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**Sampling and dilution for the measurement  
of nanoparticles from engine exhaust**

# Sampling And Dilution for the Measurement of Nanoparticles from Engine Exhaust

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## Introduction

In automotive engine development and optimization, the measurement of ultra fine particle size distributions in the range from a few nanometers to micrometer sized particles more and more becomes common practice. Instruments like SMPS and ELPI, see e.g. /1/, are widely used in the field.

Especially for the measurement of ultra fine particles in the exhaust gas of vehicle engines, lab-to-lab comparability of the results has become a serious task. Until today, there are no clear regulations on how (and where) to do the sampling and how to do sample preparation. Even if only the most important effects which can change particle size distributions are considered, it immediately becomes obvious that the results of measurements are significantly influenced by the sampling conditions, see e.g. /2/.

## Important Effects

Nanoparticle size distributions can be subject to dynamic changes due to several effects. While, for example, isokinetic sampling is not important for these fine and ultra fine particles, size selective losses, particle to particle interactions, and reactions between the particles and the carrier gas must be considered.

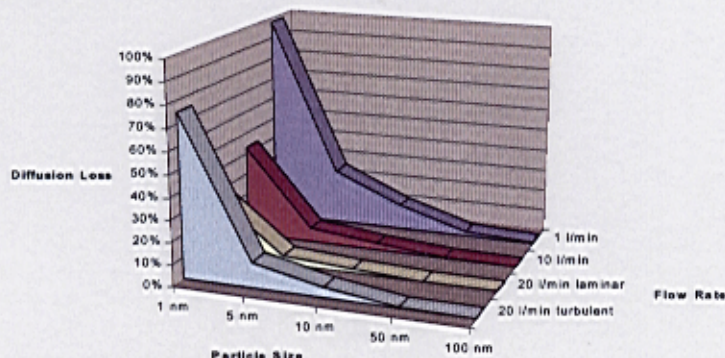
### Size selective losses

With decreasing particle size continuum physics is successively replaced by gas dynamics to describe the particle motion. Thus, diffusion losses to the walls of sampling tubing increase with decreasing particle diameter. In the presence of a temperature gradient or an electrical field, the same is true for thermophoretic losses or electrophoretic losses, respectively.

Figure 1 shows diffusion loss calculations according to the equations given in /3, 4/. The example given in Figure 1 illustrates losses for 1 m of tubing, inner diameter of 6 mm and at a temperature of 400 K. For all considered conditions, the losses can be neglected for particles larger than 50 nm. On the other hand, if the residence time is long enough (long tubing or low flow rate), particles smaller than 10 nm might be lost completely. Turbulent diffusion can outnumber the losses found in laminar flows, where only Brownian diffusion must be considered.

Fig. 1: Diffusion Losses

Example: 1 m of tubing with inner diameter of 6 mm at  $T = 400$  K



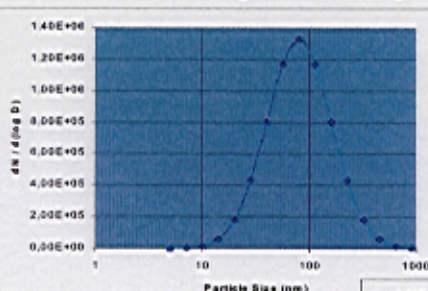
	1 nm	5 nm	10 nm	50 nm	100 nm
1 l/min	88%	24%	12%	2,50%	0,70%
10 l/min	43%	7%	3%	0,30%	0,15%
20 l/min laminar	29%	4%	2%	0,20%	0,10%
20 l/min turbulent	15%	12%	5%	0,60%	0,30%

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## Coagulation

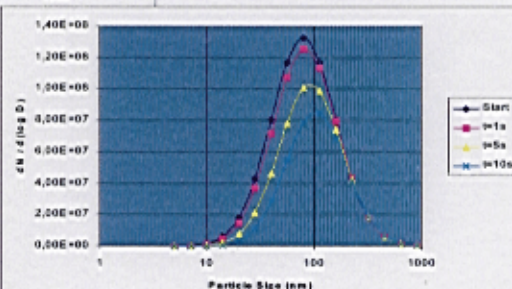
Particles getting into contact with each other are generally regarded as remaining agglomerated or to coalesce in case of droplets. This coagulation process increases with increasing particle number concentration. Figures 2 and 3 show example calculations for polydisperse coagulation, based on the equations given in /5/. Sampling of automotive exhaust aerosols typically requires a transport time in the sampling tubing which is in the order of 10 seconds. Within this time frame coagulation can be neglected if the total particle number concentration is below  $10^6$  particles per  $\text{cm}^3$ . However, the concentration can be higher in cases like direct sampling from the tail pipe. Even in a CVS tunnel, concentrations of then  $10^7$   $1/\text{cm}^3$  are reached, for example, by small truck diesel engines.

Fig. 2: Example for Coagulation



$$C_0 = 10^6 \text{ 1/cm}^3$$

$$C_0 = 10^8 \text{ 1/cm}^3$$

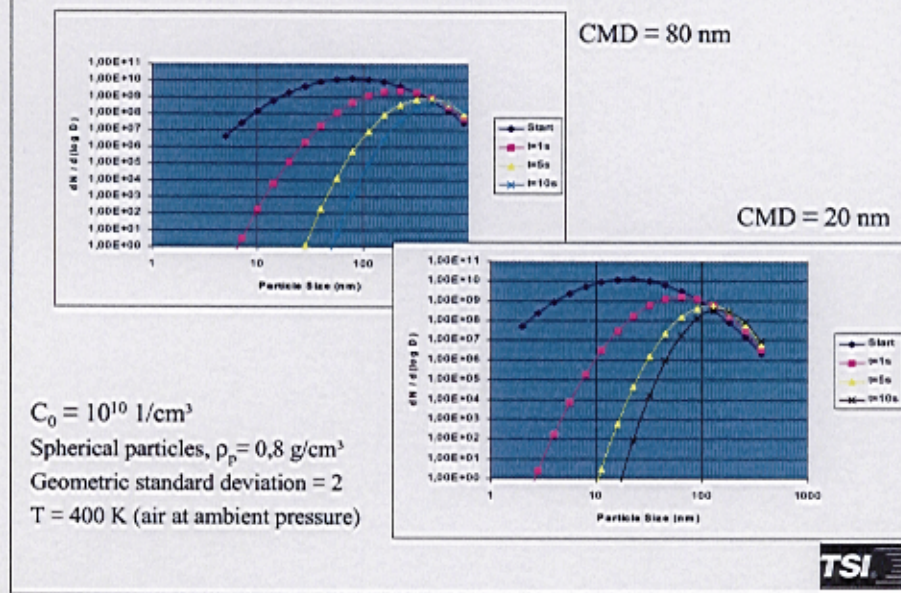


Count median diameter = 80 nm  
Spherical particles,  $\rho_p = 0,8 \text{ g/cm}^3$   
Geometric standard deviation = 2  
 $T = 400$  K (air at ambient pressure)

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Fig. 3: Example for Coagulation

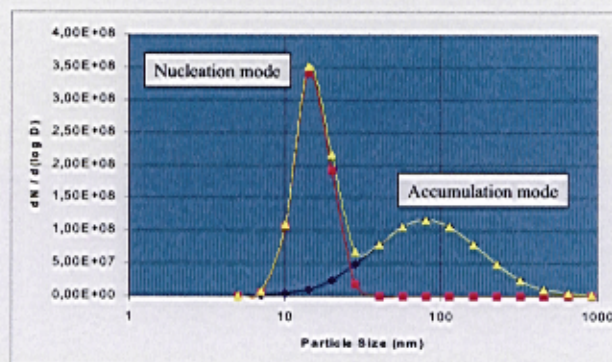


If highly concentrated aerosol particles (see figure 3) are transported with sufficient residence time, coagulation completely changes the nature of the original aerosol. Such aerosols can originate, for example, directly from internal combustion or from an undiluted aerosol source such as a flame. Highly concentrated aerosols are extremely unstable. They undergo dynamic size changes in very short times.

#### Heterogeneous condensation

In the presence of sufficient vapor content in the carrier gas, a decrease of temperature or an increase of pressure can lead to supersaturation close to the particles. The particles now act

Fig. 4: Example for Homogeneous Nucleation



Homogeneous nucleation or gas to particle conversion will add a more or less distinct small nucleation mode to the size distribution. After sufficient aging time, the nuclei will attach to the surface of the larger particles or grow due to condensation.

as condensation nuclei. Supersaturated gaseous compounds condense on the surface of the particles. This process leads to particle growth. At the same time, the particles' morphology and chemical properties will change. Heterogeneous condensation will also occur on the walls of the transport tubing if the tubing is cooler than the carrier gas.

### Homogeneous nucleation

If gaseous compounds of the effluent reach supersaturation not only near the particle surface but in general, homogeneous nucleation occurs. New particles are formed by a gas to particle conversion process now. Under these conditions, the particle size distribution shows a nucleation mode. The number median diameter of the nucleation mode typically is in the order of 10 nm. Homogeneous nucleation can either occur when hot exhaust gases are released to the cold atmosphere, or as an artifact due to the sampling conditions. Figure 4 shows an example.

## Optimizing the particle sampling process

As discussed above, sampling and measurement of high concentrations of nanoparticles, particularly at higher temperatures, is a highly dynamic and very sensitive process. If laboratory-to-laboratory comparable results must be achieved, it is very important to sample and measure under controlled conditions.

Some general recommendations can be given which help to achieve unbiased results:

To minimize losses:

- The residence time and tubing surface must be minimized.
- Temperature gradients and electrical fields must be avoided.
- Turbulent sampling flow should be avoided.

Recommended measures to minimize losses:

- Keep the tubing as short as possible
- Heat sampling tubes to gas temperature, but avoid pyrolysis ( $T < 180^{\circ}\text{C}$ )
- Use stainless steel or other conductive tubing
- Use high (but laminar) sampling flow

To reduce coagulation, nucleation and condensation:

- Minimize the residence time
- Keep the total number concentration below  $10^6 \text{ cm}^{-3}$ .
- Reduce the vapor contents to non-condensing conditions.

Recommended measures to minimize coagulation, nucleation, and condensation:

- The sampling tubing must be as short as possible
- The flow rate should be high, but the flow should be laminar



- The sample should be diluted to "safe" concentrations with less than  $10^6 \text{ cm}^{-3}$  close to the sampling point, preferably by means of a 2 stage dilution system which allows heated dilution gas.
- Dry dilution air (or dry  $\text{N}_2$ ) should be used to avoid nucleation and condensation.
- If necessary or desired, a thermodenuder can be used to remove volatiles.

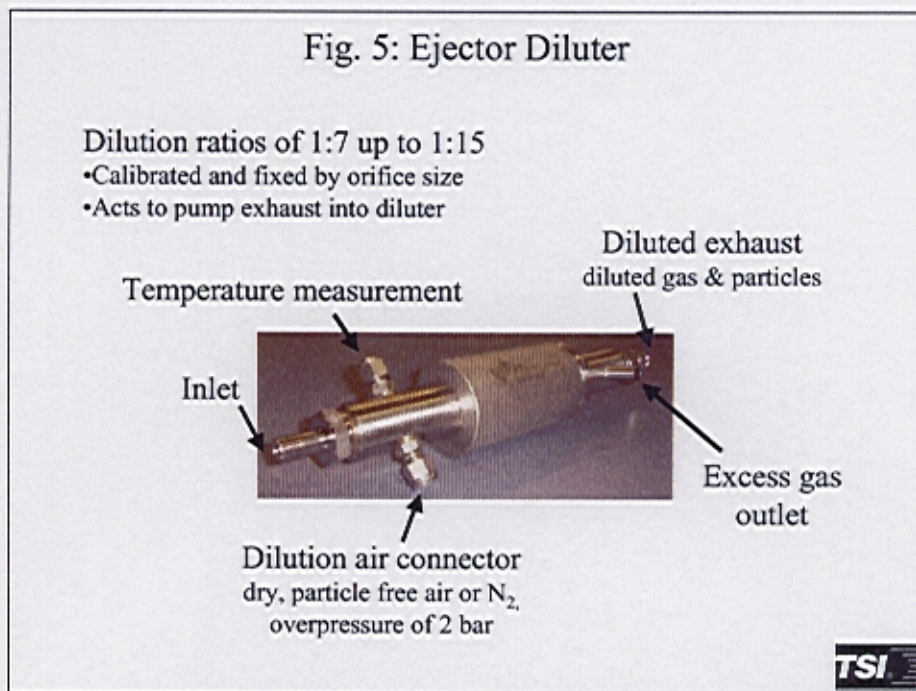


Figure 5 shows an ejector diluter. This compact device is made from stainless steel. It can be heated to avoid internal condensation and nucleation. The dilution air or gas is fed through an orifice into the venturi ejector. This section of the diluter also acts as a pump. The external

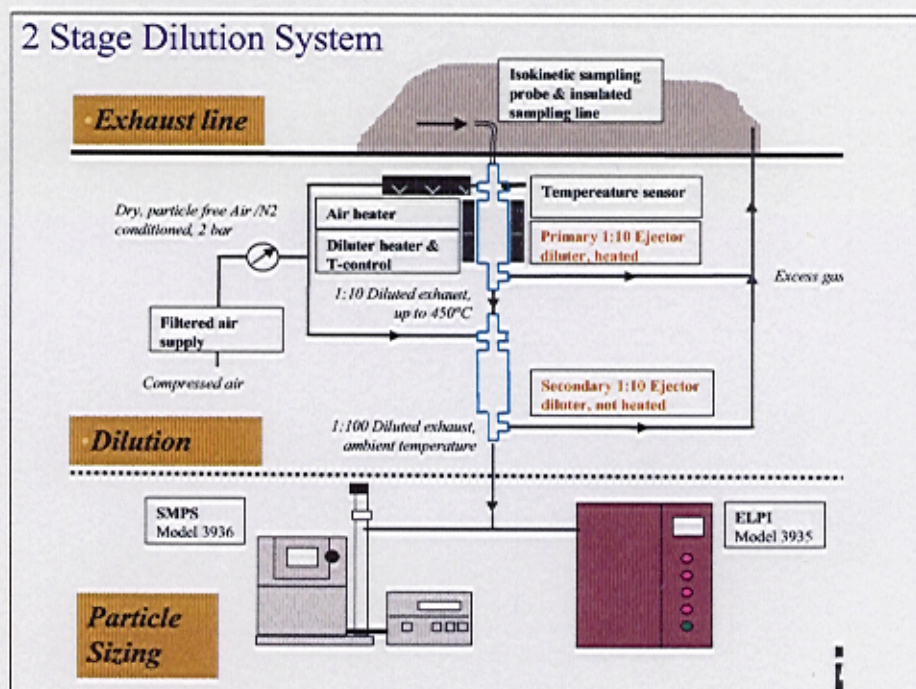


Fig. 6: Two-stage dilution system, first stage heated

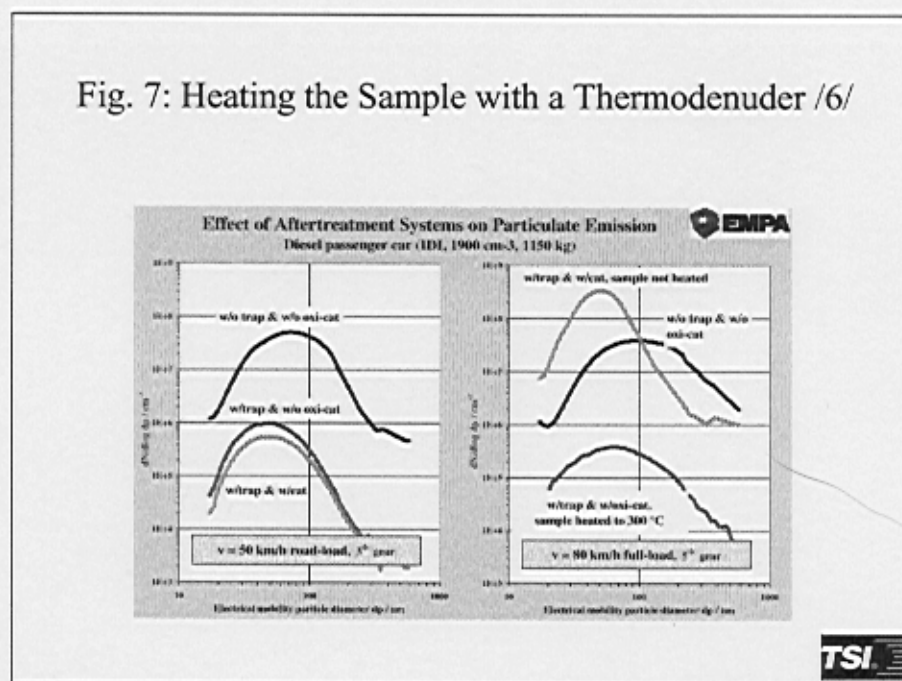


pressure of the dilution air controls both the air flow into the diluter and the sample flow through the inlet. This ensures a fixed dilution ratio at given operating conditions. The diluted exhaust can be taken from the mixing chamber into the measuring instrument by the instrument's sampling pump. A second dilution stage can also be connected to this port. The excess gas is either fed back or released. Figure 6 shows the setup of a two stage dilution system with heated first stage.

## Sample Heating with a Thermodenuder

Depending on the operating conditions, nucleation mode particles can be generated either in the dilution tunnel or in the sample tubing. Figure 7 /6/ is a good example. While the effects of the aftertreatment system can be clearly seen at 50 km/h (road load, 3<sup>rd</sup> gear) measurements, the particulate emissions at 80 km/h (full load, 5<sup>th</sup> gear) are higher with the aftertreatment than without. If the sample is heated in a thermodenuder, the nucleation mode particles disappear, allowing to measure the efficiency of the aftertreatment system.

Fig. 7: Heating the Sample with a Thermodenuder /6/



A thermodenuder (see Fig. 8 to 10) consists of two sections. First, the sample is heated to a controlled temperature. Depending on their volatility and the temperature, volatiles are removed from solid particles. Only the non-volatile residue remains as particulate matter. Next, the particle laden exhaust gas passes through a tube made from a gas-permeable membrane, surrounded by activated carbon. The vaporized volatiles are adsorbed in the activated carbon bed in order to avoid re-condensation after the exhaust gas leaves the thermodenuder.





Fig. 8: A TSI Thermodenuder for engine exhaust sampling (the picture shows a prototype)

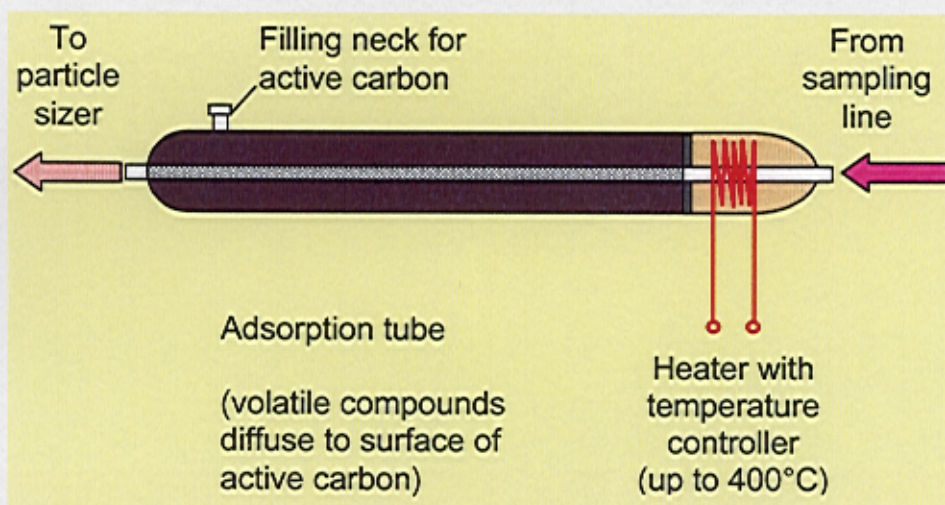


Fig. 9: The principle of a thermodenuder

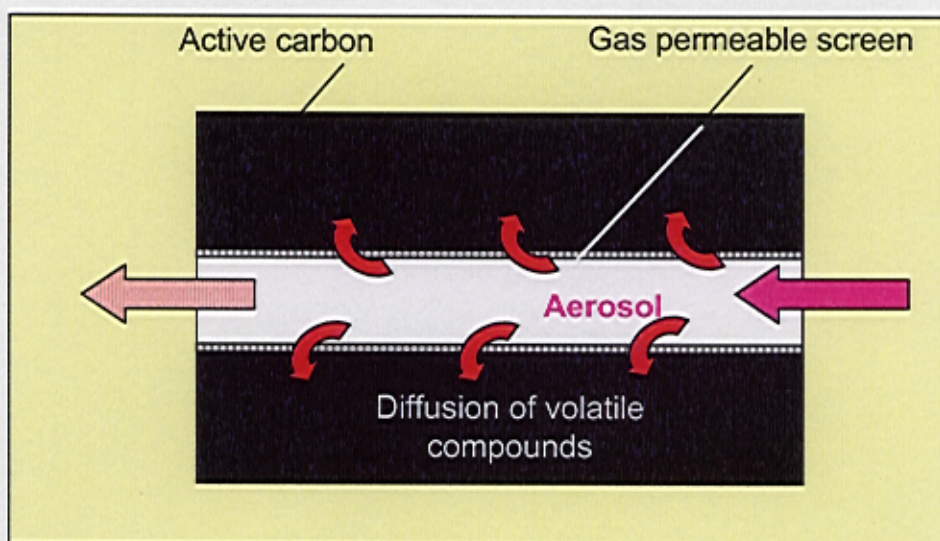


Fig. 10: Adsorption of volatile compounds in a thermodenuder



## Conclusions

The particle sampling and transport conditions for submicron to nanometer sized particles are as important for the results of measurements as the choice of the instruments. Basic rules like sampling lines being as short as possible etc. should be followed in any case. A two stage ejector dilution systems, together with the option to heat the sampling line to the first dilution stage, the first diluter itself, and the dilution air for the first stage is a very flexible tool to guarantee reproducible sampling conditions. This system can significantly reduce changes of the particle size distribution between the sampling probe and the measuring instrument.

In many cases, e.g. to evaluate the efficiency of aftertreatment systems, the measurement of the non-volatile compounds of the particles becomes necessary. A thermodenuder should be used to remove the volatile compounds and therefore allow the measurement of solid particles only.

A commonly accepted sampling standard for particulate matter in the nanometer to micrometer size range is essential for laboratory to laboratory comparability of measurement results.

## References

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- /6/ From a DEKATI newsletter, courtesy of Dr. Mohr, EMPA, Dübendorf, Switzerland