H.U. Franke, H. Tschöke, P. Veit
Otto-von-Guericke University of Magdeburg
Magdeburg / Germany

3D-Morphology of diesel oil soot particles and rape oil methylester soot particles

2nd ETH Workshop
„Nanoparticle Measurement"
Zurich, Aug 7, 1998

„3D-Morphology of diesel oil soot particles and rape oil methylester soot particles

Franke, H.-U.; Tschöke, H.; Veit, P.
Otto-von-Guericke-University of Magdeburg, Germany

The examination methods developed by the Institute of Measurement Technique and Reciprocating Engines and the Institute of Experimental Physics reveal to what extent operation parameters, combustion techniques, fuels and engine parameters influence the soot particles' size and their 3-D structure.
Our investigations are carried out using a Transmission Electron Microscope. Along with the size distribution statement, they also supply information about the form and shape of particles. These are single particles with an average diameter of approximately fourty six plus minus fourteen nm and particles with the form of agglomerates, which have a chainlike structure. An evaluation carried out by TEM photographs assumed, do not consist of continous chain-structured rows of particles, but rather they connect like links in a chain. A further view oh the particles in Diesel-engines' exhaust fumes consist of diffuse, simply structured particles, the so-called „droplets".
Fig. 1 is a typical TEM picture, where the three different particle structures are shown which appear in every test.
Note that in both transparent light photographs (TEM) and opaque light photographs (grid electron microscope and optical microscope) only the projections of the three-dimensional particles are shown.
Particles of extremly varied shapes settle on the carbon-coated copper grid while the partial exhaust gas stream flows by. The covered copper grid is placed under the TEM and images are recorded from different angles while the sample is tilted. The images taken during tilting provide a so-called multiple picture configuration which can be used for triangulation in order to determine the three-dimensional coordinates of defined points.
For sampling from raw gas a flow-related optimized sampling set-up was developed permitting a „gentle" covering of the sample carriers (copper grids with carbon layer) by removing a part of the exhaust gas from the flow vertically and having the exhaust gas pass by the copper grid in a direction parallel to its surface. This prevents the particles from impacting too harshly during the settling process. The principle is shown in a scheme in **Fig. 2**.
A simply structured agglomerate consists of particle agglomerates, which are wrapped by chain-like structures (**Fig. 3**). It is not the particles that are wrapped, but the agglomerate as a whole, so that the original form of the agglomerates, the impressive unusual three-dimensional shape of the larger agglomerate, is not recognisable.
For a better understanding some parameters of 2D-agglomerate analysis have to be described:
ECD (Equivalent Circle Diameter)
In this case is accepted that the determined surface area of the single objects are derived from a

circular area. In order to seperate the single components, first of all standard agglomeration algorithms have to be modified. The segment algorithms can be supported by density analysis. The hypothesis is that the overlapping of contact points of elementary agglomerate segments express themselves on discret leaps in blackening. The algorithms have to be extended in object persecution routines, which allow the traces of the marked picture points during the variation to be quantified.

Figure 4 shows the ECD's for two different agglomerates.

Virtual holes are completely enclosed by object points not to object-belonging picture areas. Evaluation of this information already supplies statements from 2-D pictures about the space-filling degree.

The convex cover is the area which is built by a line, that includes all the obkect points and shows exclusively a curve direction. The area which is marked on **Fig. 5** as „convex cover", is the surface area.

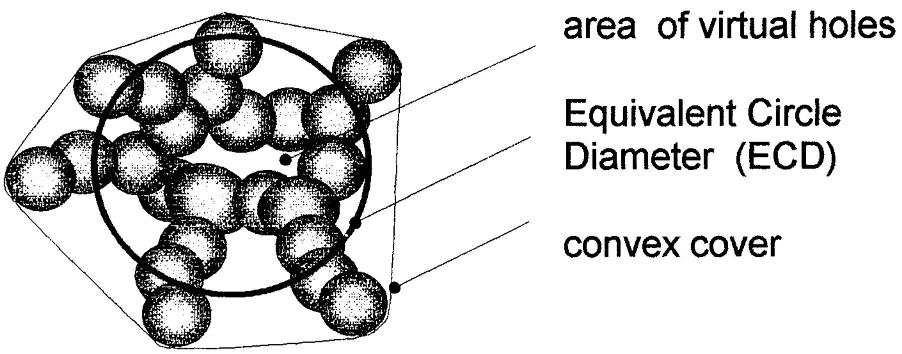


Figure 5: Schematic representation of particle agglomerates as a definition the measured quantities the form-factors

ECD	Equivalent Circle Diameter
A	area of agglomerate
H	area of virtual holes
F	2-D-shape factor / 4π area/perimeter^2
K	area of convex cover
C	2-D compactness (A/K)

The form factor contains except for information on the global shape of an object, for example circle or rectangle, also information on the local course of the contour (smooth or rough through hollows and projections). For instance through the digitize-occourance and the discrimination of the contour-course for a visual mathematical circle the value 1 can not be exactly reached. Due to an obvious fractle structure inside a structure field from 10 nm to approximately 55 µm, the application of the techniques offers a determination of the fractle dimension.

Picture	Formula	Formula – faktor
1. Circle		1
2. Square	$\pi/8$	0,39
3. Rectangle		
3.1 Length (a) : Width (b) 10 : 1	$(a+b)^2$	0,26
3.2 Length (a) : Width (b) 100 : 1		0,031
4. Sphereconglomerates		
4.1 Touch of two circles (100 % total area)		0,50
4.2 Overlapping of 2 circles (99,4 %)		0,61
4.3 Overlapping of 2 circles (95,1 %)		0,73
4.4 Overlapping of 2 circles (82,1 %)		0,88
4.5 Overlapping of 16 circles (chain similar 3.1, 63 % of the 16 circles‘ area		0,26

A way of clearing up the 3D structure can be seen in the manufacture of a series of images taken during tilting. **Fig. 6** shows such a multiple picture configuration.
By means of the technology available, the preparations were tilted around an axis between -60° and +60° in angle-steps of 10° in direction of the electron beam and against the normal of the specimen. A schematic view of the situation is represented in **Fig. 7**.
During this process a defined point of the object plane recorded from the different angles. This permits an accurate determination of the three-dimensional coordinates of the point with suitable algorithms using redundancy and determination of the angles. By repeating this procedure for other defined points it is possible to measure the three-dimensional structure of an agglomerate.

TEM pictures from different angles

↓

Measurement of defined points for orientation

↓

Triangulation

↓

Three-dimensional evaluation of points at known orientation

An agglomerate with defined points from 1 to 27 for a certain angle is situated in the upper half of **Figure 8 (8a)**. The calculated three-dimensional coordinates of these points are shown in perspective. The lower picture gives an impression of the spatial shape **(8b)**. The video which was shown during my presentation intensifies this impression.
For objects larger than 10 µm the depth-sharpness of the TEM can be used to provide information. Classic stereometric evaluation methods for complete 3D reconstruction fail to examine the subject sufficently: on the one hand due to the significant cover of the greater particle fields; and on the other hand due to the percularity of the contrast origin. The use of the multi-

ple picture association requires the clear and practical identification of single object areas and the pursuit of their three-dimensional trace during the tilt experiment. Triangulation can be used to realise this task.

Reliable commercial programmes are used to view complete analysed agglomerates. For this purpose, a sphere-simulation is used, in which the centre of gravity's 3D-coordinates and the equivalent circle diameter of the sphere-approaching particle components need to be known.

In **video** sequences the results of the three-dimensional morphology are reproduced. The unusual three-dimensional shape is shown in an impressive way.

Summary

The methods of three-dimensional representation of particle agglomerates with measurement of the three-dimensional coordinates of defined points permit a more in-depth understanding of the structures. It is hoped that continued investigations into this subject will provide further insights into the formation of agglomerates.

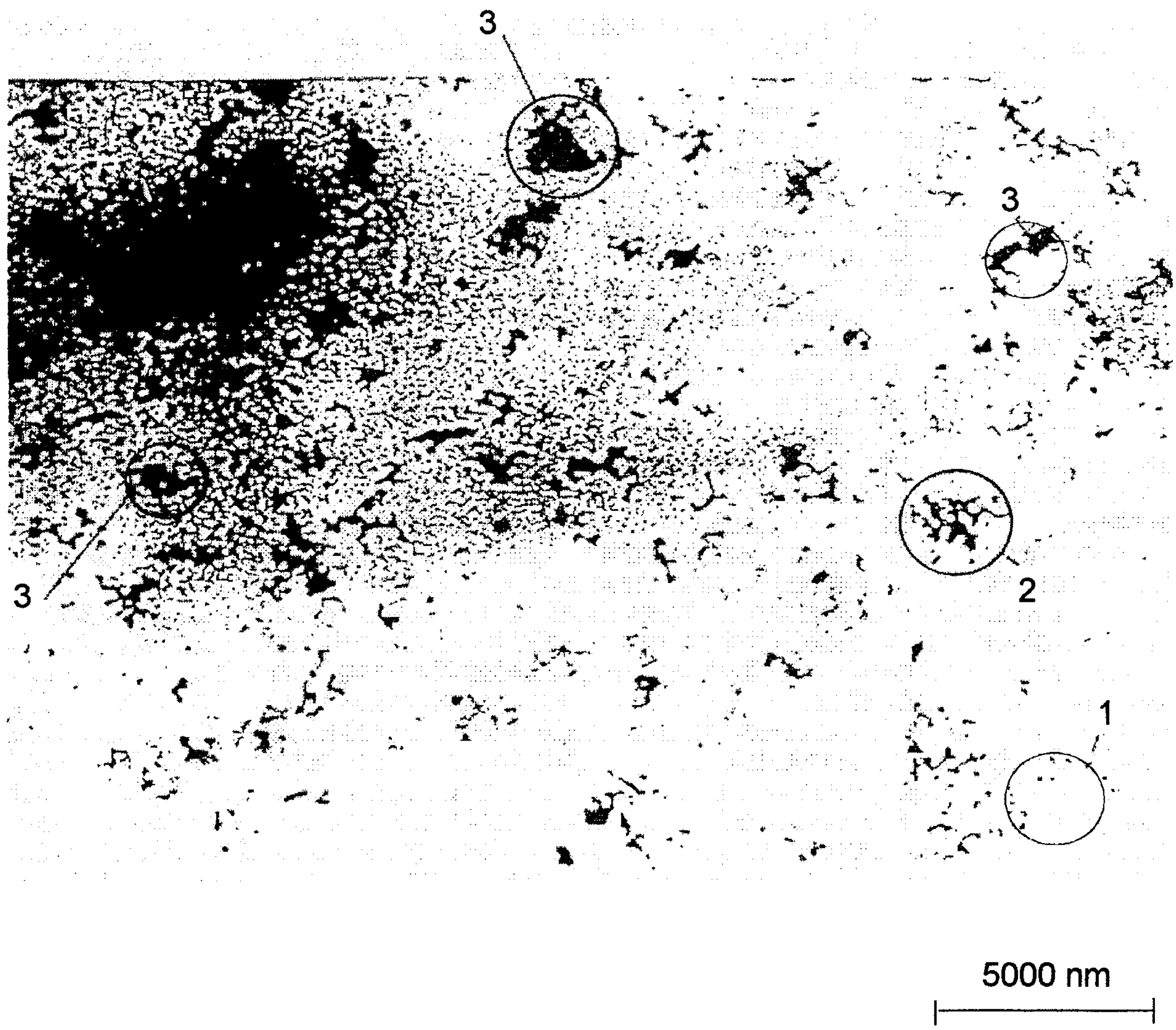


Figure 1: Typical TEM - picture with single particles (1), agglomerates (2) and „droplets“ (3)

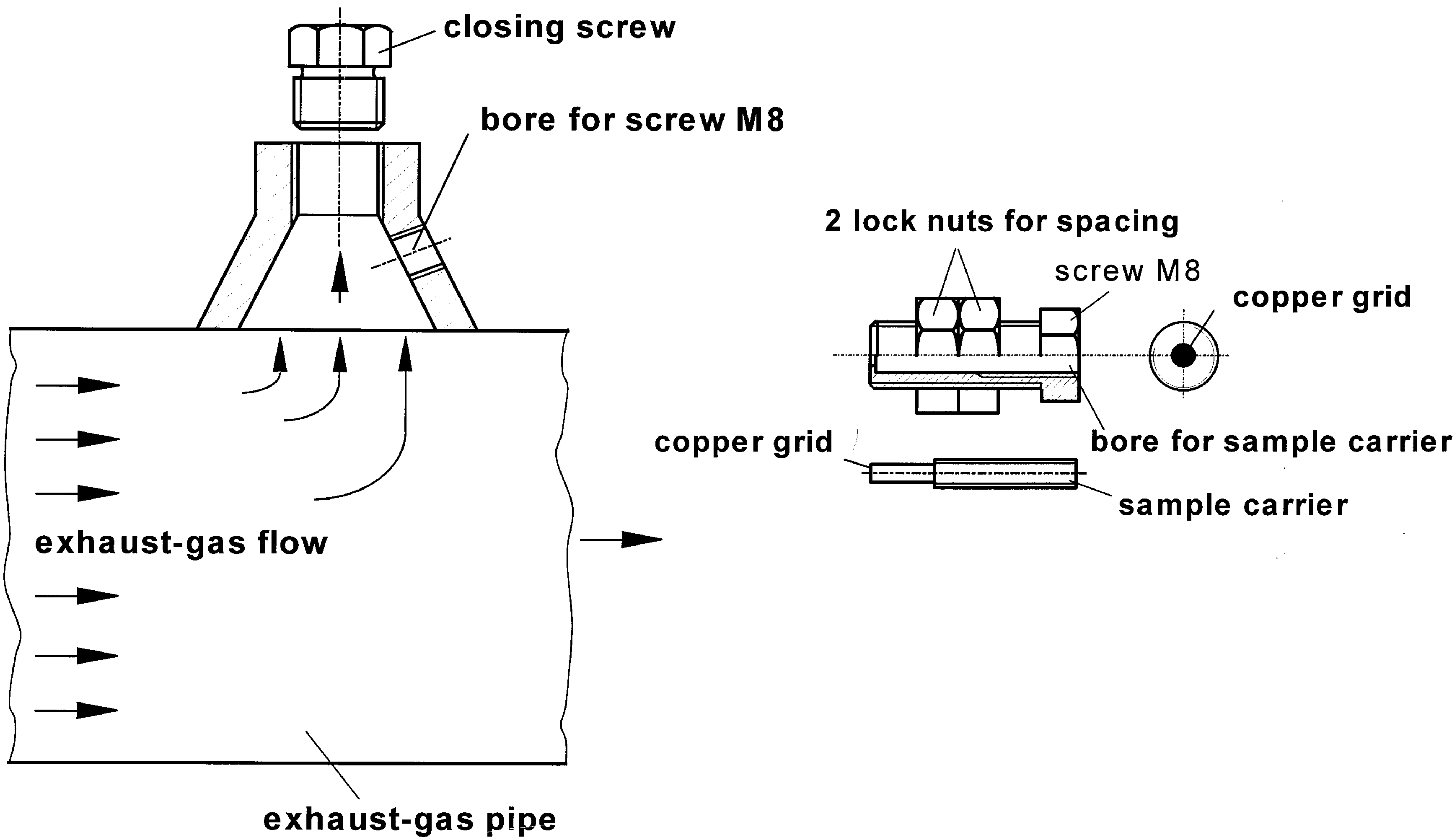


Figure 2: Scheme of sampling device for microscope investigations

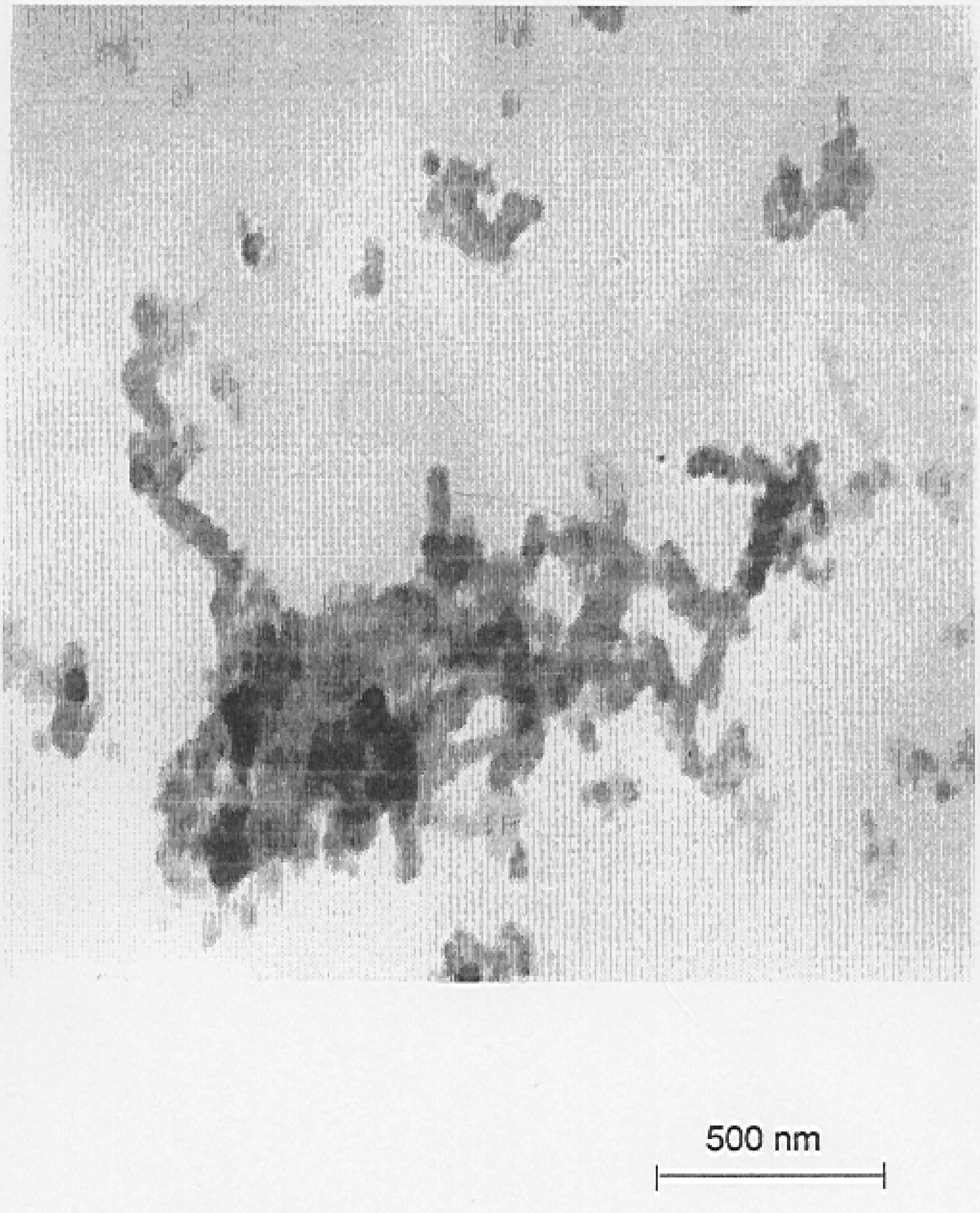
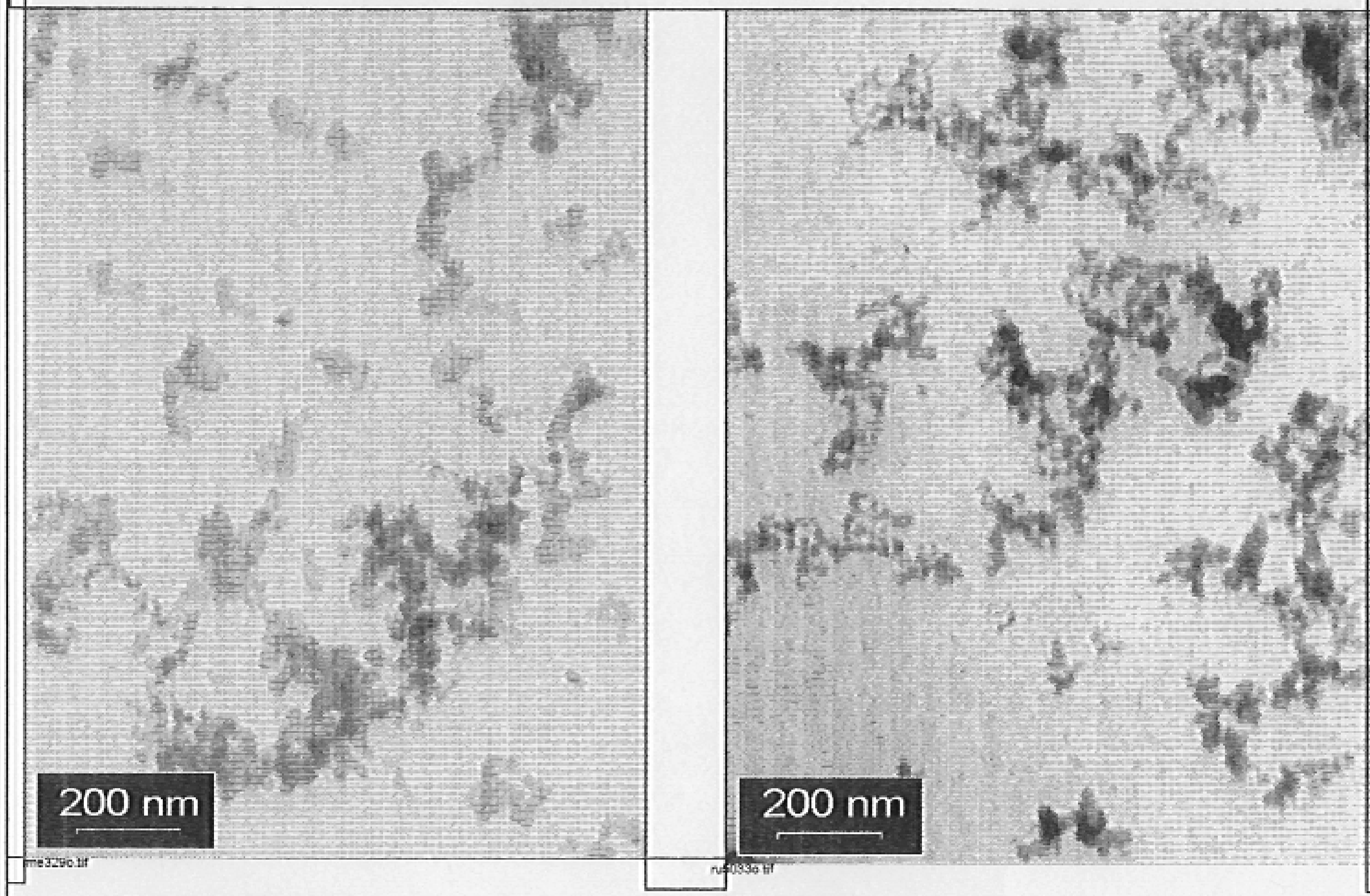


Figure 3: Simply structured agglomerates



rape oil methylester
ECD = (90 ± 4) nm

diesel oil
ECD = (70 ± 6) nm

Figure 4: TEM-micrographs of rape oil methylester soot and diesel oil soot

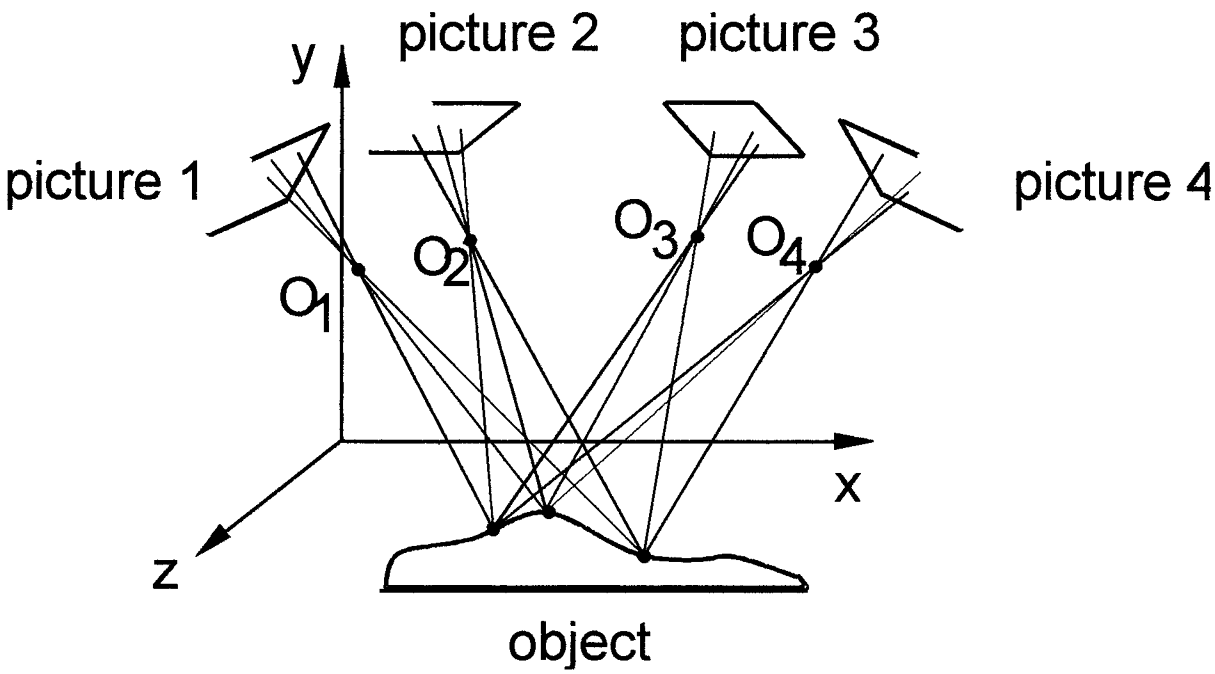


Figure 6: Multiple pictures configuration for triangulation

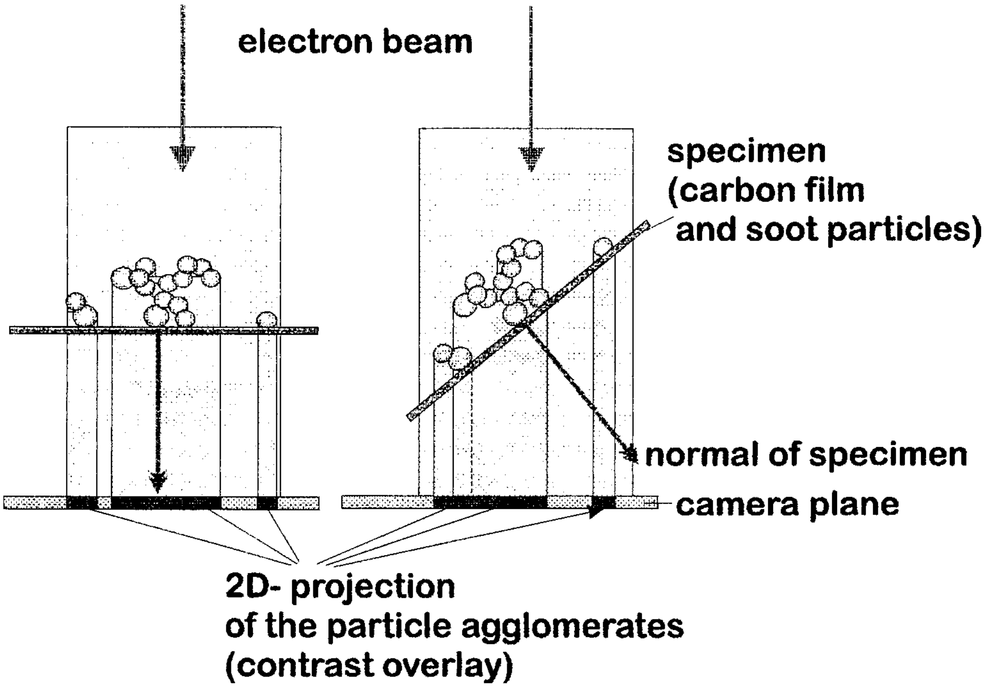


Figure 7: Schematical presentation of the 3D- to 2D-transformation by tilting transmission electron microscopy experiments

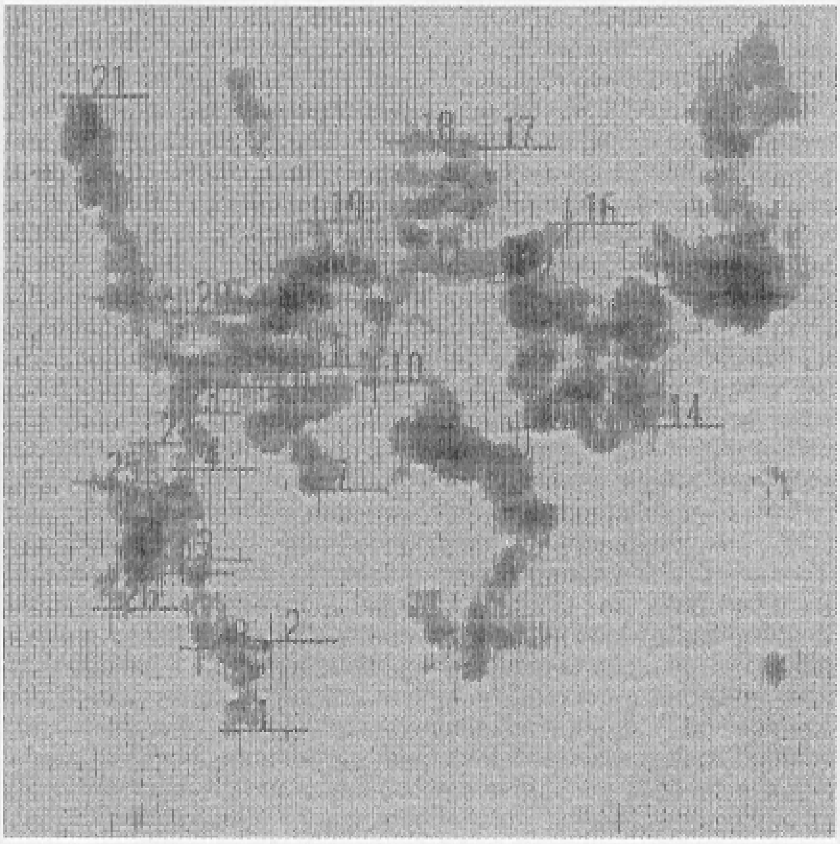


Figure 8a: TEM picture of an agglomerate with defined points

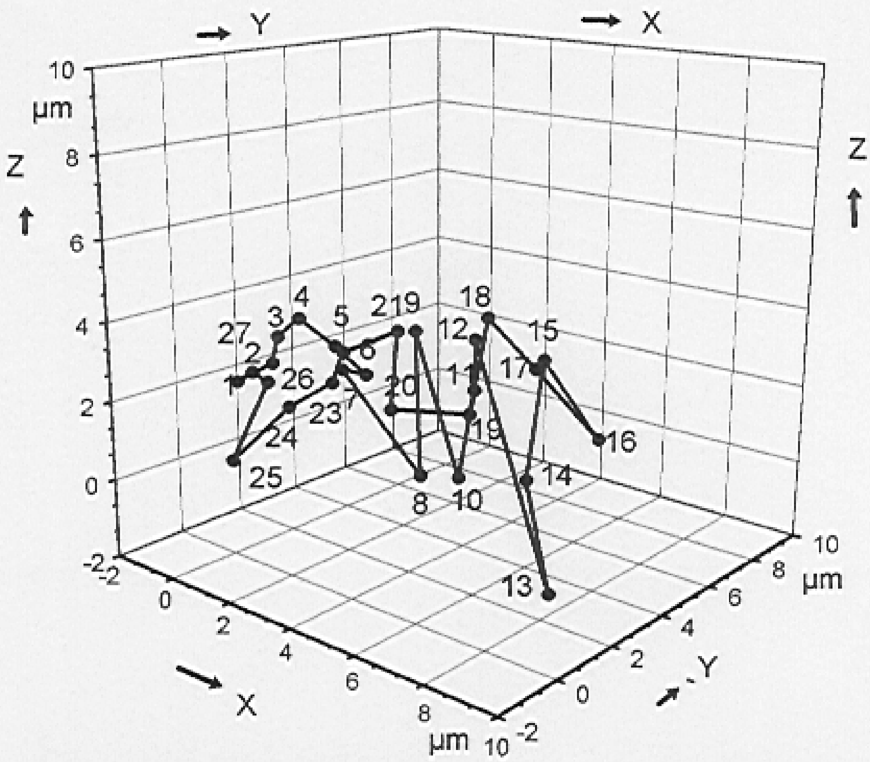


Figure 8b: Three - dimensional configuration of the agglomerate (Fig. 8a)