

## Particle Size Analysis

### 1. Overview

Several non regulated particle measurement and characterisation methods are applied.

Fig. 1 shows their possible position in the sampling process and their principal time and size resolution.

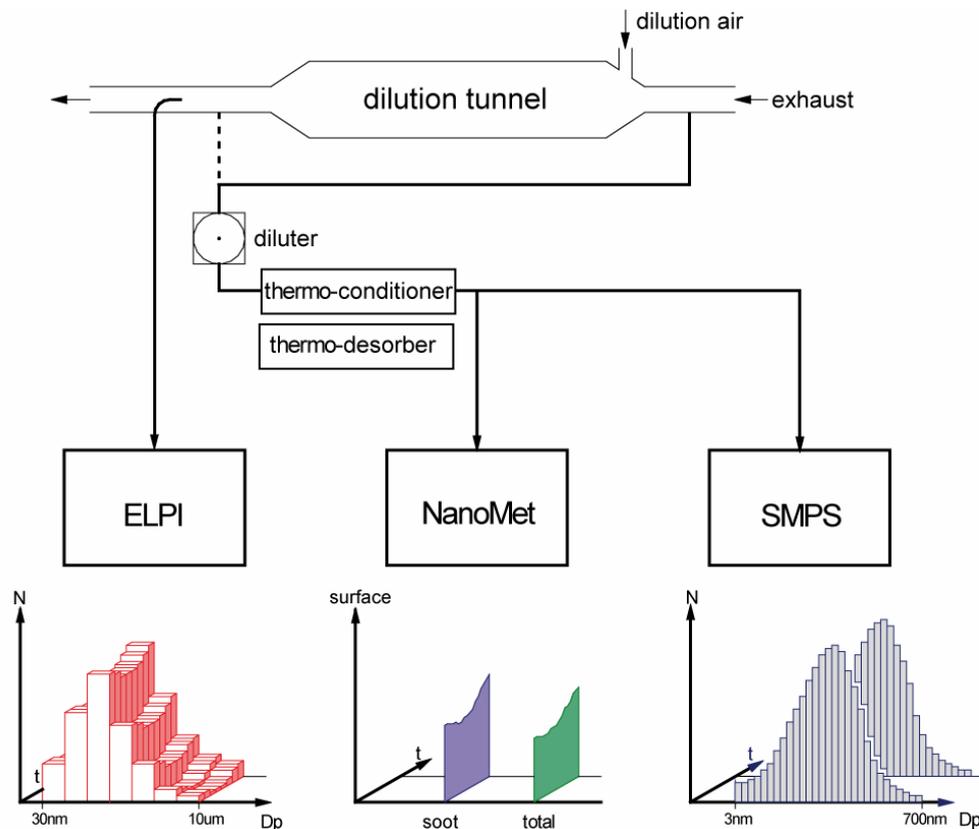


Fig. 1 Nanoparticle measurement systems, particle characterisation and time resolution

The methods and their main characteristics are as follows:

- **ELPI, Electrical Low Pressure Impactor.** Particle size distribution based on aerodynamic diameter. Low size resolution but high time resolution down to 1 second.
- **SMPS, Scanning Mobility Particle Sizer.** Particle size distribution based on mobility diameter. High size resolution but low time resolution, typically 1 – 3 min scan time.
- **Thermodesorber (or Thermoconditioner),** element to distinguish solid from volatile particles. Particle evaporation temperature is chosen by adjustable heating temperature up to 330°C.
- **DC, Diffusion Charging sensor (NanoMet).** Integral signal for total active particle surface with time resolution down to 0.5 second.
- **PAS, Photoelectric Aerosol Sensor (NanoMet).** Integral signal for soot surface with time resolution down to 0.5 second.
- **MD19, tunable minidiluter (NanoMet).** Exhaust sampling and dilution with direct connection to tail pipes.

Table 1 shows selected properties of this measurement- and sampling equipment used in the reported test. Detailed descriptions are given in chapter 2.

equipment system	type	physical property	size range selection mode	size resolution	time resolution
ELPI (DEKATI)		number concentration	30 nm ... 10 µm aerodyn. diam.	12 stages	>= 1 sec
SMPS (TSI)	DMA 3071 + CPC 3025A DMA 3081 + CPC 3010	number concentration	16 nm ... 660 nm mobility diam.	105 channels	1 – 3 min
NanoMet DC (Matter Eng.)	LQ1-DC	total active surface	1 nm ... 1 µm	integrated value	>= 0.5 sec
NanoMet PAS (EcoChem)	PAS 2000	total soot surface	1 nm ... 1 µm	integrated value	>= 0.5 sec
Thermodesorber (ETH Zürich)	own construction	distinction solid/volatile	adjustable regulated heating temp. up to 330 °C activated char coal zone water cooled		
Minidiluter (Matter Eng.)	MD19-2E	aerosol dilution	adjustable dilution ratio from 1 : 30 to 1 : 3000 undiluted zone and dil. air heated to 80 – 150 °C		

Table 1 Properties of the measurement equipment

2. Description of the measurement equipment and systems

**ELPI**

The ELPI (**E**lectrical **L**ow **P**ressure **I**mpactor) as shown in block diagram Fig. 2 is a 12 (13) stage cascade impactor that measures particle number concentrations as a function of aero-dynamic diameter.

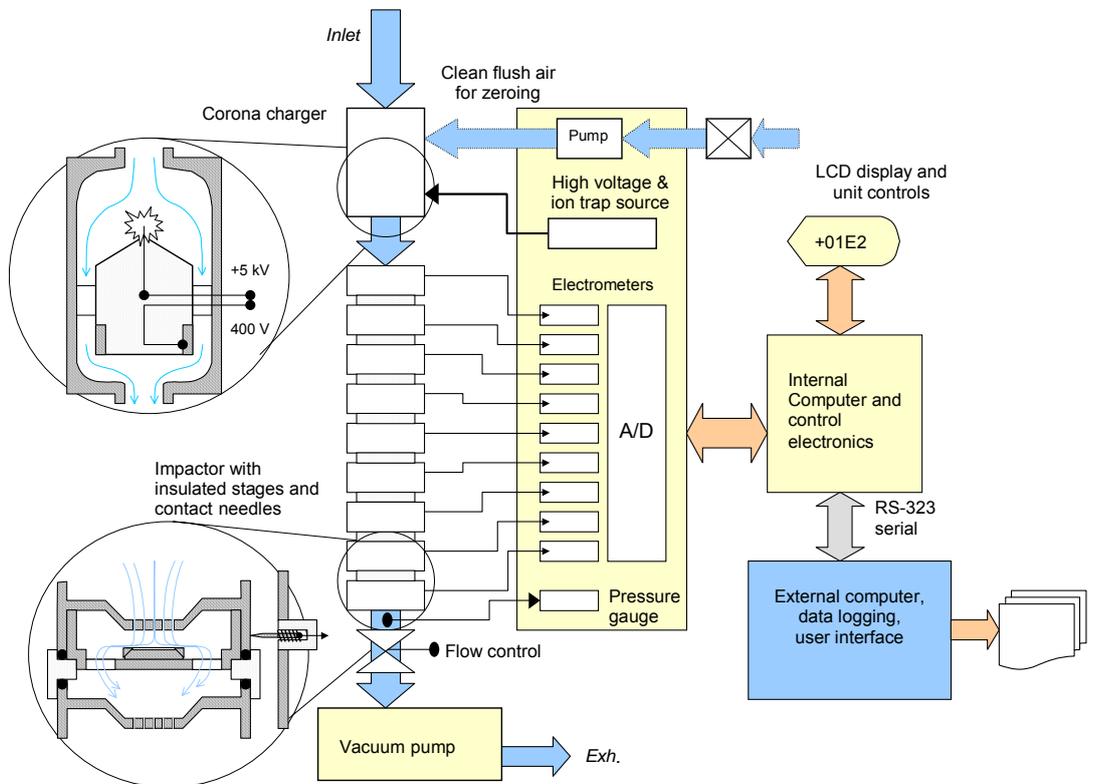


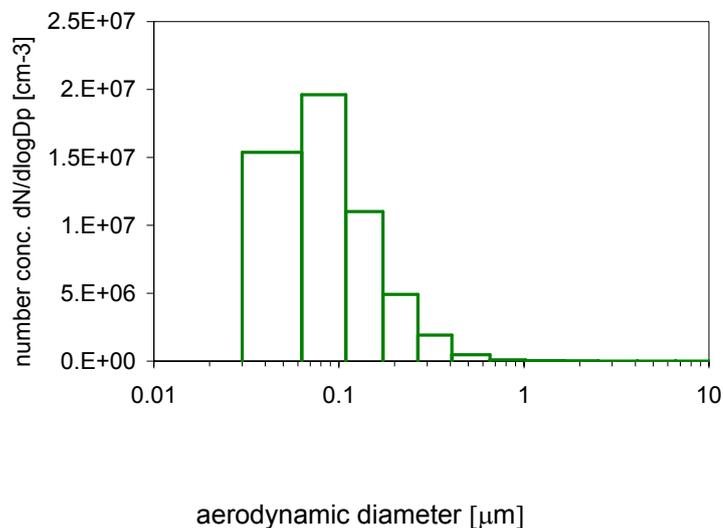
Fig. 2 ELPI block diagram

An impactor is a size selective element where the aerosol is guided through a nozzle behind which a plate forces the gas flow to change direction abruptly. Due to their inertia, particles cannot follow the bent gas streamlines but are driven towards the plate. Only friction with the gas makes them accommodate with the new flow direction. Depending on their size-to-mass ratio - that is, their mass density - the particles are deposited on the plate and thereby removed from the aerosol flow. The diameter defined by this separation process is called the aerodynamic diameter. The size limit between particles that pass the impactor and those being deposited on the plate - the cutoff diameter - depends on the velocity in and pressure drop across the nozzle, the geometry of the impactor and, as stated before, particle mass density. By variation of these parameters, usually the pressure behind the nozzle, the cutoff diameter is adjusted to the desired value.

In the ELPI, 12 impactor stages operate in sequence, each with a smaller cutoff diameter. Thus, particles collected in one stage belong to one size class which is limited by the cutoff diameters of the two subsequent impactor stages.

After size classification, the deposited particle load has to be quantified. In classical impactor design, the particle mass deposited on the plate is determined by gravimetric analysis, but this technique has shortcomings as it needs high particle loads to be accurate, and analysis is carried out after measurement - the method is off-line. In order to make ELPI an on-line instrument, aerosol particles are electrically charged before they enter the cascade impactor. Each impactor collector plate is connected to an electrometer amplifier. Thus, instead of collecting deposited particle mass, the plates take up the electric charge of the impinging particles and pass it on as measurement current.

Number size distributions are calculated from the measured current, the size dependent average charge per particle, and the deposition probability per impactor stage. The time resolution is around one second; the covered particle size range is from 30 nm to 10  $\mu\text{m}$  (Fig.3).



**Fig. 3** Typical ELPI size distribution. Particles were sampled from the exhaust pipe of a common rail diesel passenger car at 70 km/h on a roller dynamometer.

## SMPS

SMPS (**Scanning Mobility Particle Sizer**) illustrated in block diagram Fig. 4 is a method to determine the number size distribution of submicron aerosol particles. It uses a measurement system consisting of an electric charger, a mobility classifier, a counter, and PC control [4].

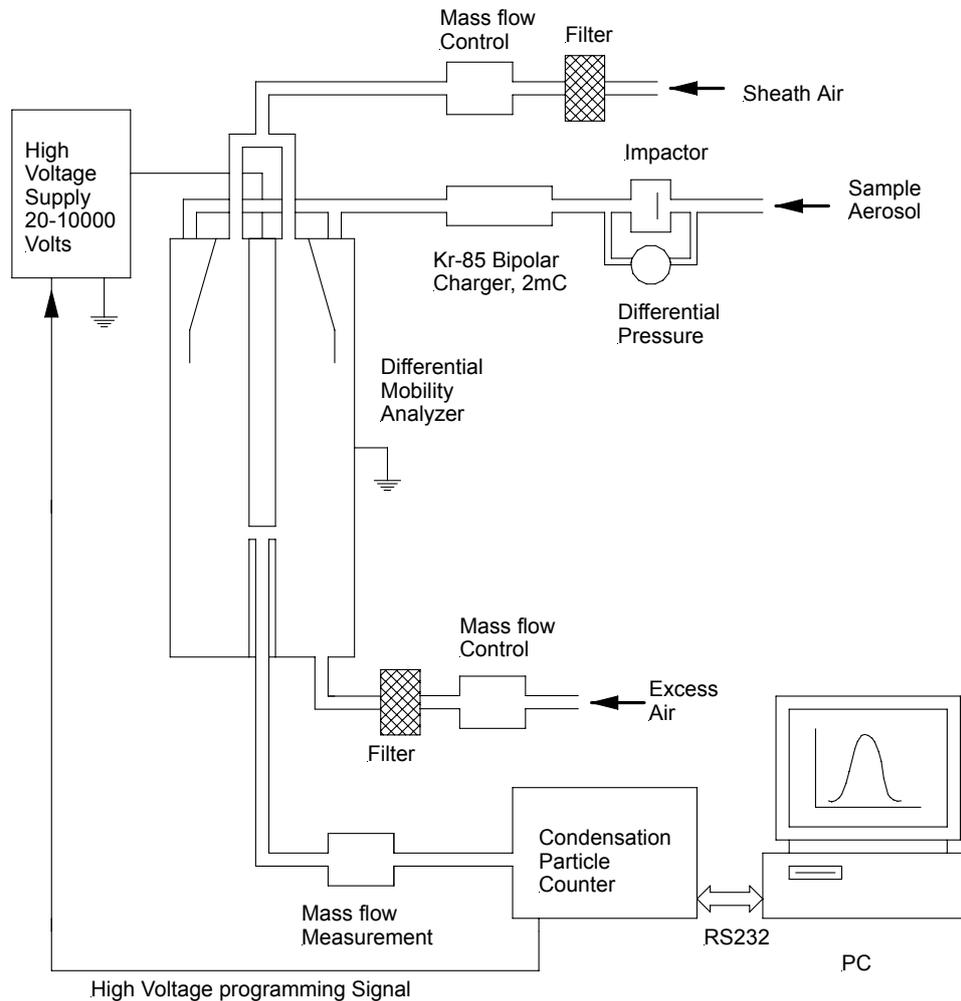


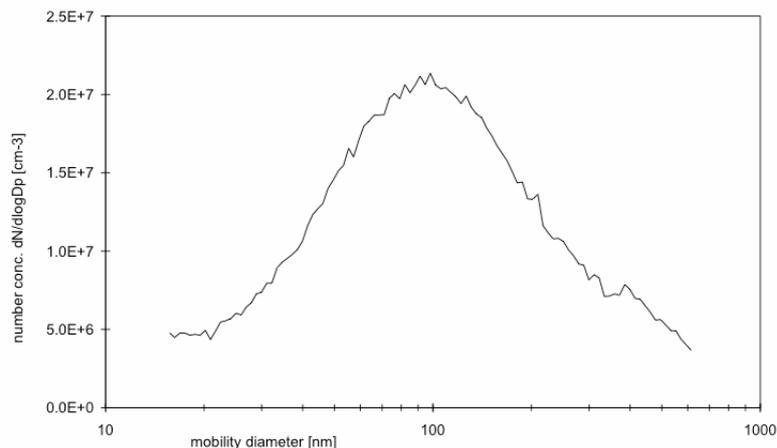
Fig. 4 Block diagram of SMPS particle sizer system

The aerosol is first guided into a neutralizer [6]. This is a chamber in which the air is ionized by beta rays from a radioactive source ( $^{85}\text{Kr}$ ). Positively and negatively charged ions diffuse onto the surface of the aerosol particles until a charge equilibrium is established. The probability for 100 nm particles to carry one elementary charge is about 20% for positive and 40% for negative charging, while the rest of the particles leave the neutralizer with zero electric charge - hence the name "neutralizer".

The charged aerosol particles are now classified by their mobility in a Differential Mobility Analyzer (DMA) [7]. The DMA is a long condenser through which a laminar flow of particle free air is guided. For practical reasons it has cylindrical geometry. The aerosol particles enter through a narrow slit at the upper end of the DMA. When a voltage is applied between outer and inner electrode, the charged particles are dragged towards the centre. Their velocity is determined by the equilibrium of electric force and friction with the suspension air - small particles move faster, larger ones are slower. While the particles move in radial direction, the laminar air flow carries them along the cylinder axis. Thus, they hit the centre electrode below the inlet, large particles later and further downstream than small ones. At its lower end the centre rod has a narrow outlet slit where particles of a certain size arrive. This size can be tuned by varying the voltage applied to the electrodes. The other particles are either deposited on the walls or they are transported out of the DMA with the sheath air.

The number concentration of the size selected particles is determined using a Condensation Particle Counter (CPC). Since the particles are too small for optical detection, they have to be magnified by condensing volatile material onto their surface. This is accomplished by guiding the fine particles through saturated vapour of butanol (or vapour of another volatile substance) and subsequently cooling the mixture. The vapour molecules use the aerosol particles as condensation nuclei for the formation of droplets, one out of each aerosol particle. The final size of the butanol droplets is around one micron which is just large enough to be detected using light scattering.

By computer control the DMA voltage is increased so that larger and larger particles are fed into the CPC. The software combines CPC counts with particle size calculated from the DMA voltage and calculates a size spectrum (Fig. 5).



**Fig. 5** Typical size spectrum from SMPS measurement. The particles were emitted from a diesel engine at low rpm and high load.

## NanoMet

NanoMet is a modular measurement system for on-line characterization of aerosols, consisting of a diluter, an evaporation tube, two sensors and various accessories [2, 3]. Being both robust and user friendly NanoMet is also well suited for field use. The following NanoMet components are used in the reported test:

- a mini-diluter to reduce the aerosol concentrations to levels within the nominal ranges of the NanoMet sensors,
- a thermal conditioner (evaporation tube) to evaporate remaining droplets of volatile material still present after the diluter,
- two real time sensors, the diffusion charging sensor (DC) for active surface and the photoelectric aerosol sensor (PAS) for soot surface.

## MD19 minidiluter

A compact minidiluter is used as a stand alone direct sampling and dilution device [8]. Its main features are its simple and stable operation, the wide adjustable dilution range over 2 decades and the possible connection to closed systems with undiluted exhaust. The setup is shown in Fig. 6.

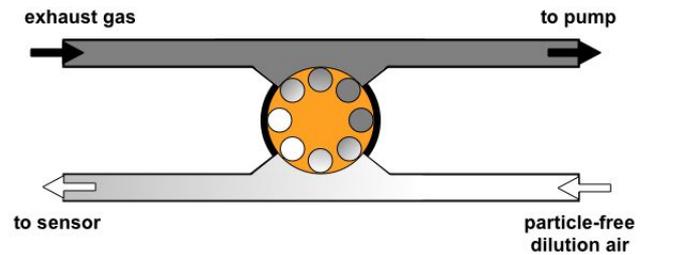


Fig. 6 Schematic diagram of the MD19 rotating disc diluter

Dilution takes place in a heated steel block with separated gas channels, one for the raw gas and one for the diluted measuring gas. A rotating disk with cavities on the side to the dilution block shifts the raw gas in the cavities into the measuring gas channel, such that the diluter works like a "revolving door" for particles. The dilution ratio depends on the rotation frequency, the gas flow in the measuring gas channel, the volume and the number of cavities on the disk.

The dilution ratio can be tuned continuously from 1:15 to 1:3000 by varying the rotation frequency and choosing between disks with 10 or 8 cavities. The undiluted gas section as well as the dilution air are heated to regulated temperatures, adjustable to 80°C, 120°C or 150°C. This heating and the large dilution ratio prevent spontaneous nucleation to volatile nanoparticles as it is often observed in dilution of combustion exhaust in standard dilution tunnels at lower dilution ratios with cold dilution air.

#### Evaporation tube (Thermoconditioner)

By definition, DPF efficiency is related to solid exhaust gas particles. In addition to solid soot and ash particles, exhaust contains many volatile substances that pass the DPF as vapour: hydrocarbons (HC), sulfate and water. When the exhaust cools down to ambient temperature these volatiles tend to nucleate and condense into nanosized droplets. As most particle analysing instruments cannot distinguish droplets from solid particles, the two fractions have to be separated in the sampling system in order to get a valid measurement of the DPF efficiency.

A very straightforward method to remove droplets of volatiles from the exhaust gas sample is to evaporate them in a heated tube [3]. If the exhaust gas sample contains volatiles in high concentration, they will re-nucleate into new droplets after the heated tube, and there will be no benefit of the thermal treatment. However, if the exhaust sample is diluted before entering the evaporation tube, concentration of the volatiles will be low enough to keep them in vapour phase after heating. This method is called post-dilution thermo-conditioning (PDTC). PDTC does not remove the volatile substances from the exhaust sample, but it keeps them in vapour phase rather than in particle phase.

Fig. 7 shows the principal setup of PDTC, consisting of an MD19 rotating disc diluter and a heated tube (thermal conditioner).

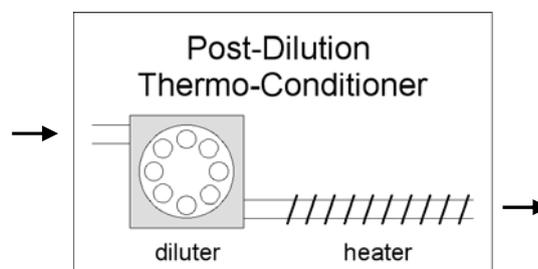


Fig. 7 PDTC, consisting of an MD19 rotating disc diluter and a heated tube

## PAS and DC sensor

The 2 particle sensors monitor submicron particles by charging them before they are deposited in a insulated particle filter. The principle of operation is illustrated in Fig. 8, [2].

Two different charging methods are used to characterise the particles depending on their size, chemical composition and number concentration. In either sensor an electrometer amplifier converts the integrated electrical charge of the particles into a dc-voltage signal with a response time below 0.5 seconds. The measured current is proportional to the charging probability of the particles.

Unipolar diffusion charging (DC) by corona discharge is used in the DC sensor to charge the particles. The charging efficiency depends on the particle size and is almost independent of the chemical composition. The charge measured in the electrometer is a measure for the active surface or Fuchs surface. The active surface is proportional to the geometric particle surface  $\pi (D_p)^2$  in the range of free molecular motion where the particle size is below the mean free path  $\lambda$  of the carrier gas molecules ( $\lambda \cong 66$  nm). For large particles, where the carrier gas is treated as a continuous fluid, the active surface scales with the mobility diameter  $D_p$  according to Stokes' law. The intermediate range is interpolated by an empirical function proportional to  $D_p^X (D_p)$  where the exponent  $X (D_p)$  is a function decreasing from 2 to 1 as  $D_p$  increases from the molecular to the Stokes range.

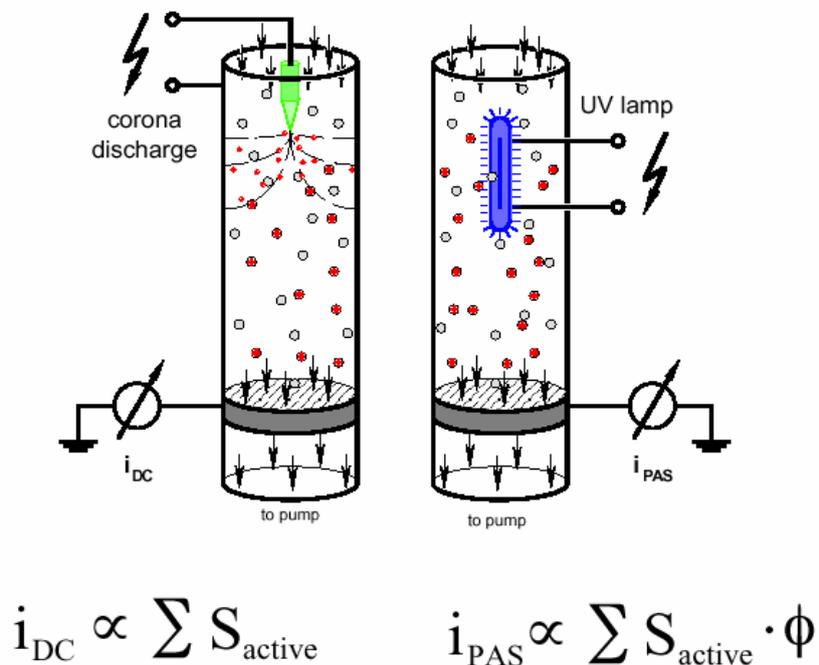


Fig. 8 Principle operation block diagram of PAS und DC sensor

- $i_{DC}, i_{PAS}$  : filter current of DC sensor / PAS
- $S_{\text{active}}$  : active surface of a single particle
- $\phi$  : material coefficient of the aerosol
- $\sum$  : sum over all particles

The calculation of the active surface is based on a relation deduced by Keller et al. [9]. The product of mobility and mass transfer coefficient for gas ions is a constant independent of the particle mobility diameter. This size independent relation allows the calibration of the DC sensor by using standard particle analysing equipment. The calibration is carried out by comparison of the DC signal with the number concentration measured in a condensation particle counter (CPC), both fed with monodisperse aerosol from a differential mobility analyser (DMA).

The photoelectric aerosol sensor (PAS) charges particles with monochromatic 222 nm UV-light from an Excimer lamp. The size dependence of the charging efficiency is similar to that of the DC sensor but the charging efficiency depends on the chemical composition of the particles. Numerous investigations have proved a high photoelectric charging efficiency for carbonaceous soot particles from fossil fuel combustion.

The PAS signal has been shown to correlate well with the concentration of particle bound aromatic hydrocarbons (PAH) for various combustion sources [10] as well as with the elemental carbon content of diesel soot [11]. For non-soot particles in combustion exhaust - e.g. fly ash or volatile particles or water droplets from spontaneous nucleation in the dilution process - the photoelectric charging efficiency with the UV wave length applied in PAS is orders of magnitude lower. PAS is therefore an ideal selective soot detector with low cross sensitivity to other particles and gas compounds.

Simultaneous monitoring of combustion aerosols with PAS and DC offers two valuable pieces of information: the PAS/DC ratio is characteristic for different combustion sources which allows source apportionment in a limited range (see Fig. 9). It is furthermore possible to identify the presence of additional soot particles in combustion exhaust.

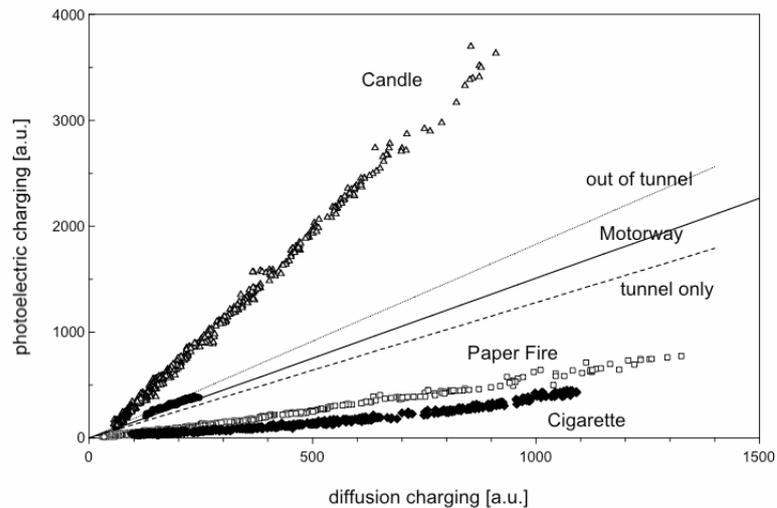


Fig. 9 PAS versus DC signal for combustion aerosols from different sources

### Thermodesorber (or thermodenuder)

The thermodesorber is used to discriminate solid from volatile components in a mixture of aerosols. It consists of a heater where the aerosol mixture can be heated to 330 °C, and a charcoal trap that absorbs evaporated aerosol components (see Fig. 10).

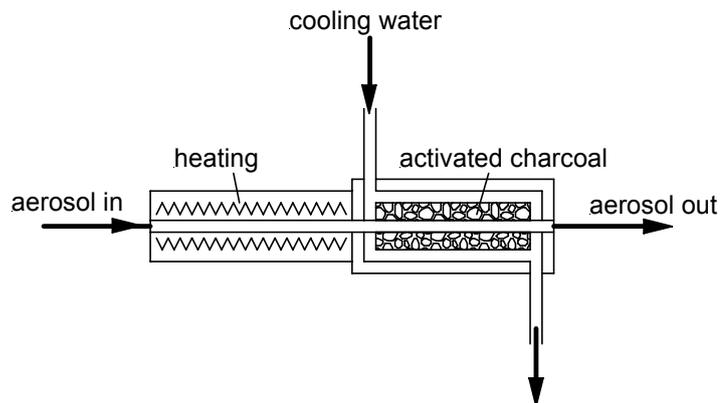
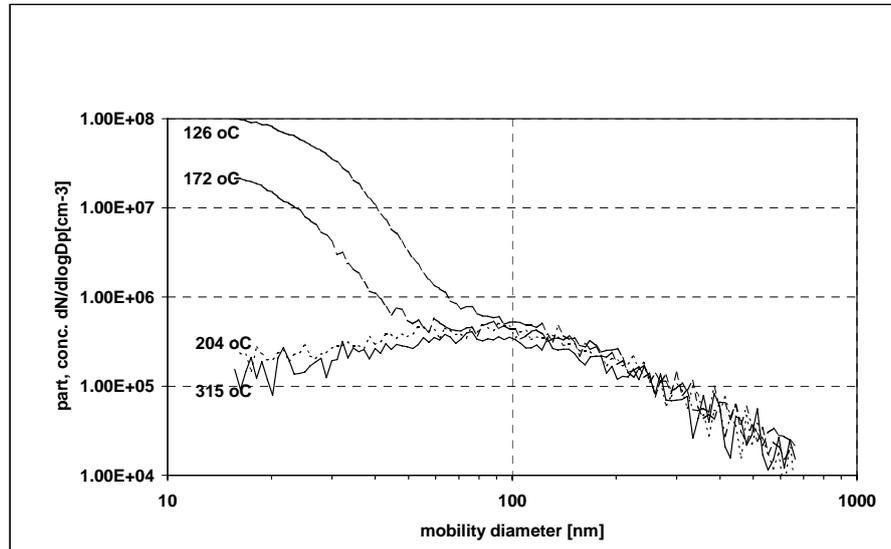


Fig. 10 Schematic diagram of thermodesorber

Due to their high mobility, vapor molecules diffuse into the pores of the charcoal granules and are absorbed while the solid, comparably heavy aerosol particles drift past the granules on almost straight trajectories. Therefore, solid, non-volatile particles are not affected by the thermodesorber.

By lowering the heating temperature, less substances evaporate due to their individual boiling point. From the temperature at which certain particles appear, their material can be concluded. This operation mode of the thermodesorber is called thermogramm (see Fig. 11).



**Fig. 11** Sample thermogram of a diesel emission. Up to a temperature of about 120 °C the SMPS measures numerous tiny particles which disappear as temperature increases. The solid particles centered around 100 nm are not affected by the thermodesorber.

### 3. References

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