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Characterization of Nanoparticles from Different Sources:

Diesel Engines, Welding Fumes, Environment, Chemical Reactions

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Introduction:

The physical and chemical characterization of airborne particles is an important aspect in health related research on particulates aiming at understanding the toxicology of inhaled particles and developing reasonable emission control strategies. In this context special attention is directed to fine and ultrafine particles. There are numerous sources of such particles potentially relevant for human exposure in the environment or at workplaces, for example: the diesel engine, welding fumes, atmospheric nucleation of gaseous precursors, emissions from chemical plants or other combustion sources. With respect to diesel engines substantial efforts were undertaken in the past decade to reduce the amount of particle mass being emitted by the engines. In recent years the issue of number concentration and particle size distribution has become an increasingly important aspect in the discussion on possible adverse health effects associated with particles. This is a very complicated issue since a large fraction of fine particles, particularly those originating from combustion sources, are agglomerated nanoparticles, i.e. agglomerates composed of many insoluble primary particles with sizes in the nanometer range (around 20 to 30 nm for diesel emissions). From a toxicological viewpoint, it is yet unclear whether to define particle number as total number of primary particles or number of agglomerates. In this presentation we report on the characterization of agglomerated nanoparticles from different sources.

Materials and Methods

We used three methods to measure the physical properties of agglomerated nanoparticles: 1) the electrical mobility spectrometer (SMPS) for the agglomerate number distribution as a function of the mobility diameter; 2) the low pressure cascade impactor for measurement of the mass distribution as a function of the aerodynamic diameter and, 3) the transmission electron microscope (TEM) for investigating the morphology and the primary particle diameter. Samples for the TEM-analysis were taken using thermophoretic particle deposition on the TEM grids. Characterization of diesel exhaust was performed by sampling from a standard dilution tunnel.

When comparing results of SMPS and impactor measurements one has to take into account that for agglomerates there is a size dependent quantitative and qualitative difference between the aerodynamic diameter and the mobility diameter (Fig 1).

Results

Diesel particles

The number and the mass size distribution of a modern diesel engine is shown in Fig. 2 a and b together with a typical transmission electron micrograph. The considerable shift in the mass size distribution towards larger aerodynamic diameters in Fig. 2b is due to a restructuring of the diesel particles from open agglomerates into dense packed agglomerates presumably caused by incomplete drying of the exhaust in the dilution tunnel under the high load conditions. The analysis shows that the particle morphology needs to be considered when comparing results obtained using the SMPS and the (electrical) impactor. SMPS measurements have been performed for various modern diesel cars (turbo charged direct injection, common rail injection). The agglomerate size distributions under constant load conditions (50 km/h, 3rd gear) look all similar and are also similar to measurements performed previously on swirl chamber engines. However, the swirl chamber engine (Nissan 2.0 d) investigated in this campaign seems to emit considerably smaller agglomerates than all other engines tested (Fig. 3). As Fig. 4 shows there seems to be no correlation between the number and mass emission rate. There is a trend that the average particle size becomes slightly smaller as the mass emission rate is reduced. This is consistent with the theory of agglomeration where the final number concentration is nearly independent of the initial number concentration and is essentially determined by the coagulation time. This has been also shown for example for soot formation in flames (Fig. 5). TEM samples have also been taken from outside air. The grid was placed on the back and the front of a diesel car running mainly on a German Autobahn. The deposits on the rear plate (Fig. 6a) originate mainly from the tailpipe emission of this car since it was located in an area affected by the vortex of the exhaust flow. The particles on the grid placed on the front of the car originate from emissions of other cars driving on the Autobahn (Fig. 6b). The „environmental" diesel particles are morphologically not much different from the particles sampled in the dilution tunnel.

Worplace

Welding is a source of ultrafine particles at the workplace. Due to the formation mechanism many of the fumes are composed of agglomerates. Unlike for soot the size and the chemical composition of the primary consituents can vary substantially as shown in Fig. 7, 8, and 9.

Laboratory generated nanoparticles

For certain applications such as filter tests, inhalation toxicology, instrument calibration there is a need to generate nanoparticles with controlled properties (size and number concentration) in a laboratory rig. This is done for example by gas to particle conversion of aerosol precursors in a turbulent free jet. Aerosol particles are formed by cooling a hot vapor or by chemical reaction (Fig. 10). If particle growth is coagulation controlled the size distributions are self preserving (Fig. 11) and the average size and the number flux of the generated particles are determined by simple process parameters (Fig. 12).

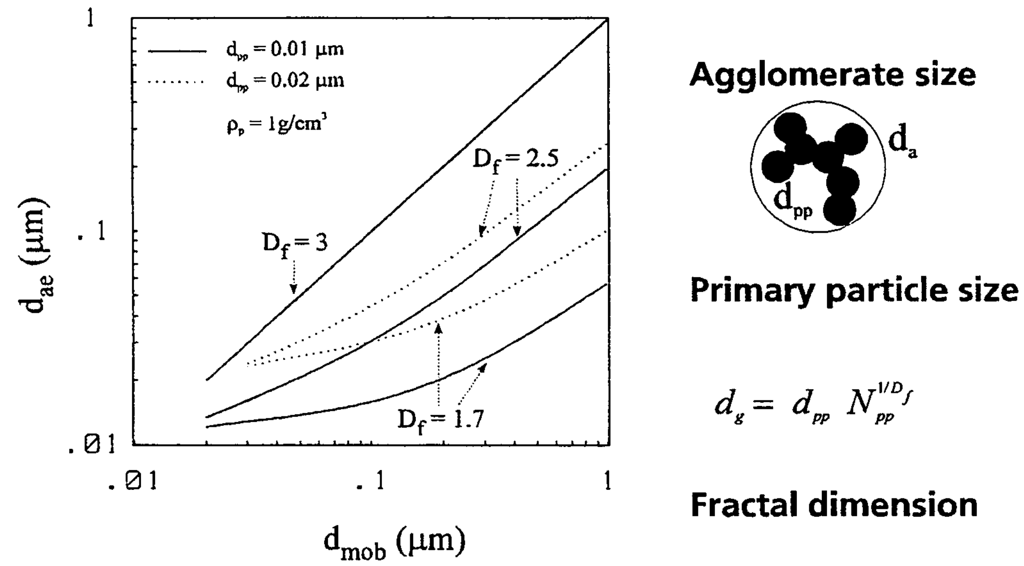


Fig. 1: The relationship between aerodynamic and mobility diameter depends strongly on the fractal dimension of the agglomerate.

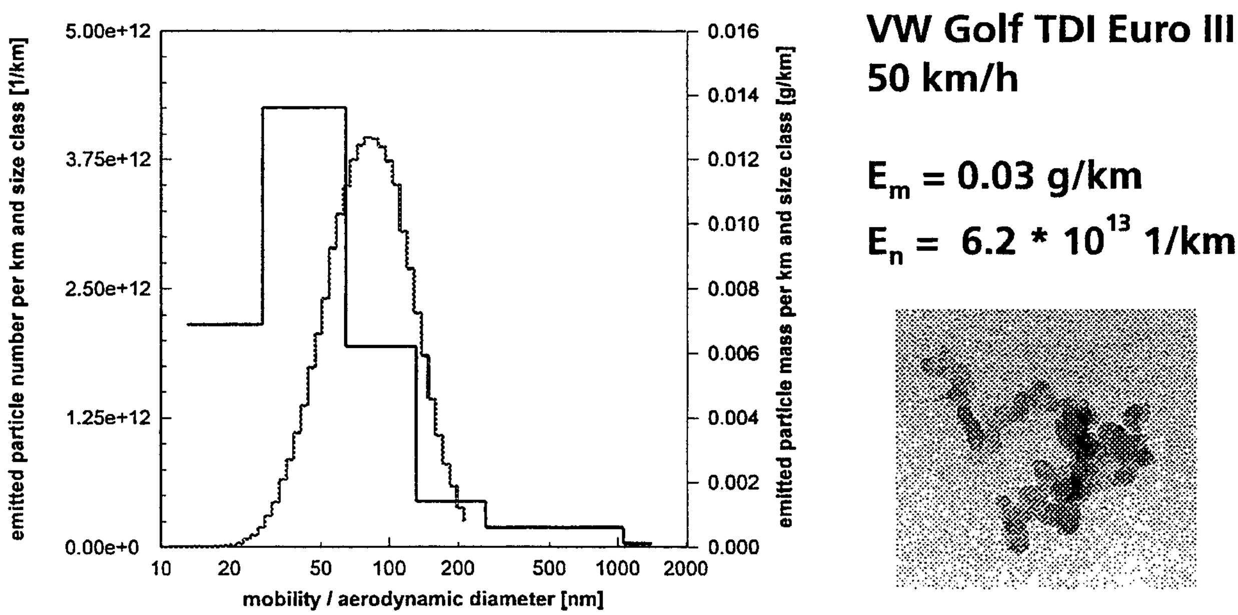
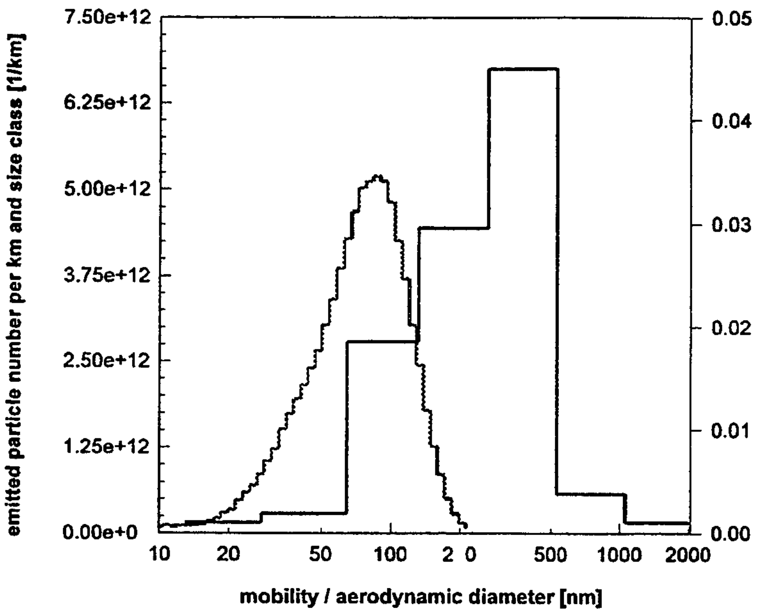


Fig. 2a: Number and mass size distribution of diesel exhaust particles. For open agglomerates the mass median aerodynamic diameter is considerably smaller than the number median mobility diameter.



VW Golf TDI Euro III
130 km/h

$E_m = 0.13$ g/km

$E_n = 8.2 * 10^{13}$ 1/km

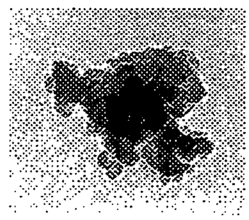
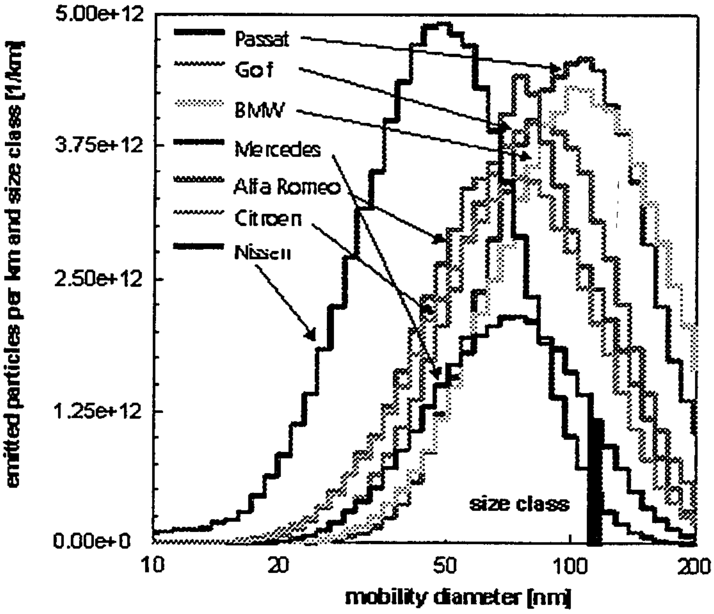
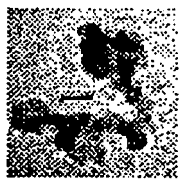


Fig. 2b: For the high load conditions the mass emission rate has increased substantially whereas the number emission rate is almost the same as under low load conditions. The aerodynamic size distribution has shifted considerably towards larger diameters due to restructuring .



Nissan:
swirl chamber engine



all others:
direct injection engines

Fig. 3: The number size distributions of the particle emissions under low load conditions peak between 70 and 100 nm, except for the Nissan emitting slightly smaller particles. The morphology of the particles emitted by all engines is similar.

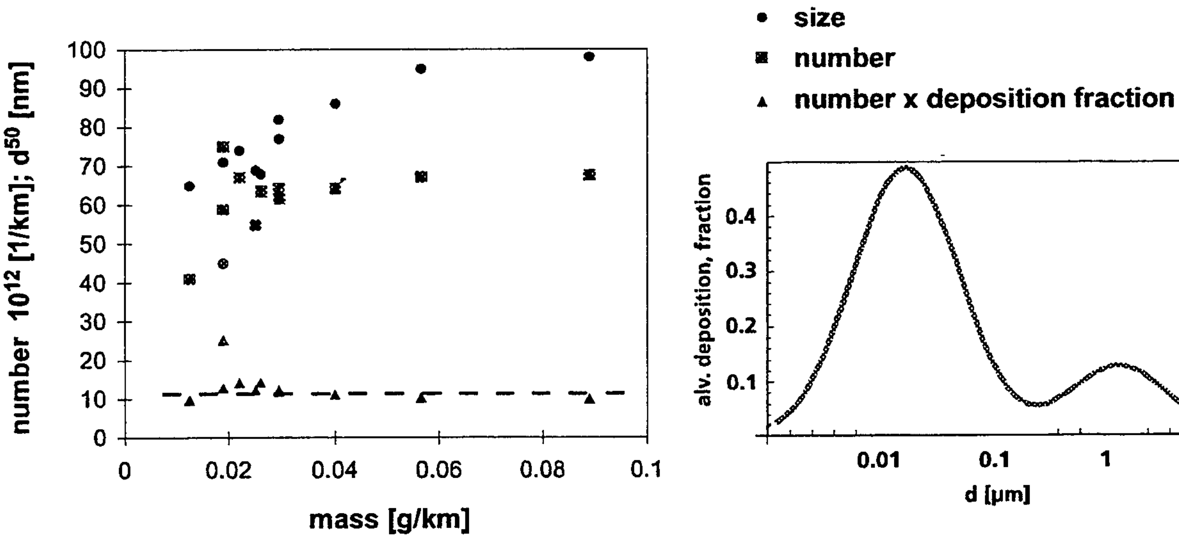
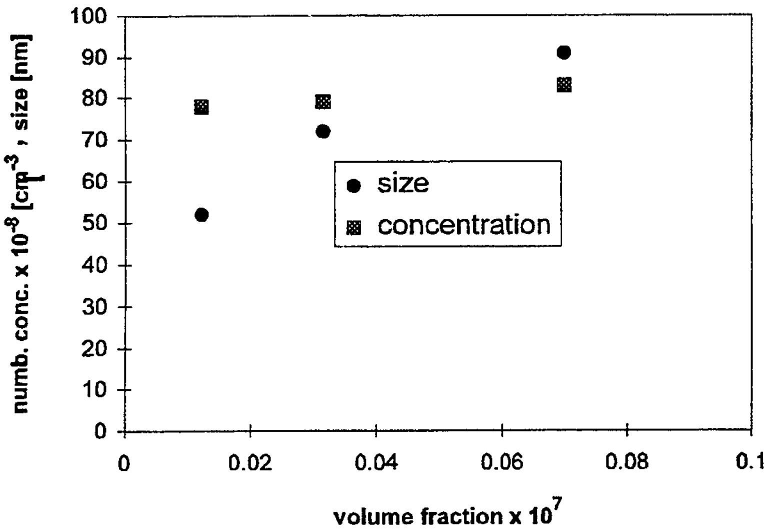


Fig. 4: The agglomerate number emission is relatively independent of the mass emission. The agglomerate size decreases slightly with decreasing mass emission. This does however not affect the number of agglomerates deposited in the lung after inhalation.



$$N = 2.84\,10^{14} \frac{1}{T^{3/5}\,\varphi^{1/5}\,t^{6/5}}$$

Fig. 5: Characteristics of soot formation in flat flames. The number concentration does not change with the amount of soot formed in the flame.

Environmental diesel particles. EM grid on rear license plate

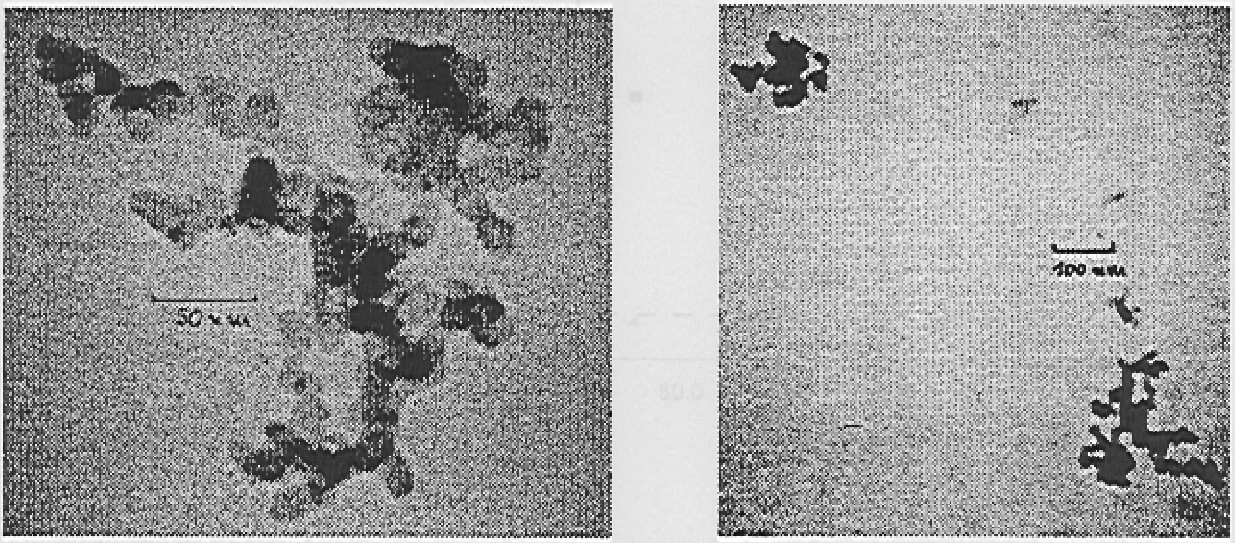


Fig. 6a: Diesel particles sampled immediately behind the tailpipe from the outside air.

Environmental diesel particles. EM grid on front license plate

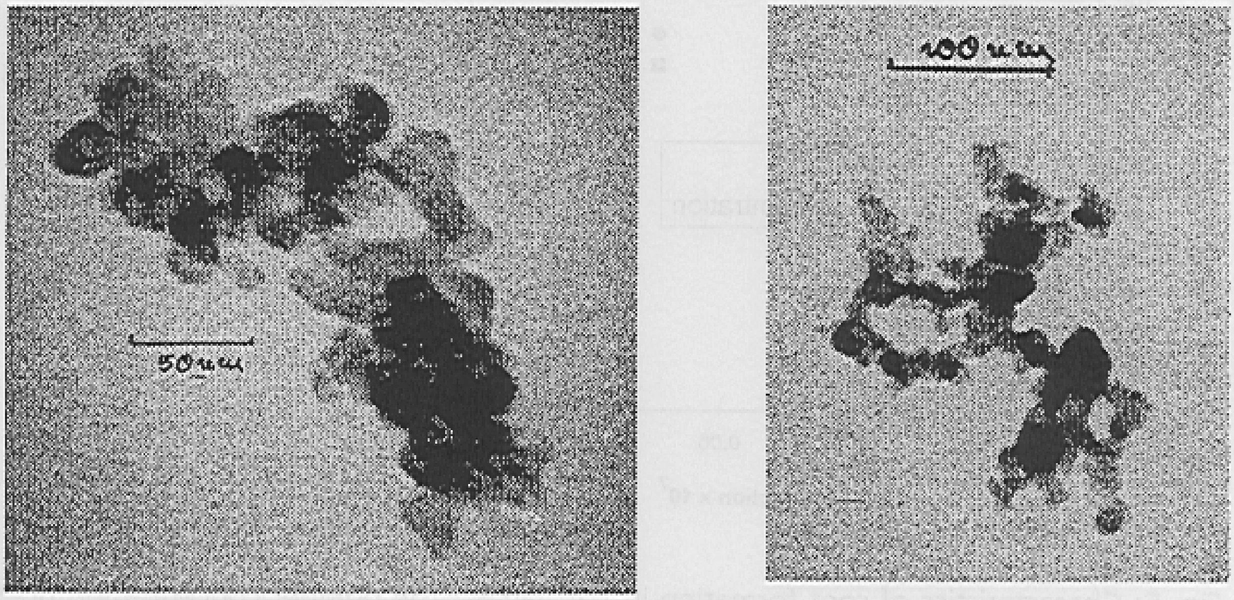


Fig. 6b: Typical diesel particles collected while driving on an Autobahn. They show similar morphology as the freshly emitted agglomerates.

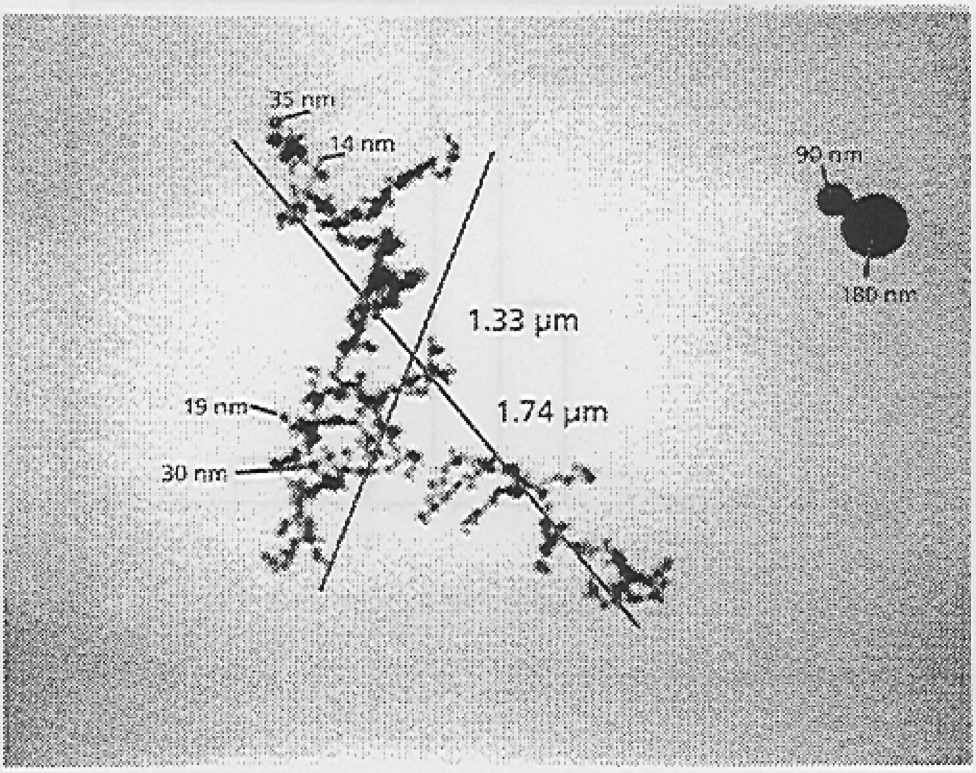


Fig. 7: TEM picture of welding fume particles.

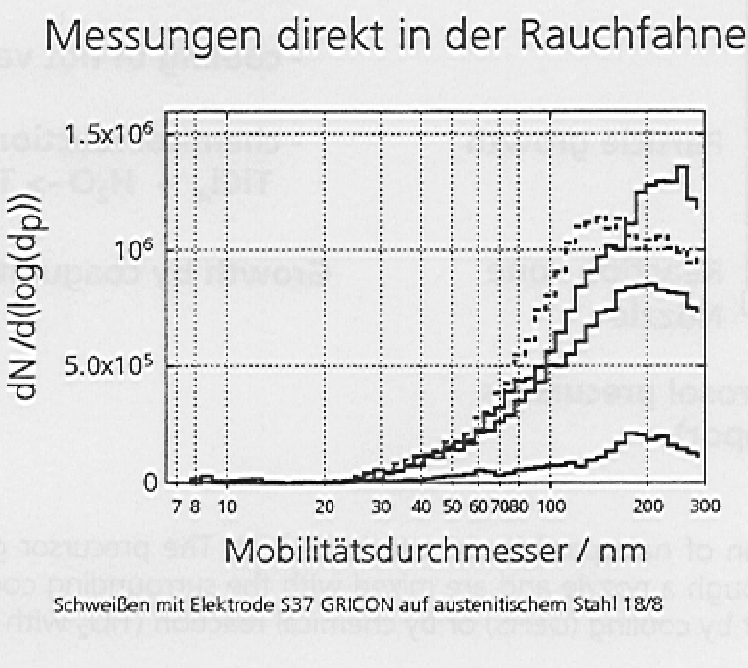


Fig. 8: Number distribution of welding fumes measured inside the plume. The fraction of particles with mobility diameters smaller than 100 nm is low.

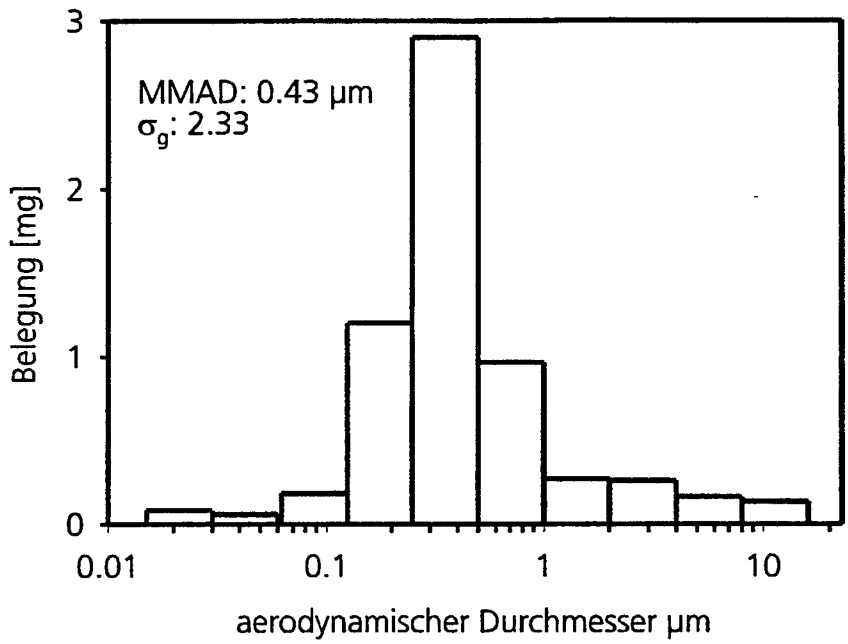


Fig. 9: Typical mass distribution of a welding fume.

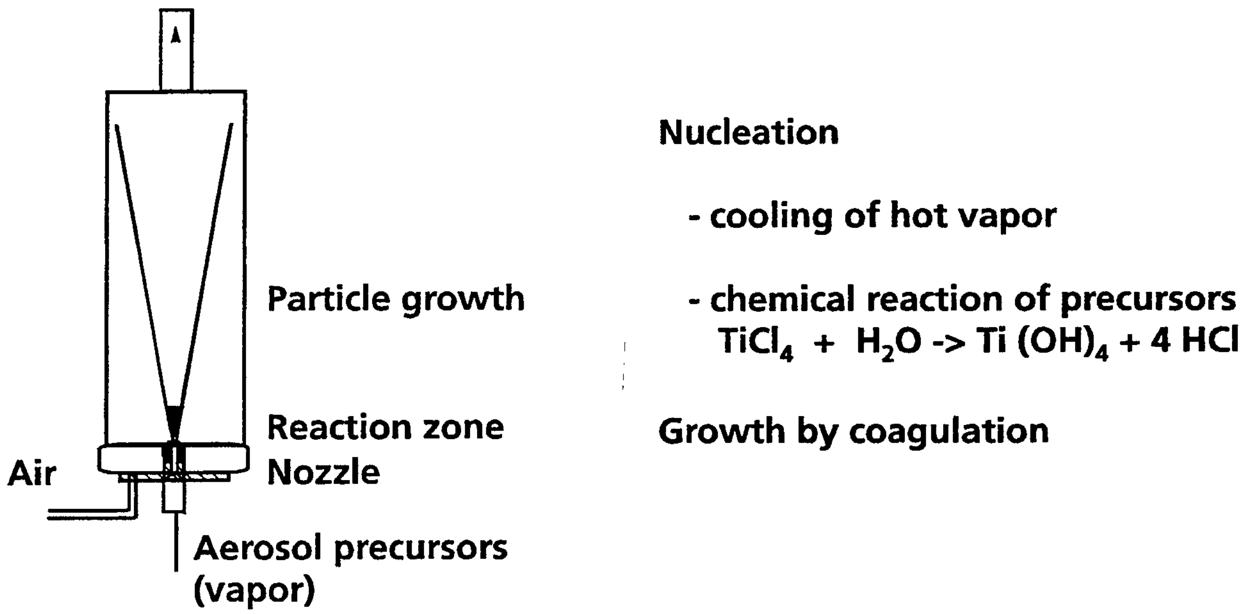
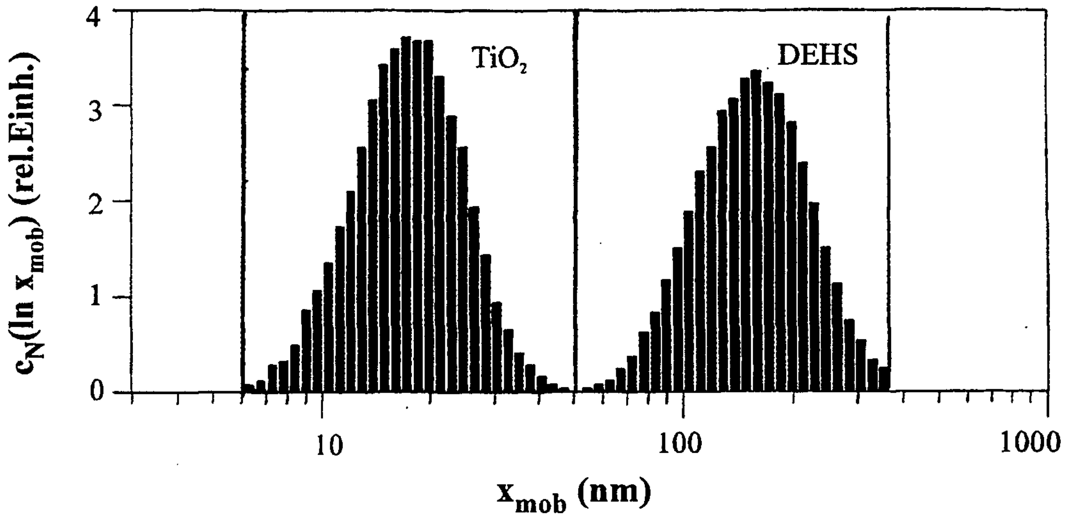


Fig. 10: Formation of nanoparticles in a turbulent jet. The precursor gases issue with a high velocity through a nozzle and are mixed with the surrounding cool gas. Nucleation takes place either by cooling (DEHS) or by chemical reaction (TiO_2 with water vapor).



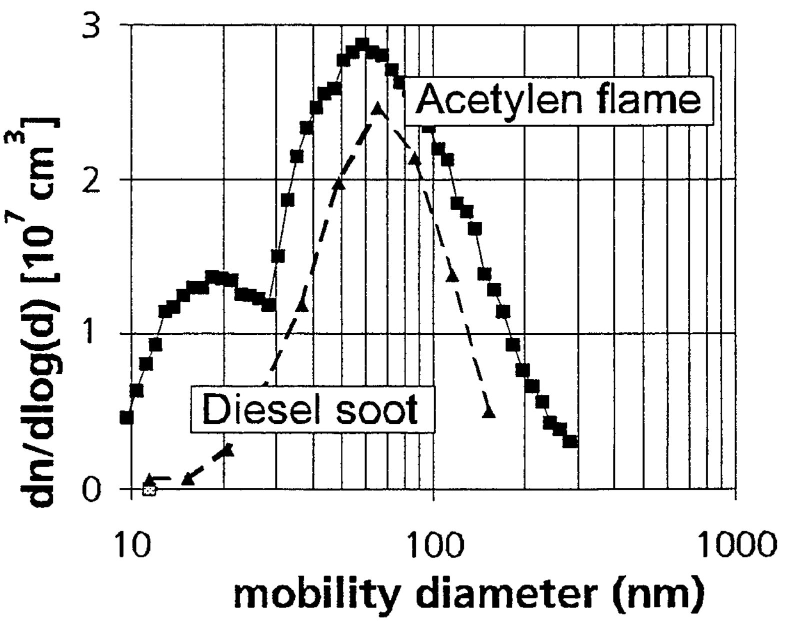


Fig. 11: The size distributions of the TiO_2 and the DEHS aerosols formed in a turbulent jet have a universal shape with a geometric standard deviation of around 1.5. It is possible to generate aerosols with an average size as small as 15 nm at very high concentrations. In a turbulent flame the situation is more complicated.