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TEM-Analysis of diesel engine particle emission to get a correlation of the geometric parameters with the SMPS mobility diameter.

W. Fr. Dreher, A. Harscher, C. Burkhardt, W. Nisch; **NMI**
W. Sebbeße, S. Weßels; **ADA**

NMI
Naturwissenschaftliches und Medizinisches Institut
www.nmi.de

ADA
Abgaszentrum der Automobilindustrie
(Audi, BMW, Daimler-Chrysler, VW, Porsche)

Abstract
The quantitative detection of airborne particles represents a challenging problem for measurement technology. The Scanning Mobility Particle Sizer (SMPS) can be used for size < 1µm in order to obtain information on particle number and size based on their electric mobility diameter. For this reason it is used, besides other methods, for the specific characterization of particles emitted from vehicle engines.

The parameter "electric mobility diameter" is not related to the well-known "aerodynamic diameter", nor has its relationship to structural parameters of the particle been defined so far.

In the present investigation we have evaluated microscopically the form and geometry of single-particle conglomerates emitted from diesel engines and established the correlation to the SMPS mobility diameter.

A. Introduction
Regulations on particle emission values mandated by law define the particle mass measured gravimetrically. Further parameters are the number and size of particles, which can be measured by a variety of methods.
In the present study the SPMS instrument of the Company TSI was used. Particles are selected by mobility classification via a DMA-classifier, and their number is subsequently measured in a CPC particle counter. The SMPS measure parameter, i.e. the electric mobility diameter Dp, is determined through the electrostatic principle of the so-called classifier.
The mobility diameter is a comparative diameter, based on the assumption that the particles are spherical. Consequently the *comparative diameter* is not directly related to the dimensions and morphology of the particle.
The goal of the present study was to use image analysis to define the shape and geometric parameters of single emitted particles. The complex shape of soot particles from diesel engine emission is greatly different from that of a perfect sphere and is best approximated by the shape of a cylinder (diameter D, length L).

B. Experimental procedures and Methods
B.1. Experimental Setup
A common rail diesel engine with exhaust-level EU3 was placed on a stationary engine test bench and operated at fixed partial load.

Sampling was done directly after the turbocharger with the partial flow dilution system NanoMet Md19-2E and the SMPS measurement. A TEM object-carrier covered with a perforated carbon-foil was placed between the DMA and the CPC. The DMA selects only a defined size of monodispersed particles (electric mobility) which are then deposited on the object-carrier.

To maintain the monodispersed character of the particles the probe-filter is loaded only to a small degree. Higher loading will lead to agglomerate formation. Evaluation by SEM is based on the image analysis of several single particles on the filter.

A plot (fig 1) of the electric mobility diameter versus particle number gives a distribution pattern which resembles the typical size-distribution parameter of particles from diesel engine emission.

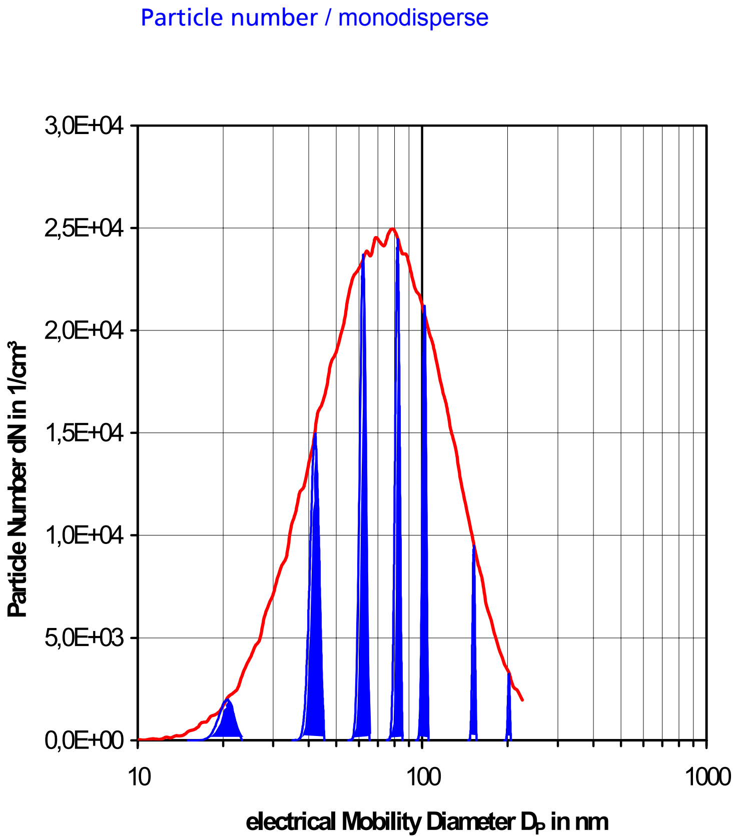

Fig.1.
Particle-size distribution measured by SMPS with selected monodipersed size classes.

Using a constant engine-load and speed setting the DMA selects the various monodispersed class-sizes which are deposited on to the probe-filter placed on the object-carrier for TEM.

B.2 TEM analysis.
TEM analysis of single particles was performed on a transmission electron microscope TEM JEOL2000 FX II (200kV with LaB6-cathode). Pictures were taken with a Gatan Multiscan CCD-camera. The emission-particles were deposited on a few nanometer thick perforated carbon foil, stretched on a small copper net with a 40µm grid. The size and local distribution of the holes on the foil was irregular.The diameter of the holes ranged from 0.1µm to several µm (Fig.3).

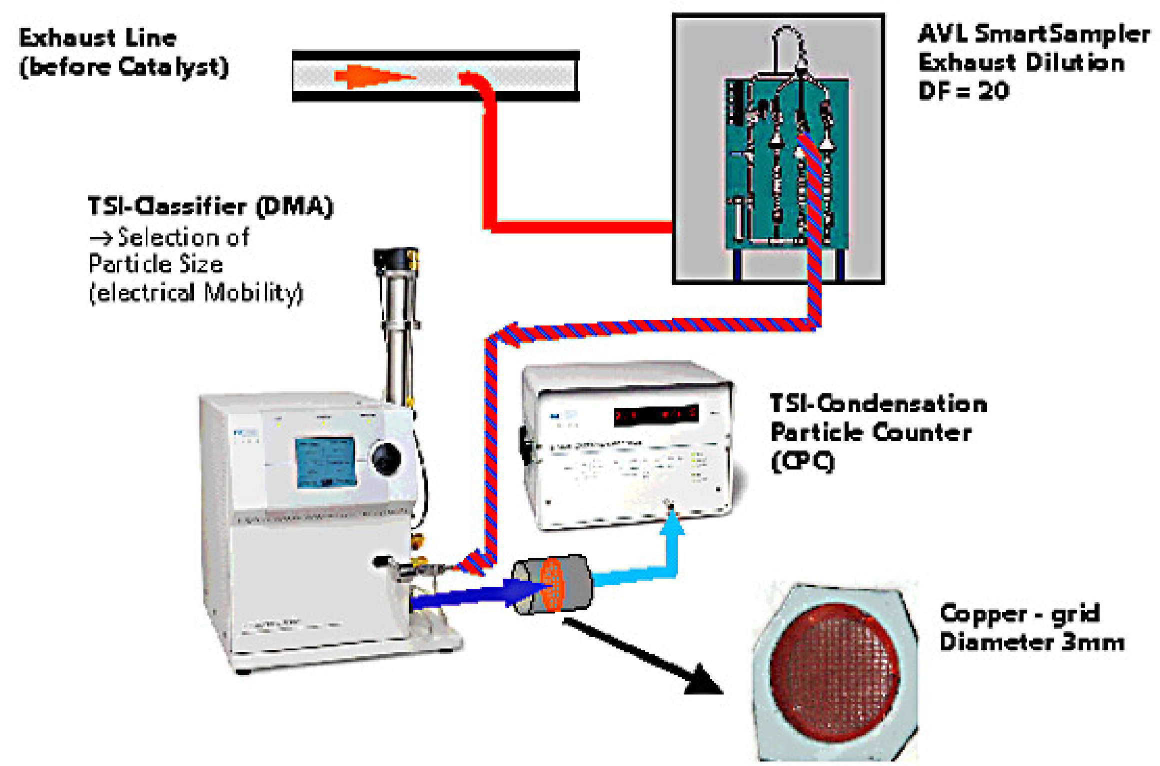

Fig.2
The TEM object-carrier is placed after the electrostatic DMA classifier into the aerosol flow.

The number and size of the pores of the carbon foil is the result of a random process. Therefor there are considerable differences between foil batches with respect to their structure. This results in variable ratios between foil surface and perforated area (Fig.3). For this reason only foils with comparable perforated to unperforated surface ratios were selected.

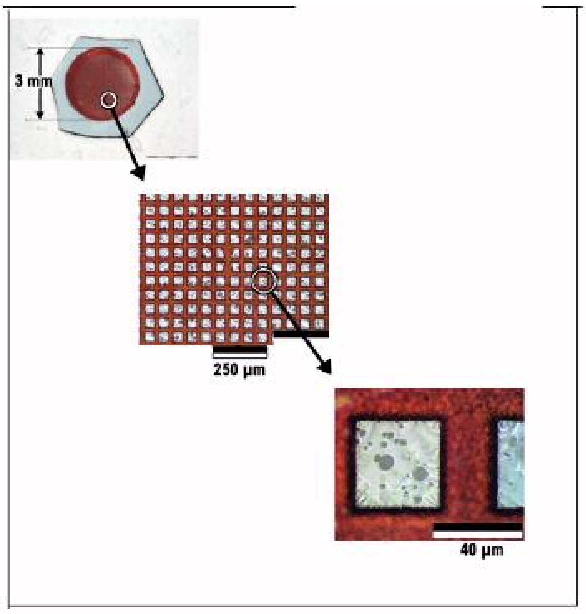

Fig.3
TEM object carrier. The perforated foil for particle collection can be recognized on the low right-hand corner.
Pilot experiments revealed that soot particles were localized preferentially on the thin struts between holes. Therefore the best foils were those with a large number of densely packed pores and narrow interspaced struts.

C Analytical methods

C.1 Determination of sample parameters

The goal of the investigations was to gain information on a possible correlation between the mobility diameter Dp (SMPS) and the geometry/morphology of the particles based on TEM analysis. Could a simple geometrical shape be described which approximates the ramified fractal structure (fig.5) of diesel soot particles?
The perfect spherical shape describes particles of 30 nm. With increasing mobility diameter, however, the particle shape changes significantly towards a fractal structure, consisting of single sphere-shaped primary particles, in which case the overall structure of the composite particle no longer resembles that of a sphere.

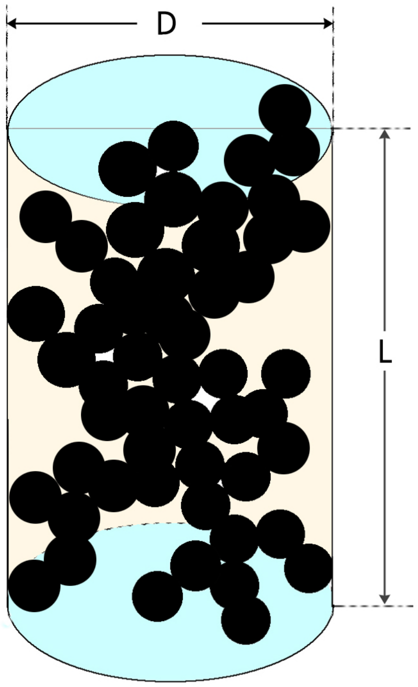

Fig.4
Cylinder model of a particle agglomerate.
The cylindrical shape outlining an agglomerate turned out to be an adequate geometric approximation. The length L and diameter D of the cylinder (fig.3) describe a particle as it is selected by the electrostatic classifier and deposited on the perforated carbon foil on the object carrier. D is the smallest diameter into which the particle fits best.

C.2 Definition of the measuring parameter.

A parallel projection of the 3-dimensional agglomerate leads to a shortened representation of the D and L axis. It is known that only those particles are stable under the electron beam which have good mechanical and electrical adhesion to the carrier. Therefore one can assume that the examined particles lay on the foil with one or both axis parallel to it with a projection factor near one. The selection of the probe carrier (see above) and the parameters for probe sampling were in preliminary experiments in order to warrant a homogeneous and low density particle probe, thereby preventing particle agglomerate formation upon deposition onto the perforated foil.
In order to obtain a statistically significant analysis, data from 50 particles (agglomerates) per foil on two foils were collected. For the determination of D and L a maximum of three particles per copper-net grid (40x40 µm) was analyzed.

D Results

D.1 TEM Analysis

The particles with a mobility diameter between 20 and 200 nm had a fractal structure. They are agglomerates consisting of spherical primary particles 20-30 nm in size. The inner structure of these nano-particles consists of few nm-large graphite leaflets ordered in onion-like fashion (fig.6).

TEM micro-graphs of agglomerates deposited on the perforated carbon foil on the object carrier are presented on fig.4 The two geometrical lengths L and D (orthogonal) can be recognized. They represent the length L and the diameter D of the cylinder in which the agglomerate fits best.

The larger the number of primary particles in an agglomerate, the greater the differences in D and L. Since primary particles during aggregation can yield a variety of structures, the larger the number of primary particles building an agglomerate, the greater the shape deviation of the latter from the ideal spherical shape.

At a mobility diameter of 10 nm only few particles are detected on the foil, because in this case the probability for ionization required for the SMPS measurement is very small (6).

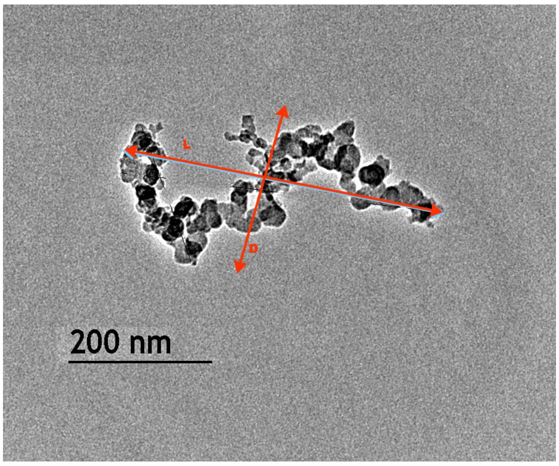

Fig.5

TEM-Picture of a single particle agglomerate with typical L and D extension. Based on the 3-dimensional cylinder model (fig.3),

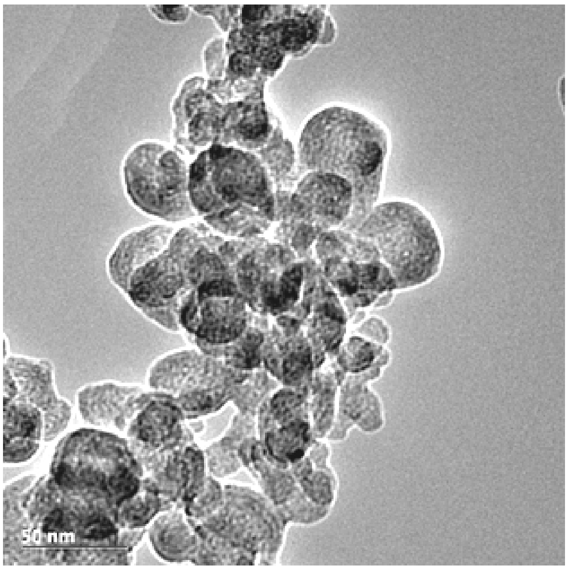

Fig.6

Typical particle agglomerate, grape-like.(TEM-picture)

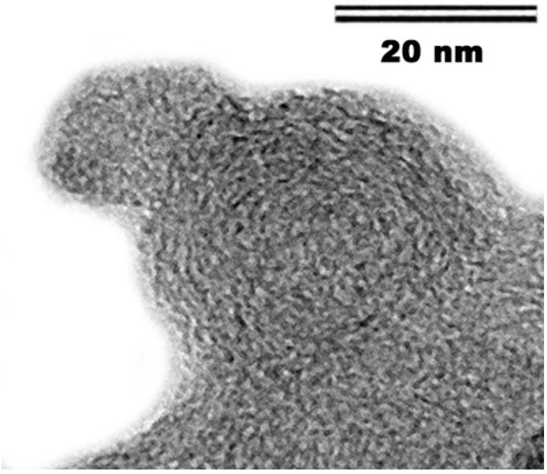

Fig.7
Primary particle in an agglomerate (TEM picture). The single leaf-shaped graphite crystals, few nanometers in size, ordered to yield an onion-like structure can be recognized.

D.2 Correlation with the parameter “electric mobility diameter”
The parameter Dp (electric mobility diameter) of the SMPS method (scanning mobility particle sizer) has been determined in emission probes from a diesel engine. Particles of a given size-class defined by the Dp value were deposited on the TEM-probe-carrier and represented by TEM. The image of the particles (aggregates) was analyzed with respect to the fractal shape with two geometrical parameters, D diameter and L length, assuming a cylinder as best fitting geometrical form.
As shown in fig.7, there was a significant correlation between the electrical mobility diameter Dp of the SMPS system and the values D and L determined by TEM analysis (Fig.7)
Dp correlated with the diameter D of the cylinder model (fig.8):

D = Dp

Furthermore, L (fig.10) was approximately twice the value of Dp:

L = 2 Dp

These results provide a rationale for the calculation of mass distribution of uniform emission particles by SMPS. For agglomerates with a Dp > primary particle size (i.e. 20-30 nm) the shape deviates greatly from that of a sphere.

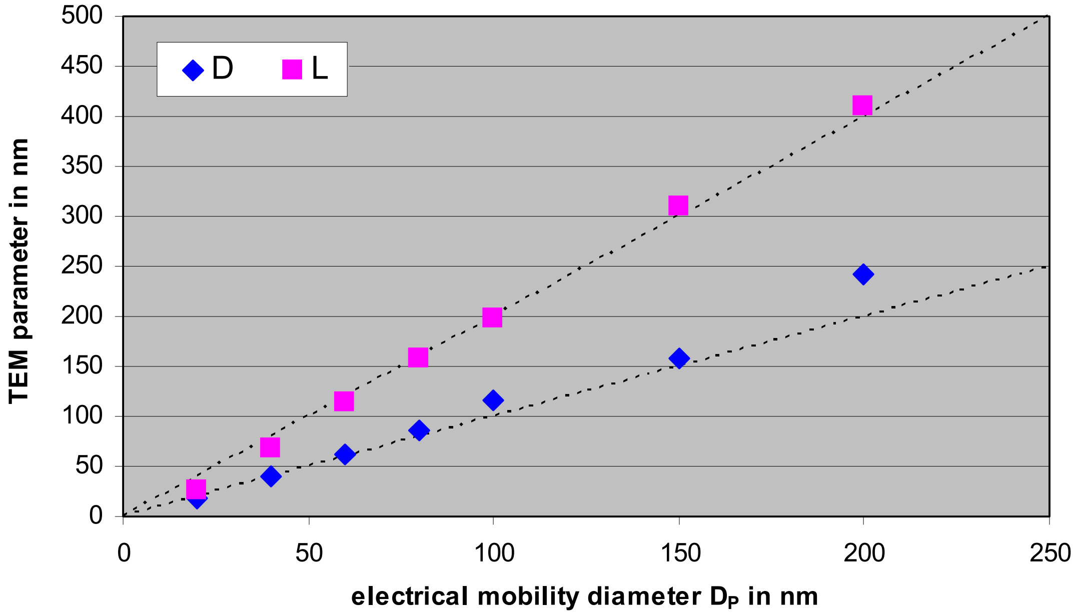

Fig.8
Median values of diameter D and length L versus mobility diameter Dp

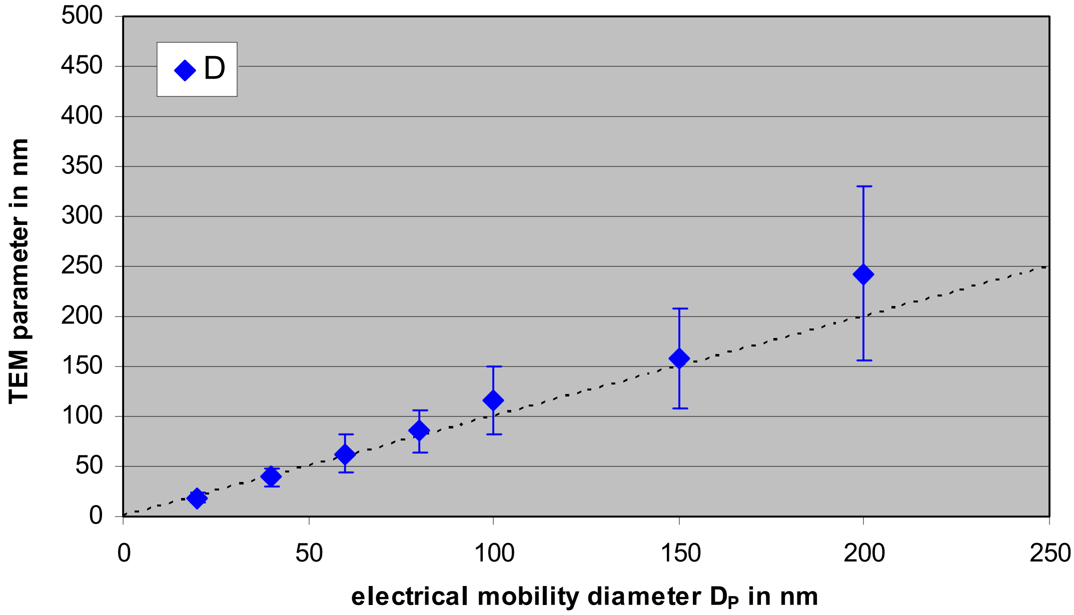

Fig.9
Diameter D (+standard deviation) based on TEM (cylinder model, fig.3) and mobility diameter Dp.
(the dotted line represents D = Dp)

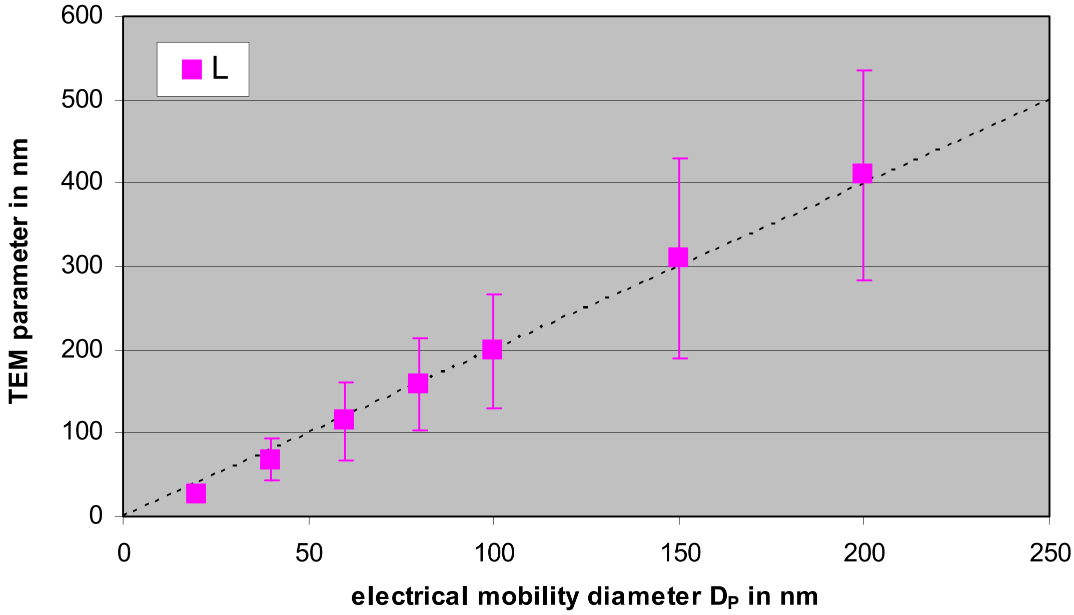

Fig.10
Length L (+standard deviation) based on TEM (cylinder model fig.3) and mobility diameter Dp (the dotted line represents L = 2 Dp)

E Summary

The SMPS measurement allows the analysis of combustion aerosol with respect to the particle size distribution in relation to the emitted particle~~s~~ numbers.
The functional principle is based on the electric mobility diameter Dp, which in itself does not give information on the geometry of the particle.
As a quantitative measurement procedure the SMPS has certain deficits with regard to calibration and reproducibility (2).
It is not suitable for instationary test bench and therefore it cannot be used for test cycles, as mandated.

In order to correlate the electric mobility diameter determined by SMPS with the geometrical structure and composition of agglomerate in engine emission, we collected classes of aggregates by size and analyzed them by TEM.

Using geometrical parameters for shape description of particle aggregates a correlation between the mobility diameter Dp determined by SMPS and particle size was established. Assuming that an agglomerate best fits to the shape of a cylinder, its diameter corresponds to Dp, its length to 2 x Dp.

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Abbreviations

TEM Transmission Electron Microscope
SMPS Scanning Mobility Particle Sizer
CPC Condensation Particle Counter
DMA Differential Mobility Analyser