# Case study – fumed silica

# Comparison of different particle size analysis methods

When comparing particle size data for a material that was characterised with different techniques, one realizes that the results often vary significantly. The answer to the question "How big is a particle?" often depends as much on the measurement technique as on the actual particle size.

This application note explores that challenge using fumed silicas as test material. We compare results from dynamic light scattering, sedimentation size analysis against the new PowMaster particle analyser. We provide some theoretical background to the different diameter definitions that allow us to convert different results into each other.

This shows that the new PowMaster instrument delivers comparable diameter results, in addition to measuring the mass and effective packing density of single aggregates.

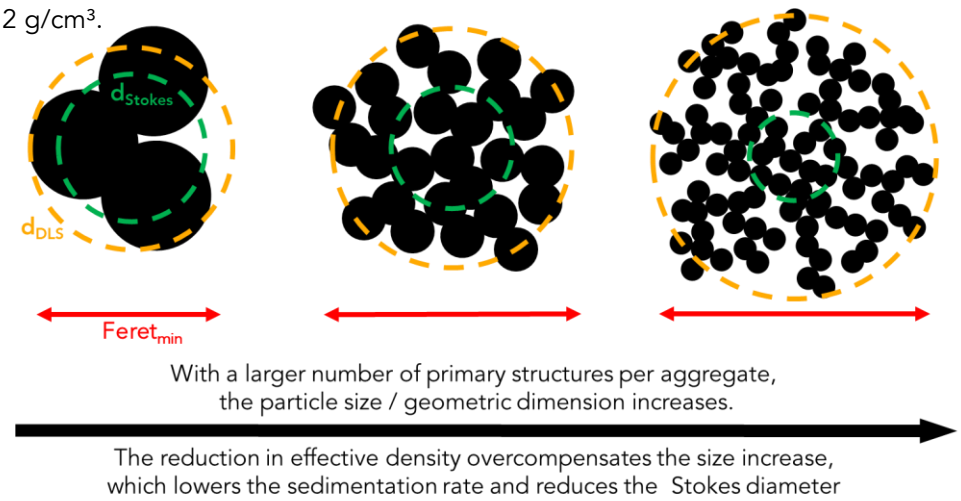
Although only fumed silica is discussed here, the findings equally apply to a broad range of other materials such as carbon black, titanium dioxide, colour pigments, or effect pigments.

## On snowflakes, water droplets and aggregated particles

To understand the difference between different particle diameter definitions, one can think of the difference between snowflakes and water droplets. A snowflake is a particle with large geometric dimensions (~$Feret_{min}$) and with a high drag-force coefficient (~low diffusion coefficient). The snowflake's diameter ($d_{DLS}$) would be high if it were measured with dynamic light scattering. As a snowflake is fluffy i.e. complex structured with a low packing density, it falls slowly through the air. A measurement of this sedimentation velocity is used to obtain the Stokes-diameter ($d_{Stokes}$). In contrast to the $d_{DLS}$ this $d_{Stokes}$ is relatively low for snowflakes. If one would "restructure" the particle by melting it (or compacting, sintering, … ) into a water droplet, the particle size and structure changes.

1. The particle's size and drag-force coefficient decrease, and with it, the **$d_{DLS}$ decreases**.
2. The particle packing density increases, which results in a higher sedimentation velocity. Consequently, the **$d_{Stokes}$ increases**.

In this example, the mass of the snowflake/water droplet is preserved. While there is a difference in the density between water and ice, it is negligible compared to the influence of the effective density. A general rule is that **the larger the difference between the true material density ($\rho_{true}$) and the effective density ($\rho_{eff}$) of a particle is, the larger the difference between the results from DLS and any sedimentation analysis becomes.** The same correlations can be applied to fumed silica aggregates, which all vary greatly in their particle packing density, although the material density is always 2.2 g/cm³.



### Comparison of PowMaster data with DLS, CPS and Lumisizer

Dynamic light scattering (DLS), Centrifugal photosedimentation (CPS) and the Lumisizer are widely used methods to measure particle sizes. However, they use different physical measurement concepts and yield different results. DLS calculates the particle diameter based on its diffusion coefficient, while the CPS and Lumisizer probe the sedimentation rate in a fluid and calculate a diameter based on Stokes' law. The same physical properties can be used to measure the particle size when the particles are suspended in air, i.e., are aerosolized. Here we speak of the mobility diameter ($d_{mob}$) and aerodynamic diameter ($d_{aero}$).
To compare results from different sizing methods, the different diameter equivalents must be converted into each other using the equations in the table. (see appendix for more details).

| | Drag-force coefficient<br>~(Diffusion-coefficient)$^{-1}$ | Terminal settling velocity<br>(Stokes ' law) |
|---|---|---|
| **Air** | $d_{mob}$ Mobility diameter<br>PowMaster | $d_{aero}$ Aerodynamic diameter<br>calculated from PowMaster |
| **Water** | $d_{DLS}$ Dynamic light scattering | $d_{CPS}$ Centrifugal photo-sedimentation<br>$d_{LUM}$ Lumisizer |
| | $d_{DLS} \approx 1.1 \cdot d_{mob}$ (±20%) | $d_{LUM/CPS} = \sqrt{\frac{\rho_{eff}}{\rho_{true}}} \cdot d_{mob} \cdot 0.953$ |

*Table 1 Comparison of equivalent diameters based on the physical effect and fluid used.*

***NOTE: The term "hydrodynamic diameter" is used frequently for the equivalent diameters measured with DLS and any sedimentation analysis, like CPS, despite their fundamental differences. To avoid confusion $d_{DLS}$ , $d_{CPS}$ and $d_{LUM}$ are used instead.***

Further, the weighting of the results has to be taken into account. The PowMaster system relies on counting single particles, i.e., measures number-weighted distributions of the particle mass and diameter, which allows for a direct calculation of mass-weighted distributions.
DLS, CPS and the Lumisizer measure light-intensity-weighted size distributions, which can be converted into volume-weighted distributions after making assumptions on the optical properties of the particles. Mass-weighted and volume-weighted size distributions are not the same since the density of the particle changes with the particle size. Those differences are not considered here, as the differences that arise from the diameter conversion are much larger.

## Diameter, mass and density of fumed silica aggregate

### Sample preparation

Three fumed silica samples with different specific surface areas (SSA) were analysed with the PowMaster, CPS, Lumisizer and two different DLS systems. For that, stock suspensions of three fumed silica in water (conc. 10g/L) were prepared and deagglomerated with ultrasound (400 J/ml). For the PowMaster, it is necessary to aerosolize the isolated silica aggregates, which is achieved by diluting the stock suspension down to 0.01 to 0.5 g/L (depending on the sample), nebulizing it, and drying the suspension droplets.

## Results from the PowMaster analysis

With the PowMaster, the number-weighted distributions of the particles' mass and (mobility) diameter are measured directly (dark blue). The mass-weighted distribution (light blue) and the particle density (red dots) are calculated from that. Fumed silica forms aggregated particles; therefore, the effective (apparent) density ($\rho_{eff}$) is below the true material density of fumed silica ($\rho_{true}$; 2.2 g/cm³). Figure 1 shows that the $\rho_{eff}$ declines as particle size increases, which is a direct result of more branched-out, less densely packed particles. Generally, the correlation between mass and diameter is different from that of spherical particles.
The particle mass is directly proportional to the diameter to the power of 2.62. This exponent, frequently called "fractal dimension," would be 3 for a spherical particle.

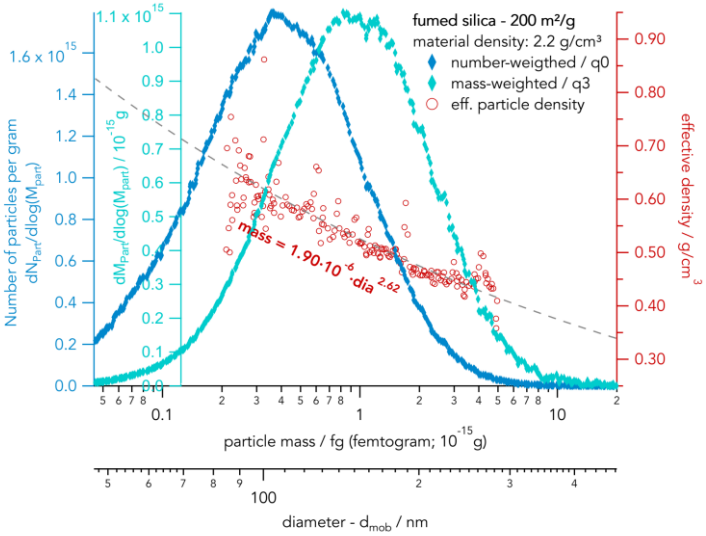



*Figure 1 Number- and mass-weighted distribution of that mass and diameter of a fumed silica with 200 m²/g SSA*

Since mass and diameter are measured independently from each other, more than one median value can be used to describe the particle size distribution. Further, by integrating the particle number distribution over the mass, the absolute number of particles per gram of powder can be obtained. This represents a **"particle concentration in a powder"**, which is a valuable parameter to like powder-specific properties (price, SSA, oil absorption number, ...) with the level of the isolated particle.

| median values | number-weigthed | mass-weigthed |
|---|---|---|
| $mass_{50}$ | 0.386 fg | 0.908 fg |
| $d_{mob,50}$ | 106.8 nm | 148.2 nm |
| $\rho_{eff,50}$ | 0.604 g/cm³ | 0.533 g/cm³ |
| Mass-diameter correlation: $mass = 1.90 \cdot 10^{-6} \cdot dia^{2.62}$ | | |
| Number of particles per gram: $1.61 \cdot 10^{15}$ | | |

*Table 2: Median values and characteristic parameters*

## Comparing PowMaster data with CPS, Lumisizer and DLS

The CPS, Lumisizer and DLS particle size distributions were measured in water using different measurement concepts. To be comparable to the CPS and Lumisizer data, the PowMaster data were converted into an approximate Stokes diameter ($d_{stokes}$) using the equations in Table 1. For the Lumisizer and CPS, light-extinction-weighted distributions were available. No Mie-scattering correction was applied, which would result in smaller diameter values. The results from DLS were measured in back-scatter mode, are intensity-weighted and can be compared with the mass-weighted $d_{mob}$. In Figure 2, the $d_{10}$, $d_{50}$, $d_{90}$ and mean values from the CPS, Lumisizer and DLS are plotted.

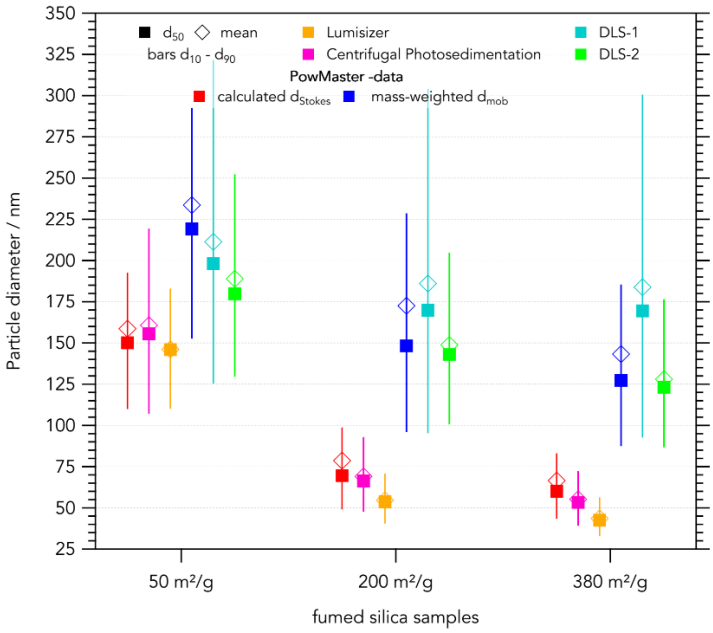



*Figure 2 Diameter values ($d_{10}$, $d_{50}$, $d_{90}$, mean) from different sizing methods.*

The $d_{CPS}$ and $d_{LUM}$ values are a factor of 2 to 4 below the $d_{DLS-1}$ and $d_{DLS-2}$. The same difference can be observed in the diameter results from the PowMaster ($d_{stokes}$ vs. $d_{mob}$). The leading cause for this difference is that the $\rho_{eff}$ of the silica aggregate is significantly below the $\rho_{true}$ for silica, 2.2 g/cm³. This also implies that the values from $d_{CPS}$ and $d_{LUM}$ are significantly below the aggregates geometric dimensions.
Theoretically, CPS and Lumisizer should yield the same result, as both instruments use the same concept. However, the data differ significantly due to different instrument designs and data processing routines. The same applies to the DLS data.
Even though, CPS, Lumiszer and DLS are liquid-based analysis methods and the PowMaster relies on aerosolized particles, the diameter estimates agree with each other within the considerable uncertainties.

*There is no "true particle diameter" for non-spherical particles. The results are always dependent on the measurement methods. The particle mass is independent of the measurement method.*

## Using the PowMaster

If you are working with material of unknown or difficult to analyse particle size, femtoG can help. Our advanced particle analysis technology offers unprecedented insight into particle size, structure, and other parameters critical for your material's properties.

**Contact us today:**

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# Appendix

## Understanding particle diameter

Fumed silica forms highly aggregated particles, which are analysed here. Since those particles are not spherical, any particle diameter is an equivalent diameter. Any reported diameter value must be understood as: "Within the chosen test conditions, this silica aggregate behaves like a sphere with a defined density, refractive index, … that has a diameter of X nanometers".
Unsurprisingly, different test methods that rely on different physical effects yield different particle diameter values. However, there are theoretical frameworks to predict particle diameter and to compare equivalent diameters from different methods.

The PowMaster system measured a so-called mobility diameter ($d_{mob}$), which compares the drag-force coefficient of a particle with a reference sphere using the concept of electrophoresis. Dynamic light scattering measures the same physical parameter, but uses a different concept. Here, the Brownian motion of a particle in water is detected via photon-correlation spectroscopy, from which a diffusion coefficient is calculated. The latter is indirectly proportional to the drag force coefficient. The $d_{mob}$ and $d_{DLS}$ are similar, since both scale with the geometric dimension of a particle, but effects like the slip of gas molecules and the existence of hydration layers prevent a 1:1 comparison. As a **rule of thumb, the $d_{DLS}$ is ~10% (±20%) larger than the $d_{mob}$** for aggregated particles whose formation can be described with the diffusion-limited cluster aggregation model (DLCA).

Centrifugal Photosedimentation analysis and the Lumisizer rely on detecting a particle's sedimentation time (or velocity) in a liquid due to gravity or centrifugation—particles with a larger diameter and higher density sediment faster than smaller and less dense particles. If the density is known, this sedimentation rate can be converted into the so-called Stokes diameter ($d_{Stokes}$) by applying Stokes ' law. Hereby, it is important to acknowledge that the effective density of structured or porous particles is below the material density. Since the former is rarely known and dependent on the particle structure, the material density is used for the diameter calculation. Following this convention, the $d_{Stokes}$ and $d_{DLS}$ can be converted into each other if the effective particle density ($\rho_{eff}$) is known. The ratio between $\rho_{eff}$ and $\rho_{true}$ is hereby equal to the particle's porosity.

$$d_{Stokes} = \sqrt{1\text{-porosity}} \cdot d_{DLS} = \sqrt{\frac{\rho_{eff}}{\rho_{true}}} \cdot d_{DLS}$$

This approach allows for a standardized analysis, but in the case of fumed silica, this can result in an underestimation of the diameter by a factor of 5 or more.
The aerodynamic diameter is equivalent to the $d_{Stokes}$, with the difference that it is measured in air. Further, there is the convention that the particle density is 1 g/cm³. The effective density or material density is not considered. Consequently, the $d_{aero}$ is primarily used to describe the aerodynamic behaviour of particles instead of their size.

## Calculating theoretical particle diameters

Fumed silica is produced via flame-spray pyrolysis. The formation of aggregates can be described by the diffusion-limited cluster aggregation model (DLCA), which allows for the description of aggregate structures and the calculation of particle diameter. To illustrate the influence the particle structure has on the different diameter analyses, we compare theoretically calculated particle diameters for particles with the same mass of 1 fg (femtogram, $10^{-15}$g). Detailed theoretical description and the used equations can be found in Sorensen 2011 [1], and Babick et al. 2012 [2,3]
For the calculation, the diameter of primary structures ($d_{PS}$) is estimated based on the SSA for the fumed silica sample characterized here. The number of primary structures per aggregate ($N_{PS}$) is

calculated from their theoretical mass. From $N_{PS}$ and $d_{PS}$, various equivalent particle diameters can be calculated (Table 3).

1. As the SSA increases, the $d_{PS}$ declines. At a constant mass, an aggregate then consists of a larger number of primary structures, i.e., the aggregation level increases
2. With an increase in the aggregation level, the geometric dimensions of the particle increase, which leads to a higher drag-force coefficient / lower diffusion coefficient, and therefore, **DLS reports a higher particle diameter**
3. The higher structural level increases porosity, reduces the effective particle density and thus reduces the sedimentation velocity i.e. the stokes-diameter. **The CPS and Lumisizer report a lower diameter.**

| Specific surface area of the fumed silica sample: | | 50 m²/g | 200 m²/g | 380 m²/g |
|---|---|---|---|---|
| Diameter of primary structure $d_{PS}$ | $\frac{6}{SSA \cdot \rho_{silica}}$ | 55 nm | 14 nm | 7 nm |
| Number of primary structures per aggregate … $N_{PS}$ | $\frac{1\ fg}{\frac{\pi}{6} \cdot d_{PP}^3 \cdot \rho_{silica}}$ | 5 | 342 | 2348 |
| Mobility diameter - $d_{mob}$ | $d_{PS} \cdot N^{0.46}$ ; $N_{PS} < 100$<br>$0.65 \cdot d_{PS} \cdot N^{0.56}$ ; $N_{PS} > 100$ | 118 nm | 233 nm | 360 nm |
| Dynamic light scattering - $d_{DLS}$ | $d_{PP} \cdot \left(\frac{N_{PS}}{1.2}\right)^{1/1.89}$ | **120 nm** | **272 nm** | **396 nm** |
| Stokes diameter - $d_{Stokes}$ (Lumisizer, CPS) | $\sqrt{\frac{N_{PS} \cdot d_{PS}^3}{d_{DLS}}} = \sqrt{\frac{\rho_{eff}}{\rho_{true}}} \cdot d_{DLS}$ | **85 nm** | **57 nm** | **47 nm** |
| Effective (apparent) hydrodynamic density – $\rho_{eff,DLS}$ | $\frac{m}{\frac{\pi}{6} \cdot d_{DLS}^3}$ | 1.16 g/cm³ | 0.15 g/cm³ | 0.04 g/cm³ |
| Ratio $d_{DLS}$ to $d_{mob}$ | $\frac{d_{DLS}}{d_{mob}}$ | 1.02 | 1.17 | 1.10 |

*Table 3 Calculation of three equivalent diameters for fumed silica with different specific surface areas*

# References

[1] C. M. Sorensen The Mobility of Fractal Aggregates: A Review https://doi.org/10.1080/02786826.2011.560909 Aerosol Science and Technology, 45:7, 765-779

[2] Frank Babick, Manuel Vorbau, Michael Stintz, Characterization of Pyrogenic Powders with Conventional Particle Sizing Technique: II. Experimental Data https://doi.org/10.1002/ppsc.201000025 Part. Part. Syst. Charact. 29 (2012) 29 116-127

[3] Frank Babick, Karin Schießl, Michael Stintz Characterization of Pyrogenic Powders with Conventional Particle Sizing Technique: I. Prediction of Measured Size Distributions https://doi.org/10.1002/ppsc.201000024 Part.Part.Syst.Charact. 29 (2012) 104-115