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NanoMet: online Characterization of Nanoparticle Size and Composition

NanoMet: On-line Characterization of Nanoparticle Size and Composition

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Introduction

The results of the VERT project have demonstrated that particle emissions from diesel engines can be reduced to toxicologically tolerable limits only by means of particulate traps. Once in use, however, such traps have to be periodically assessed for precipitation efficiency, as well as the total particle emissions of the vehicle. In order to keep interruptions of vehicle availability for the owner as short as possible, efficiency tests are to be carried out “in the field” without the need to dismount the trap from the vehicle, and the duration of the test itself should be in the range of minutes. Furthermore, the test method must be sensitive both at high and low particle concentrations as are found upstream and downstream the trap, respectively, and it should be easy to operate for the user.

One of the merits of the VERT project is that particle measurement was not restricted to the legal methods but extended to any available laboratory technique. From this large pool of methods, it were not the legal ones that fulfilled all above criteria as they are either not accurate enough or may not be applied under field conditions. Instead, a combination of a diluter and at least two on-line sensor principles turned out to be the most suitable choice.

This result lead to the VERT follow-up project “NanoMet”, the goal of which is to integrate the on-line sensors and diluter in a portable, easy-to-use instrument for trap survey in the field. This paper reports results and experiences with a unit from the first series and discusses applications and accessories beyond the present state.

Setup and Working Principles

NanoMet

Fig. 1 shows a principal view of the NanoMet set up. A detailed description of it has been given by Matter (1998), which will be briefly reviewed here. NanoMet consists of a heatable diluter with sampling interface for emission measurements and two on-line sensors. A particle sizing unit with a diffusion battery and a centrifuge is under development.

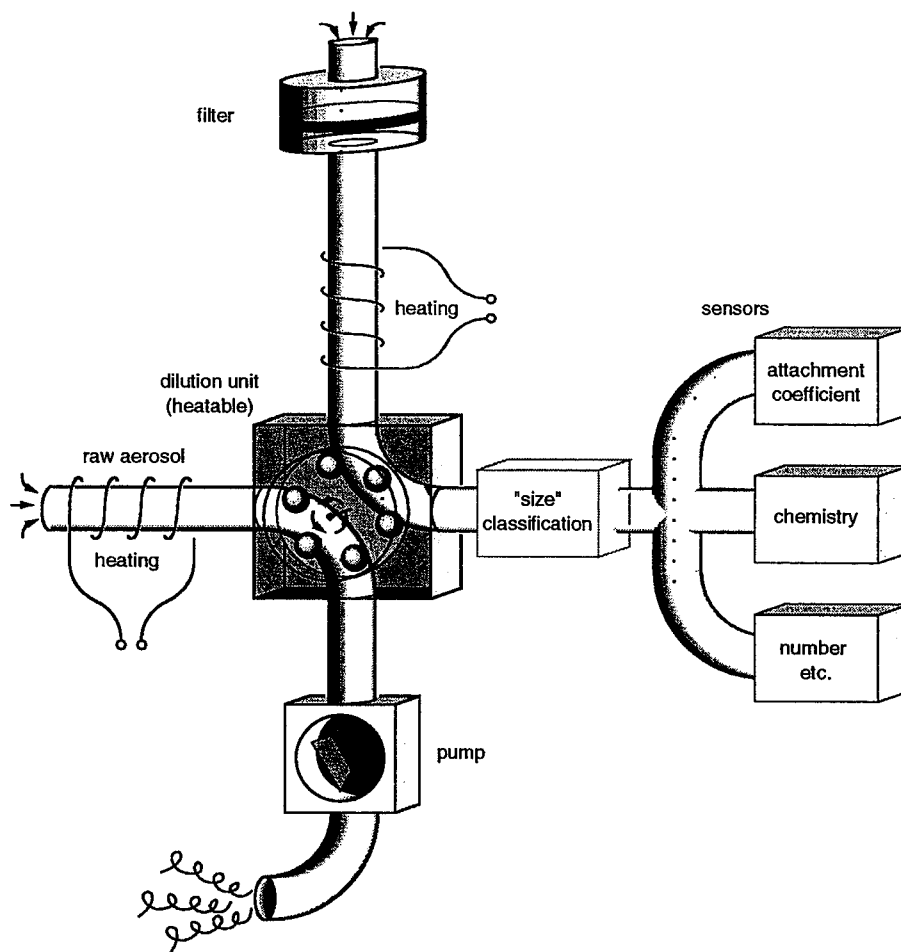


Figure 1: Schematic drawing of the NanoMet set up showing the heated diluter, size classifier and sensors. Details are given in the text.

The NanoMet modules can be used as stand alone devices or in combination to best fit the user's needs. For example, ambient air measurements or occupational exposure assessment do not require the diluter due to low particle concentrations, but the use of both sensor types may be desirable. In another situation the user may wish to complement or even replace the NanoMet sensors by his own technology but still use the heatable diluter.

Given the rotation frequency of the diluter disk and the response time of the sensors a time resolution of 0.1 seconds is achievable. Measurements are reproducible within an error of a few percent.

Diluter

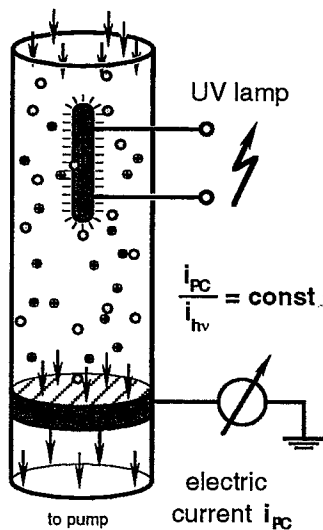
The pocket size diluter consists of a block of stainless steel through which two aerosol ducts are drilled, one for the undiluted aerosol as sampled from the source, the other bearing a flow of particle free air (Hueglin *et al.*, 1997). The channels, milled open at the

top side of the steel block, are sealed against the environment and each other by a rotating disk pressed against the block. Small cavities in the bottom side of the disk exchange tiny volumes between the channels, especially from the raw aerosol on the primary side into the particle free air on the secondary side. The stainless steel block is designed so that the two channels are never in direct contact. Thus pressure waves on the primary side cannot cause disturbance on the secondary side from where the now diluted aerosol flows to the sensors. The dilution ratio is determined by the rotation frequency of the disk and the flow rate on the secondary side of the diluter. In order to separate the processes of dilution and cooling, steel block and particle free air can be heated to 80°C, 120°C, or 150°C.

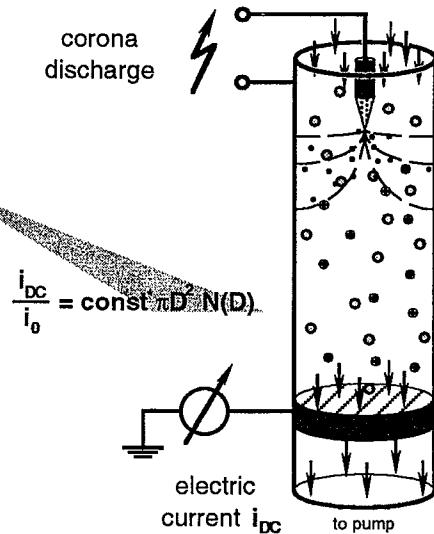
The sensors

NanoMet comes with two on-line sensors where particles are electrically charged and subsequently precipitated on a filter (Fig. 2). The electric current flowing from the filter is amplified and measured. The sensors differ in the charging principle - in the diffusion charger (referred to as DC) positive ions from a corona discharge diffuse onto the

Photoelectric Charging



Diffusion Charging



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Figure 2: Working principles of the photoelectric aerosol sensor (PAS) and the diffusion charging sensor (DC). The measured current is proportional to the total "Fuchs" surface of the aerosol. The PAS signal further depends on a material coefficient.

particles. Therefore, the filter current is proportional to the total “scattering” surface or active surface of the aerosol (“Fuchs” surface). In the other sensor (referred to as PAS, photoelectric aerosol sensor) aerosol particles are illuminated by ultraviolet light and photoelectrically charged. The electrons are then quickly removed from the gas by an electric filter. 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 is proportional to the active surface and a material coefficient. This material coefficient is especially large for particles from fossil fuel combustion.

For both sensors the measurable particle size range is in principle unlimited towards the lower end. At the upper end, the PAS cuts at approximately 1 micron because the emitted electrons will return to the surface of the charged particle. Only if the particle is smaller than the mean free path of the electron in the gas (~ 1 micron) the electrons will fail to return to the particle and be lost in the gas. Thus only submicron particles remain charged and contribute to the signal. For diffusion charging with the DC sensor no upper size limit exists, but NanoMet is equipped with a coarse particle trap (cyclone) in order to keep grains over 5 microns out of the system.

Size classification

A particle sizing unit with a diffusion battery and a centrifuge is being developed. Details are presented in this very volume by Schegk (1999). Size classification facilitates the measurement of size spectra; in combination with the DC sensor reading the number concentration per size class can be calculated.

Aerosol Characterization

Solid particles and condensates

Nanoparticles emitted from Diesel engines are not just “soot” but a highly complex mixture of varying physical and chemical properties. The simplest way to classify them is to distinguish between liquid droplets and solid particles of carbonaceous soot and ash. The droplets normally consist of dilute sulfuric acid or condensed VOC that were formed during the cooling and dilution process, e.g., in a dilution tunnel. Being condensates they cannot be expected to be removed from the exhaust by a trap designed to precipitate solid particles. The strategies to avoid the condensates rather imply the use of low sulphur fuel and oxidation catalysts to burn the VOC (Mayer *et al.*, 1999a). Neglecting the fact that the nature of the droplets differs so basically from solid particles often yields highly misleading results in the assessment of particle trap efficiency. According to gravimetric analyses some traps used during the VERT project seemed to have negative efficiency: more particulate mass left them than was fed in on the upstream side. A thorough investigation using a thermodenuder, scanning mobility particle sizer (SMPS) and NanoMet revealed that the particles downstream from the trap consisted almost entirely of slightly acid water, while solid particles were reduced in number by the trap by typically 2 to 4 orders of magnitude (Mayer *et al.*, 1999b).

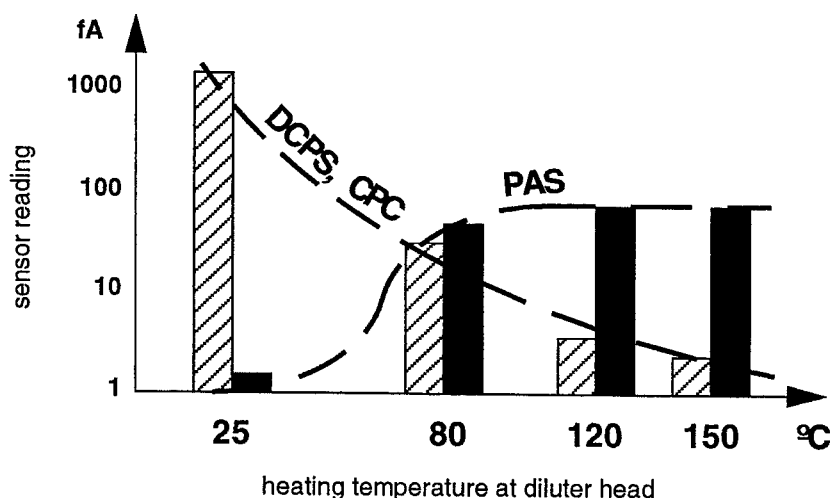


Figure 3: Droplets are detected by the DC sensor but not by the PAS. As the diluter head is heated to higher temperature less volatiles condense. The DC signal decreases while the PAS displays a constant value because solid soot particles are not affected by heating.

The NanoMet approach to treat droplets as different species aims at preventing them from ever condensing at all. This is accomplished by heating the diluter head and dilution air to 150°C, which sets the process of aerosol dilution prior to cooling of the mixture to room temperature. Thereby the order of the two processes - dilution and cooling - is reversed, as opposed to the dilution tunnel where conditions are most favorable for the formation of droplets. Furthermore, two lower heating temperatures can be chosen (120°C, 80°C) at which some of the less volatile compounds may condense while others remain in gas phase. This allows one to further characterize the volatile components of the aerosol, e.g., weakly acid water vapor will not condense at 120°C while vapor of more concentrated sulfuric acid will.

The principle is illustrated in Fig. 3. As temperature in the heated diluter head is increased, the reading of the “overall surface” DC sensor decreases. The PAS detects an almost constant concentration of solid carbonaceous soot particles at any temperature; only in the presence of high droplet concentrations, i.e. at low temperature the PAS signal approaches zero because the electrons photo-emitted by soot particles cannot be extracted by the electric filter. Instead, they are captured by the droplets which now carry a negative charge when precipitated on the measurement filter, thereby compensating the positive contribution of the soot particles to the PAS signal.

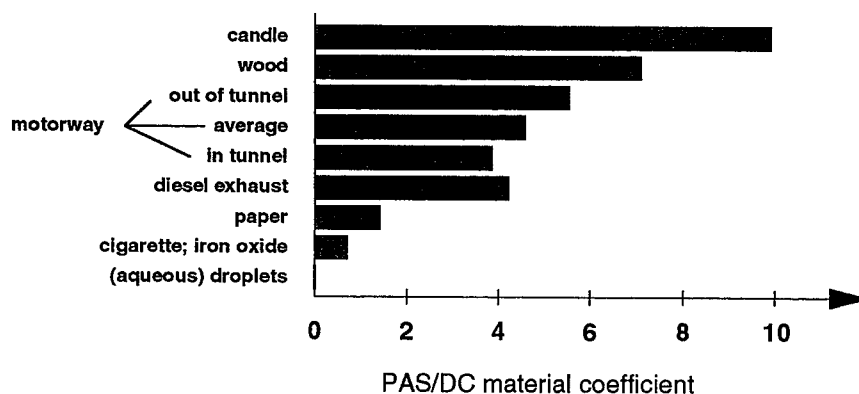


Figure 4: Material coefficients of particles from different sources.

Source apportionment

Simultaneous operation of the two NanoMet 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. Fig. 4 shows a list of particle sources and the respective material coefficients. A very high photoelectric activity is observed for soot from candles and wood fire while cigarette smoke and iron oxide exhibit little such activity. Droplets do not undergo photoemission at all - their material coefficient is zero.

An application of the source apportionment feature of NanoMet is shown in Fig. 5. Emissions of a diesel engine operated with two types of fuel were characterized using SMPS and NanoMet. With standard fuel the SMPS spectrum shows the usual log-normal distribution peaking at 70 nm. The NanoMet reading is equal for both sensors, which can be interpreted as “all particles” (DC) are “soot particles” (PAS). In the second case the fuel was doped with some organo-metallic compound. The effects of this additive on the emission spectrum (SMPS) are twofold: (a) The number of soot particles is reduced by half an order of magnitude. This result is reflected in a reduction of the PAS signal by the same factor 3. (b) The additive generates new small particles in high numbers which are suspected not to be soot particles. NanoMet confirms this suggestion by an almost tripled DC reading. Thus the relevant information (soot reduction; increase of total particle emissions) is obtained in a very straightforward manner without the need for further data reduction.

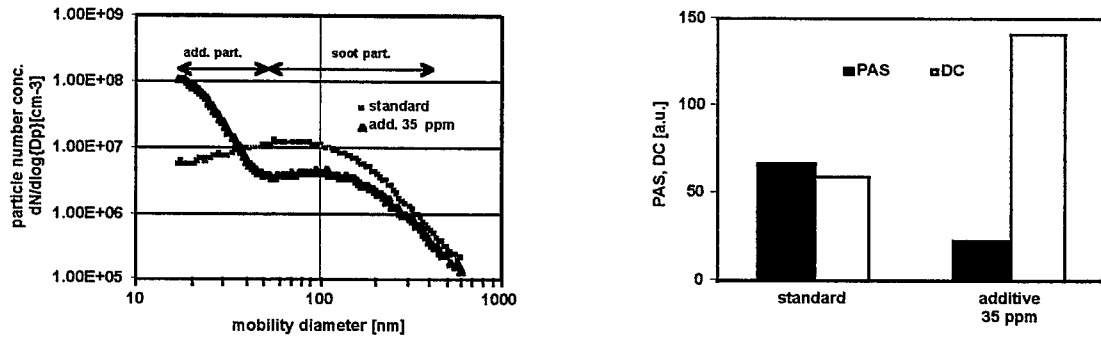


Figure 5: Emission measurements with SMPS and NanoMet at a diesel engine operated with standard fuel and cerium doped fuel. Due to the additive the number of soot particles is decreased while the total particle number increases (SMPS spectra). This result is also reflected in the PAS and DC signals.

Calibration

Attachment coefficient and mobility

The DC sensor signal is proportional to the number of aerosol particles and to the probability that ions from the corona discharge reach the particle surface. This probability is called the attachment coefficient, K . Particles much smaller than the mean free path in the surrounding gas (approx. 66 nm) are said to be in the molecular regime because the gas flow around the particle is best described as a shower of impinging molecules. In this case the attachment coefficient scales with the geometric particle surface. For large particles the surrounding gas is treated as continuous fluid with which the particle interacts through Stokes friction. The latter is determined by zones of maximal flow velocity which are found at the equator of the particle. Thus the attachment coefficient in the Stokes regime is proportional to the particle diameter. The diameter range between molecular and Stokes regime is interpolated by the Cunningham slip correction. The “scattering” or “friction” surface related to the attachment coefficient is also referred to as the “Fuchs” surface.

Another important physical property of aerosol particles is their mobility, b , which determines the velocity v a particle obtains as response to the action of an external force: $v = b \cdot F$. The mobility is measured with a differential mobility analyzer (DMA) where it is inversely proportional to the applied voltage. Furthermore, b is related to the diffusion

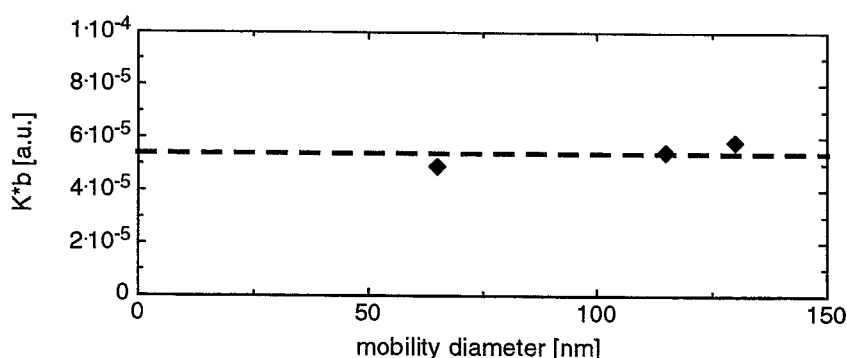


Figure 6: The product $K \cdot b$ is almost constant over a vast diameter range. The attachment coefficient, K , is measured with the DC sensor. The mobility, b , is determined by the voltage applied to a differential mobility analyzer (DMA).

constant, D , from which it differs only by a factor of kT where k is Boltzmann's constant and T the temperature. D , in turn, determines the probability that the particle will diffuse to the walls of a vessel containing the aerosol.

The two concepts of microscopic attachment coefficient, K , and macroscopic mobility, b , are connected by an astonishingly simple relation, $K \cdot b \approx \text{const}$, which holds over the whole diameter range within a few percent variation (Siegmann *et al.*, 1999). Thus, inverse proportionality of the DC signal with the diffusion coefficient is established via attachment coefficient and mobility. The reading of the DC sensor may then be considered a direct measure of the amount of particles deposited in a tube system such as the bronchial epithelium of the human lungs.

Calibration of the diffusion charging particle sensor (DC)

Calibration of the DC sensor is now very easy. Test aerosol is fed into a DMA where a mobility class is selected. This monodisperse aerosol flow is split in two and guided to a condensation nucleus counter (CNC) and the DC sensor. Without further calibration, the DMA voltage determines particle mobility, b , the CNC measures their number, N , and the DC sensor captures the overall attachment, $K \cdot N$. The only parameter remaining to be tuned is the amplification factor in the DC Sensor. This concludes the calibration process.

Calibration of the photoelectric aerosol sensor (PAS)

As has been stated before the reading of the PAS differs from that of the DC sensor by a multiplicative material coefficient. This requires a test aerosol of constant and reproducible photoelectric properties. Only recently has this condition been fulfilled by a new aerosol generator (Jing, 1999). Using this test aerosol allows one to calibrate the PAS against the DC sensor by tuning the PAS/DC ratio to the desired fixed value.

3 Ranges - 1 Method

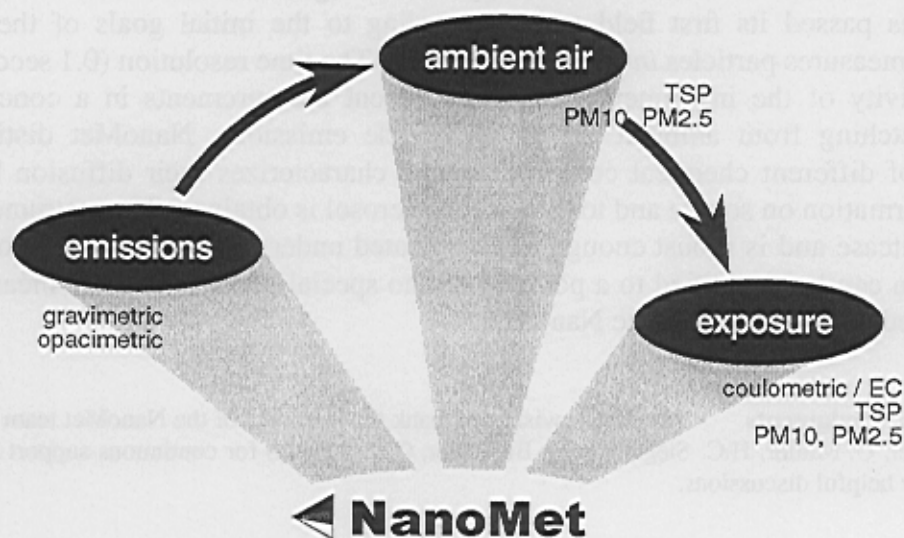


Figure 7: Due to its high sensitivity NanoMet is amply suited for emission measurements as well as ambient air and occupational exposure measurements.

Applications

Owing to the high sensitivity of the PAS and DC sensor, combined with the diluter, the whole concentration range between emission and ambient air / occupational exposure measurement can be covered. With NanoMet one has an instrument at hand which solves the unsatisfactory situation that the same particles are measured and legally limited by different, often not even correlating methods, only depending on the actual legal situation (Fig. 7). Numerous ambient air measurements have been carried out during the last years, mainly by the Swiss authorities and within scientific research projects (e.g., BRISKA). Several sensors are used for ventilation control in garages and halls with truck traffic.

During the VERT project the modules of NanoMet were used independently for emission measurement at test benches and chassis dynamometers. NanoMet passed its first test under harsh field conditions earlier this year in the NORANDA ore mine near Bathurst / Canada. Within the framework of the DEEP project emissions were measured from scoops and trucks belonging to the mining equipment. A test program including various load conditions and free acceleration runs facilitated almost complete characterization of vehicle emissions and trap efficiency within less than one hour.

Summary

The newly developed NanoMet technology that emerged from the results of the VERT project has passed its first field tests. According to the initial goals of the project, NanoMet measures particles *in-situ*, i.e. as aerosol. The time resolution (0.1 seconds) and the sensitivity of the instrument facilitate transient measurements in a concentration range stretching from ambient air up to vehicle emissions. NanoMet distinguishes particles of different chemical composition and characterizes their diffusion behavior. Thus, information on source and toxicity of the aerosol is obtained. The instrument fits in a large suitcase and is robust enough to be operated under fairly rough field conditions. The design can be simplified to a point where no special skills in particle measurement are required any more to operate NanoMet.

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