposition of small particles it makes more sense to directly use the mobility diameter.
- Under steady state conditions the SMPS yields a repeatable and reproducible result for particle size and concentration. Under transient conditions it requires either multiple drive cycles or the parallel use of several instruments. Both are very expensive ways.
- The only sizing methods which are really fast enough for transient measurements are ELPI and electrical diffusion battery.

The effect of density and particle structure (in terms of a fractal-like dimension df) on the relation of the most frequently used diameter definitions (mobility- and aerodynamc diameter) is demonstrated in Fig. 23.

Fig. 24 shows a comparison of a size distribution measurement with SMPS and ELPI, both operated from a CVS dilution tunnel.

Whereas the upper graph shows a fairly good match between the two systems, a mismatch is observed in the lower graph. The differences are engine load and fuel sulphur content, leading to different particle properties.

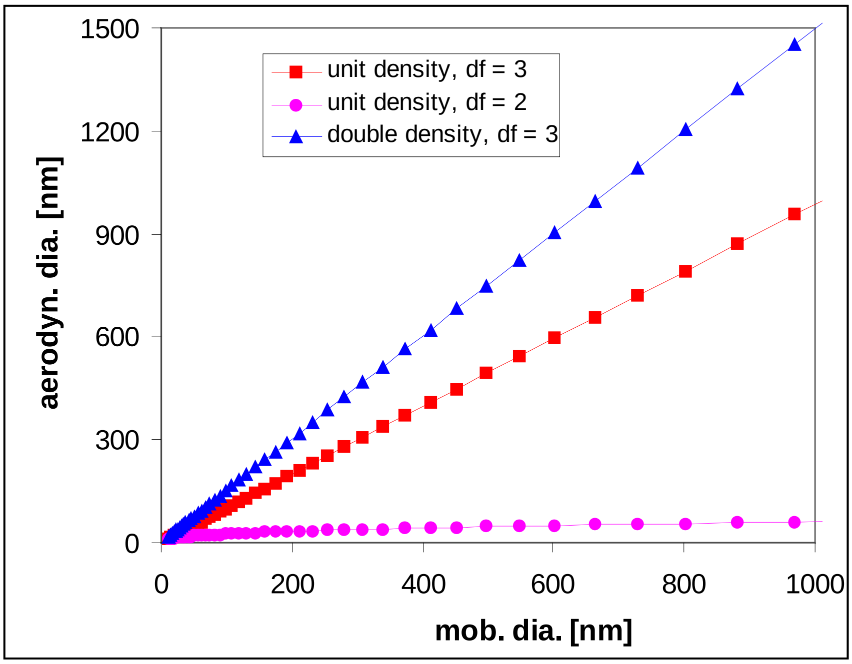

Fig. 23 Relation between mobility diameter and aerodynamic diameter, when particle density or fractal dimension df vary.

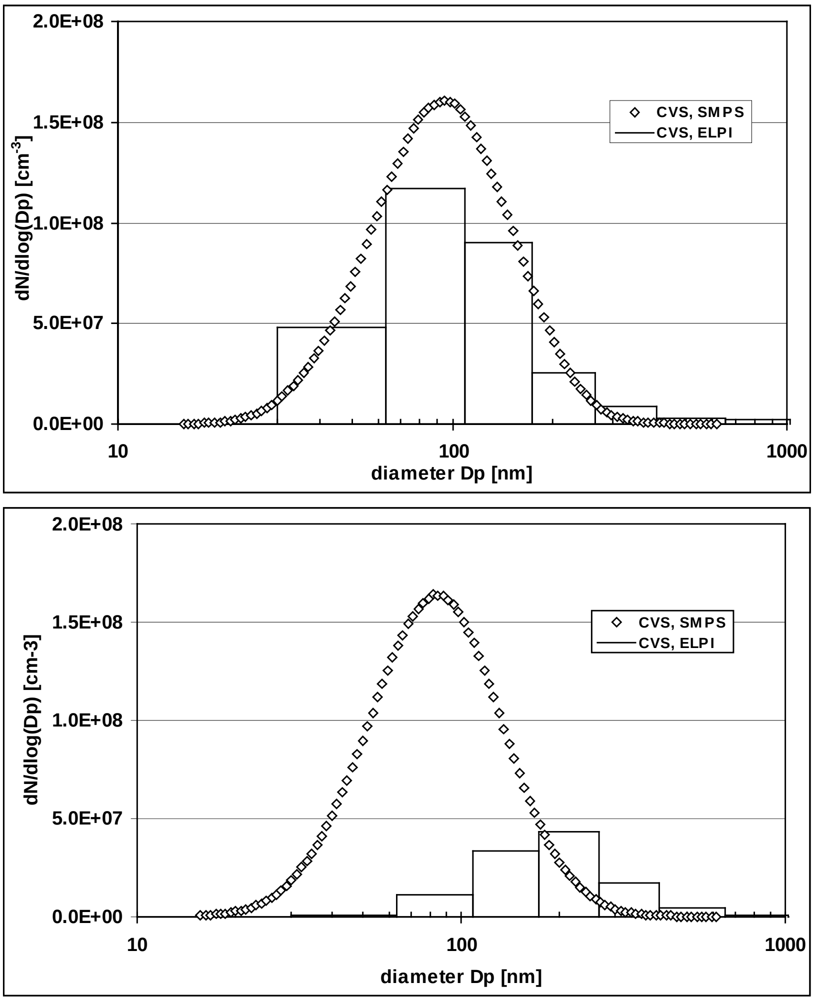

Fig. 24: Comparison of a parallel measurement with an SMPS and an ELPI. The upper result is with low sulphur (<10ppm) fuel and low engine load, the lower with 500ppm sulphur and higher load. The significant difference in the match between the two systems is mainly ascribed to a different particle density and structure.

6.5. Calibration

As no aerosol standard exists, calibration of aerosol instruments is very problematic. Most calibration procedures used do not really fulfil criteria of traceability to a standard, but are based on comparison to another method. Often mainly reproducibility and comparability, but not absolute correctness, are assured by instrument calibration. Round robin tests therefore are very important.

A soot particle generator for calibration purposes has recently been developed at the Swiss Federal Office of Metrology (Jing, 2000). Particles are produced by a sooting gas diffusion flame. The generator has a good reproducibility and may be a useful device to calibrate combustion particle measurement devices.

7. Summary and qualification

In the following table the different techniques will be summarised and their applicability according to the following criteria is given:

- Detection limit
- Cross sensitivity
- Transient measurement possible
- Emission, working place and ambient air measurement possible
- Stability, reproducibility
- Calibration
- Applicability for field measurements

Judgement:
+: good
p: problematic
-: not possible
?: undefined

Recommendations

- As the health effect of solid and solvable fraction is completely different, they should be treated separately.
- A way to deal with the solid fraction is to measure elemental carbon. This would be in agreement with occupational health standards. The reference method is Coulometric analysis, a commercially available monitoring device is the PAS. Other systems, based on optical absorption as the photoacoustic sensor or LII may be used in the future.
- The volatile fraction can be removed or kept in the gas phase by hot dilution or a thermodesorber. Then a measurement of number concentration (by CPC) or surface concentration (DC sensor, Epiphaniometer) yield results which are closely related to EC, but also include ash.
- As mainly particles <300nm are relevant, which are deposited by diffusion in the respiratory system, size classification – if done at all - should also be made according to a diffusion-relevant size parameter, which is the mobility diameter.
- An accurate size measurement is not required. Separating nucleation mode, soot mode and reentrained material is sufficient.
- If the solvable material is considered too, this has to be on a mass basis. In contrast to the solid fraction, where the particle material seems to be of minor importance, the solvable fraction has to be judged material specific. Otherwise materials like water will have a decisive influence.
- Today's knowledge on effects of the solvable fraction is not sufficient for a limit.

Summary of techniques

Procedure/ device	**quantity**	**range**	Det. lim	Cross.Sens	Trans.	Em.-amb	Field appl.	Stabil	Calibr.	**remarks**
CPC	Total number	5nm -10μm $1 – 10^6$ #/cm^3	+	+	+	+	p	p	+	The total number conc. is dominated by the nucleation mode, can hardly be measured reproducible. When using number concentration: condensation particles have sizes where CPC is at its lower limit, leads to uncertainty. Sensitivity sufficient for all cases, comparison difficult because total number concentration rapidly changes due to coagulation and nucleation, strongly depends on way dilution occurs after emission. Due to the limited range of operation temperature and position sensitivity the CPC is mainly a laboratory instrument.
CPC + hot dilution or thermodesorber	Number of solid particles	5nm -10μm $1 – 10^6$ #/cm^3	+	+	+	+	p	+	+	The problem of reproducibility can be overcome by removing the condensable fraction in a thermodesorber or by preventing nucleation by hot dilution with sufficiently high dilution factor. Comparison easier than for total number (no nucleation problem), coagulation remains.
Gravimetric analysis	Total mass	Dep. on sampling line	p	+	-	+	p	+	+	Sensitivity problem after trap, condensable material (sulphates, water...) dominates mass if trap used. Needs long sampling times for ambient air concentrations, problem with volatile material, comparison difficult.
TEOM	Total mass	< 10Mm	+	+	p	+	+	+	+	Same problems with volatile material as gravimetry, continuous measurements, but too slow for transient cycles.
Coulometric analysis	EC-mass		+	+	-	+	p	+	+	Reference method for EC-determination, high cost, EC is a very stable quantity.
Opacimetry	Light extinction		-	p	+	-	+	+	p	Sensitivity too low for low emission engines unless optical path is elongated by mirror system. Signal may be dominated by few large particles
Aethalometer	EC-mass		+	p	p	+	+	+	p	Cross sensitivity to non-EC material, continuous measurements, but too slow for transient cycles.

Procedure/ device	**quantity**	**range**	Det. lim	Cross.Sens	Trans.	Em.-amb	Field appl.	Stabil	Calibr.	**remarks**
PAS	Elemental carbon for diesel particles	< 1 µm det. limit 100ng/m^3	+	p	+	+	+	+	p	Indirect measurement, good correlation with EC found for diesel engines, fast and simple measurement, sensitivity sufficient for ambient air in urban areas. Calibration may change due to aging processes (change on the particle surface by photochemistry...) and other processes which change the particle surface
Photoacoustic sensor	EC	not reported	p	p	+	p	+	+	p	No commercial instrument, still problems with cross-sensitivities (water, NOx), has potential to become an easy-to-use device, should be kept in mind Sensitivity for ambient air not jet sufficient
Laser induced incandescence	EC	not reported	+	+	+	?	?	?	?	Interesting for engine development, as it allows in-cylinder measurements, fast, yields primary particle size.
BET	BET surface		-	?	-	p	-	?	+	Very expensive procedure, needs much material, sensitivity problem, esp. after trap, extremely long sampling times for ambient air samples.
DC	Active surface	5 nm - 1µm	+	+	+	+	+	+	+	Yields active surface, easy fast measurement, fast, simple, sensitivity sufficient for ambient air measurements in urban area
Epiphaniometer	Active surface	<7µm	+	+	-	+	+	+	+	Yields active surface, time resolution limited to some minutes, very high sensitivity, requires high dilution for emission measurement, also applicable in remote areas.
SMPS	Size distribution, based on mob. diameter	10 – 700 nm	+	+	p	+	p	+	p	High-resolution instrument, scan times for emission measurement ca 1 min, not sufficient for transient measurement, very expensive, laboratory instrument, can be used for all cases, sensitivity sufficient for measurement in clean areas (with scan times of some minutes)
DMA + CPC	Number in small size interval	5nm – 700nm	+	+	+	+	p	+	+	If a size in the accumulation mode is chosen a stable measurement is possible but information is limited, as mean diameter may vary. As size changes by coagulation, no comparison possible. Parallel measurement of several intervals yields good information, but causes very high costs (several DMA+CPC), serial measurements with one system require multiple measurement cycles

Procedure/ device	**quantity**	**range**	Det. lim	Cross.Sens	Trans.	Em.-amb	Field appl.	Stabil	Calibr.	**remarks**
El. Diffusion battery	Size distribution, based on mob. diameter	5 – 300 nm	p	+	+	+		+	+	Fast and simple instrument, no good size resolution, but sufficient to distinguish modes, new, not much experience so far, should be commercially available in a few months. Can be used for all cases, sensitivity too low for measurement in clean areas
Impactor	Mass in size intervals	Dep. on type >30nm	p	+	-	+	p	+	+	Same problem with condensable material as gravimetric analysis, only low pressure impactors cover size range of interest, requires very long sampling times, even longer sampling times than total mass measurement by gravimetric analysis
ELPI	Size distr., based on Aerodynamic Diameter	30nm - 10µm	+	+	+	+	+	+	p	Measures aerodynamic diameter, for deposition depends on mobility diameter, problem with evaporation of volatile material Can be used for all cases, sensitivity too low for measurement in clean areas

8. References

Abdul-Khalek et al. (1998) Diesel exhaust particle size: Measurement Issues and trends. SAE Paper No. 98P-353.

ACEA programme on emissions of fine particles from passenger cars (1999). www.acea.be.

ACEA (1999b) Problems associated with the measurement of low particulate levels. Report ACEA99000524.

Adams, K.M. (1988) Real time in situ measurements of atmospheric optical absorption in the visible via photoacoustic spectroscopy. 1. Evaluation of photoacoustic cells. *Appl. Opt*. **27**, 4052-4056.

Ahlvik, P., et al. (1998). Real Time Measurements of Diesel Particle Size Distribution with an Electrical Low Pressure Impactor. SAE Paper No. 980410.

Allouis, C, A. D'Alessio, C. Noviello, F. Beretta, (2000) Time resolved laser induced incandescence for soot and cenospheres measurements in oil flames. *Combust. Sci. Technol*., **153**, 51-63.

Ammann, M., L. Scherrer, W. Müller, H. Burtscher, and H.C. Siegmann (1992) Continuous monitoring of ultrafine aerosol emissions at Mt. Etna. *Geophys. Res. Lett*. **19**, 1387-1390.

Arnott, W.P., H. Moosmüller, and C.F. Rogers (1999) Photoacoustic spectrometer for measuring light absorption by aerosol: Instrument description. *Atm. Environ*. **33**, 2845-2852.

Bagley, S.T., K.J. Baumgard, L.D. Gratz, J.H. Johnson, and D.G. Leddy (1996) Characterisation of Fuel and Aftertreatment Device Effects on Diesel Emissions. Health Effects Institute Res. Rep. Nr. 76.

Bell, S.P., C.J. Dickens, E.A. Feest, A.P. Smith and A.M. Tope (1999) Experimental assessment of particulate measurement instrumentation. AEA-Report AEAT-4978.

Booker D. (2001) Development of a real-time transient cycle mass monitor. Proc. ETH Conference on Nanoparticle measurement, Aug. 2000, paper 20, ed. A. Mayer.

BRISKA (1999) Gesundheitsrisiko durch Luftschadstoffe in der Region Basel. 1. Bericht zur Studie BRISKA, Lufthygieneamt beider Basel.

Bryce, D.J., N. Ladommatos, H. Zhao (2000) Quantitative investigation of soot distribution by laser-induced incandescence. *Appl. Opt*. **39**, 5012-5022.

Burtscher, H. (1992) Measurement and Characterization of comustion aerosols with special consideration of photoelectric charging and charging by flame ions. *J. Aerosol Sci*., **23**, 549-595.

Burtscher, H. and H.C. Siegmann(1994) Monitoring PAH-emissions from combustion processes by photoelectric charging. *Combust. Sci. Technol*. **101,** 327-332.

Burtscher, H., S. Künzel, and Ch. Hüglin (1998) Characterization of particles in combustion exhaust. *J. Aerosol Sci*. **29**, 389-396.

Burtscher, H. (2000) Characterisation of ultrafine particle emissions from combustion systems. *SAE technical paper series*, 2000-01-1997.

Burtscher, H. L. Scherrer, and H.C. Siegmann (2001) The electrical diffusion battery for dynamic classification of nanoparticles. Proc. 4. ETH-Conference on Nanoparticle Measurement.

Burtscher, H., U. Baltensperger, N. Bukowiecki, C. Hüglin, M. Mohr, U. Matter, S. Nyeki, N. Streit, E. Weingartner (2001) Separation of Volatile and Non-volatile Aerosol Fractions by Thermodesorption: Instrumental Development and Applications. *J. Aerosol Sci*. **32**, 427-442.

Cartus, T., F. Dorfer, W. Schindler und G.P. Reischl: (1999) Messverfahren und Bewertung vonPartikelemissionen, VDA – Technischer Kongress.

Cheng, Y.S. and C. H. Yeh. 1984. Analysis of Screen Diffusion Battery Data. *Am. Ind. Hyg. Assoc. J.*, 45(8):556-561.

Christian R. et al., (1993), MTZ **54**, 1, p16.

Dahmann, D., T. Mosimann, and U. Matter (2000) Validation of On-line Sensors for Monitoring Occupational Exposures from Diesel Engines, *J. Aerosol Sci*. **31**, Suppl. 1, S21-S22.

Dankers, S., S.Schraml, S. Will, and A. Leipertz (2000) On-line diesel soot diagnostics by time-resolved laser induced incnadescence (TIRE-LII), Proc. 4. ETH Conference on Nanoparticle Measurement. Ed. A. Mayer.

Dickens, C.J., M.E.H. Ball, D. Booker, J.R. Donald, A.M. Tope and M. Hughes (1997) Evaluation of Instruments for Vehicle Emission Particle Sizing. AEA Technology Report AEAT-1180.

Fauser, P. (1999) Particulate Air Pollution with Emphasis on Traffic Generated Aerosols. Risø Report Nr. Risø -R-1053(EN), Roskilde, Denmark.

Fairchild, C.I. and L.D. Wheat (1984) Calibration and evaluation of a real-time cascade impactor. *Am. Ind. Hyg. Assoc. J.* **45**(4) 205-211.

Fernandez de la Mora, J., N. Rao, and P.H. McMurry (1990) Inertial impaction of fine particles at moderate Reynolds numbers and in the transsonic regime with a thinplate orifice nozzle. *J. Aerosol Sci.*, **21**, 889-909.

Gard, E., J. E. Mayer, B. D. Morrical, T. Dienes, D. P. Fergenson, and K. A. Prather (1997) Real-time analysis of individual atmospheric aerosol particles: Design and performance of a portable ATOFMS, *Anal. Chem.*, **69**, 4083-4091.

Gifhorn, A., H. Tieber, J. Wiebrecht, and R. Ballik (2000) Grundlegende Untersuchungen zur Nutzung der CVS-Messtechnik für niedrig emittierende Fahrzeuge mit Ottomotoren. *MTZ*, **61**, 106-115.

Hall, D.E., D.J. King, T.D.B. Morgan, S.J. Baverstock, P. Heinze, and B.J. Simpson (1998) A review of recent literature investigating the measurement of automotive particulate; the relationship with environmental aerosol, air quality and health effects. SAE 982602.

Hansen, A.D. and T. Novakov (1990) Real-time measurement of aerosol black carbon during the carbonaceous species methods comparison study. *Aerosol Sci. Technol.* **12**, 194-199.

Hillamo, R.E. and E.I. Kauppinen (1991) On the performance of the Berner low pressure impactor. *J. Aerosol Sci.*, **14**, 33-47.

Hinds, W. C. (1999) *Aerosol Technology*, J. Wiley & Sons, New York.

Hüglin, Ch., L. Scherrer and H. Burtscher (1997) An accurate, continuously adjustable dilution system (1:10 to 1:10^4) for submicron aerosols. *J. Aerosol Sci*. **28**, 1049-1055.

The Inspection of In-Use Cars in Order to Attain Minimum Emissions of Pollutants and Optimum Energy Efficincy, Main Report (1998), European Commission, Directorate Generals for Environment (DG XI), Transport)DG VII) and Energy (DG XVII).

Jaklevic, J.M., N.W. Madden, and C.E. Wiegand (1983). A precision beta gauge using a plastic scintillator and photomultiplier detector. *Nucl. Inst. and Methods.* **214,** 517-518.

Jing, L. (2000) Properties of soot particles produced by a combustion aerosol standard. Proc. 4th ETH workshop 'Nanoparticle measurement'. BUWAL.

Kasper M., U. Matter and H. Burtscher (2000) NanoMet: On-lin Characterization of Nanoparticle size and composition, SAE Technical Paper Series 2000-01-1998.

Keskinen, J., K. Pietarinen, M. Lehtimaki (1992) Electrical Low Pressure Impactor. *J. Aerosol Sci.* **23**, 353-360.

Kinney, P.D., D.Y.H. Pui, G.W. Mulholland, and N.P. Bryner (1991) Use of the electrostatic classification method to size 0.1 μm SRM Particles – a feasibility study. *J. Res. National Inst. of Stand. and Technol.*, **96**, 147-176.

Kittelson, D.B. et al. (1990) Particulate Emissions from Diesel Engines: Influence of In-Cylinder Surface. SAE Paper Nr. 900645.

Kittelson, D.B. (1998) Engines and Nanoparticles: A Review. *J. Aerosol Sci*. **29**, 575-588.

Kittelson, D.B., W.F. Watts, M. Arnold (1998) Review of diesel particulate matter sampling methods, Supplemental Report #1: Diesel exhaust particle measurements systems. Univ. of Minnesota, Center for Diesel Research.

Kittelson, D.B., M. Arnold and W.F. Watts (1999) Review of diesel particulate matter sampling methods, Final Report. Univ. of Minnesota, Center for Diesel Research.

Kittelson D.B., and W. Watts (2000) Nanoparticle Emissions from engines. Proc. Third Joint ESF-NSF Symposium on "Nanoparticles: Applications in Material Science and Environmental Science and Engineering, Dublin, Ireland, Sept. 2000, p19-21.

Kopp, C., A. Petzold, and R. Niessner (1999) Investigation of the specific attenuation cross-section of aerosols deposited on fiber filters with a polar photometer to determine black carbon. *J. Aerosol Sci*. **30,** 1153-1163.

Krämer, L., Z. Bozoki, and R. Niessner (2000) Setup, calibration and characterization of a mobile photoacoustic soot sensor. *J. Aerosol Sci*. **31**S1, 72-73.

Liousse, C., H. Cachier, and S.G. Jennings (1993) Optical and thermal measuremnts of black carbon aerosol content in different environments: variation of the specific attenuation cross section, sigma *Atmospheric environment*, **27A**, 1203-1211.

Liu, B.Y.H. and D.Y.H. Pui, (1974) On the performance of the Electrical Aerosol Analyser. *J. Aerosol Sci*., **6**, 249-264.

Maricq M.M., Chase R.E., Podsiadlik D.H., Vogt R. (1999); Vehicle Exhaust Particle Size Distributions: A Comparison of Tailpipe and Dilution Tunnel Measurements. SAE 01-1461; 1999.

Maricq, M.M., D.H. Podsiadlik, and R.E. Chase (2000) Size distributions of motor vehicle exhaust PM: a comparison between ELPI and SMPS measurements. *Aerosol Sci. Technol*. **33**, 239-260.

Marple, V. A, K. L. Rubow and S. M. Behm. (1991). A Microorifice Uniform Deposit Impactor (MOUDI): Description, Calibration, and Use. *J. Aerosol Sci. Technol*., **14**, 434-446.

Marple, V. A., K. L. Rubow, and B. A. Olson. (1994). Low Pressure Stages for the Micro-orificeUniform Deposit Impactor (MOUDI). Fourth International Aerosol Conference, Abstracts, ed. R.C. Flagan, Vol. 2, 6 pp.

Matter, U., H. C. Siegmann, and H. Burtscher (1999) Dynamic field measurements of submicron particles from diesel engine, *Environ. Sci. Technol., **33***, 1946-1952.

Matter et al. (1999b) Formation of volatile particles in traps. 3rd ETH Zürich Workshop Proc. "Nanoparticle Measurement", BUWAL.

Mayer, A. et al. (1999) Particulate traps for retro-fitting construction site engines VERT: final measurement and implementation. SAE 1999-01-0116.

McAughey, J.(2000) Vehicle Particle Emissions, A report for European Comission Directorate General III, May 2000.AEA report Nr. AEAT/R/ENV/0047 Issue 1.

Mewes, B, J.M. Seitzman (1997) Soot volume fraction and particle size measurements with laser-induced incandescence. *Appl. Opt*., **36**, 709-717.

Mohr, M., A.M. Forss, and D. Steffen (2000) Particulate Emissions of Gasoline Vehicles and the Influence of the Sampling Procedure, *SAE 2000-01-1137*.

Moosmüller, H., W.P. Arnott, and C.F. Rogers (1997) Methods for real time, in situ measurement of light absorption. *J. Air&Waste Managmenet Assoc*., **47**, 157-166.

Neuroth, R., L. Laskus, and D. Dahmann (1999) Interner VDI/DIN-Ringversuch zur Bestimmung von elementarem Kohlenstoff, *Gefahrstoffe, Reinhaltung der Luft* **59**, 91-94.

Oberdörster, G. (1996) *InhalationToxicology*, **8**, p73.

Oberdörster, G. (1998) Health effects of ultrafine particles experimental studies. In: Gesungheitsgefährdung durch Feinstäube am Arbeitsplatz, Quantifizierung mechanischer Belastungen, Arbeitsmedizin in der EU, ed. E. Baumgartner, Österreichische Gesellschaft für Arbeitsmedizin.

Patashnick, H. and G. Rupprecht (1983) Personal dust exposure monitor based on the tapered element oscillating microbalance. *Bul. Mines* OFR 56-84, NTIS PB 84-173749.

Petzold, A. and R. Niessner (1996) Photoacoustic soot sensor for in-sizu black carbon monitoring. *Appl. Phys. B- Lasers O*, **63**, 191-197.

Ricardo (2001) DETR/SMMT/CONCAWE Particulate Research Programme: Summary Report. Final Draft, March 2001.

Schlatter, J. (2000) Internationaler Ringversuch mit Partikelgrössenmessgeräten. Swiss Federal Office of Metrology, Bern, Report No. 2000-230-436.

Scheibel, H. G. and J. Porstendörfer (1984) Penetration measurements for tube and screen-type diffusion batteries in the ultrafine particle size range. *J. Aerosol Sci*. **15,** 673-682.

Schindler, W. and W. Silvis (2000) Einflussfaktoren von Systemparametern bei verdünnter gravimetrischer Partikelmessung. Forum Partikelemissionen 2000, AVL-Deutschland GmbH, 55252 Mainz.Kastel.

Schleicher, B., S. Künzel and H. Burtscher: In-situ measurement of size and density of submicron aerosol particles. J. Appl. Phys., **78** (1995) 4416-4422.

Schmid, H. et al. (2001) Results of the carbon conference international aerosol carbon round robin test stage I. *Atmos. Environ*. **35**, 2111-2121.

Schraml, S, S. Dankers, K. Bader, S. Will, and A. Leipertz (2000a) Soot temperature measurements and implications for time-resolved laser-induced incandescence (TIRE-LII). *Comb. Flame,* **120**, 439-450.

Schraml, S, S. Will, A. Leipertz, T. Zens, and N. D'Alsonso (2000b) Performance Caracteristics of TIRE-LII Soot Diagnostics in Exhaust Gases of Diesel Engines. SAE 2000-01-2002.

Shoemaker, D.P. and C.W. Garland (1967) Experiments in Physical Chemistry, 2nd ed, McGraw-Hill, New York.

Siegmann K. and H.C. Siegmann (1997) The formation of carbon in combustion and how to quantify the impact on human health. *Europhys. News*, **28**, 50-57.

Siegmann K. and H.C. Siegmann (2000) Fast and reliable 'in situ' evaluation of particles and their surfaces with special reference to diesel exhaust. SAE Technical Paper Series 2000-01-1995.

Silva, P.J. and K.A. Prather. (1997). On-line Characterization of Individual Particles from Automobile Emissions. *Environ. Sci. Tech.*, **31**, 3074-3080.

Singer, W., E. Unger, and E. Schiefer (2000) Reproduzierbare messtechnische Erfassung niedriger Russkonzentrationen mit der Filterpapiermethode. Forum Partikelemissionen 2000, AVL-Deutschland GmbH, 55252 Mainz.Kastel.

Skillas, G., Z. Qiuan, U. Baltensperger, U. Matter, and H. Burtscher (2000) The influence of additives on the size distribution and composition of particles produced by diesel engines, *Combustion Sci. Technol*. **154**, 259-273

Stein, H.J. (2001) Worldwide harmonized heavy duty emission certification procedure, exhaust emission measurement ISO 2nd interim report. ECE-GRPE WHDC Subgroup "ISO Activities", Jan. 2001.

Stratmann, F., and H. Fissan (1988) Convection, diffusion and thermophoresis in cooled laminar flow, *J. Aerosol Sci.,* **19**, 793-796.

Stratmann F., Kauffeldt Th., Hummes D., Fissan H.(1997) Differential Electrical Mobility Analysis: A Theoretical Study; *Aerosol Sci. Tech.*; **27**; 368-383.

Thaller, W., W. Schindler, and W. Singer (2000) Transiente Erfassung niedriger Rauchwerte mittels Opazimetrie. Forum Partikelemissionen 2000, AVL-Deutschland GmbH, 55252 Mainz.Kastel.

Turpin, B.J., J. Huntzicker and K.M. Adams (1990) Intercomparison of photoacoustic and thermal-optical methods for the measurement of atmospheric elemental carbon. , *Atm. Environm*., **24A**, 1831-1835.

VDI (1996) Chemisch-analytische Bestimmung des elementaren Kohlenstoffes nach Extraktion und Thermodesorption des organische Kohlenstoffes. VDI 2465.

Wang, S.C. and R.C. Flagan (1990) Scanning electrical mobility spectrometer. *Aerosol Sci. Technol*. **13**, 230-240.

Weingartner, E., H. Burtscher, and U. Baltensperger (1997) Hygroscopic properties of carbon and diesel soot particles. *Atm. Environ*. **31**, 2311-2327.

Wichmann, HE and A. Peters (2000) Epidemiological evidence of the effects of ultrafine particle exposure. *Philos. Trans. R. Soc. Lond. Ser. A,* **358**, 2751-2768.

Willeke, K. and P. A. Baron (1993) Aerosol Measurement, Principles, Techniques and Applications. Van Nostrand Reinhold, New York.

Wiedensohler A., Orsini D., Covert D.S., Coffmann D., Cantrell W., Havileck M., Brechtel F.J., Russel L.M., Weber R.J., Gras J., Hudson J.G., Litchy M.(1997) Intercomparison Study of the Size-Dependent Counting Efficiency of 26 Condensation Particle Counters; *Aerosol Sci. Technol.*; **27**; 224-242.

Winklmayr W.; Reischel G.P.; Lindner A.O.; Berner A.(1991) A new Electromobility Spectrometer for the measurement of aerosol size distributions in the size range from 1 to 100 nm; *J. Aerosol Sci.*; **22**; 289-296.

Zahoransky, R.A., E. Laile, B. Terwey, and A. Konstandopoulos (2001) Proc. ETH Conference on Nanoparticle Measurement, paper 26, Aug. 2000, ed. A. Mayer.