Department of Glass and Ceramics
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Characterization of particles via laser diffraction

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1. Theory

Information about particle size is one of the most important parameters in material science and technology, pharmacology and ecology.

1.1. Particle size and equivalent diameters

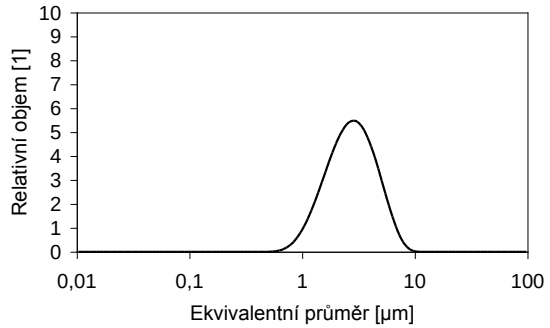
In this context, the quantity describing the particle size is a linear dimension, the length (meter in the International System of Units). In this meaning, size can be clearly defined only for spheres, where the size corresponds to the diameter (or radius). The size of particles with other shapes must be defined with respect to the method of measurement. The derived diameters are determined by the measurement of a selected property, which is dependent on the particle size and relating this to some linear dimension. The most commonly used of them are the **equivalent diameters**, which primarily are the diameters of equivalent spheres.

Important equivalent diameters are: volume equivalent diameter (diameter of sphere with identical volume as given irregular particle), surface equivalent diameter (diameter of sphere with identical surface as given irregular particle), **Stokes diameter** (equivalent diameter corresponding to sphere diameter with the same settling velocity as the non-spherical particle), hydrodynamic equivalent diameter, sieve diameter (equivalent diameter corresponding to a sphere diameter which can pass through a sieve with defined grid size), equivalent diameter determined via laser diffraction (diameter of a sphere providing the identical electronic response to optical signal as the non-spherical particle), area-equivalent diameter, volume-surface diameter (also called natural or Sauter diameter) etc. Another way to describe the particle size, widely used in image analysis, are statistical diameters (e.g. chord length, Feret diameters).

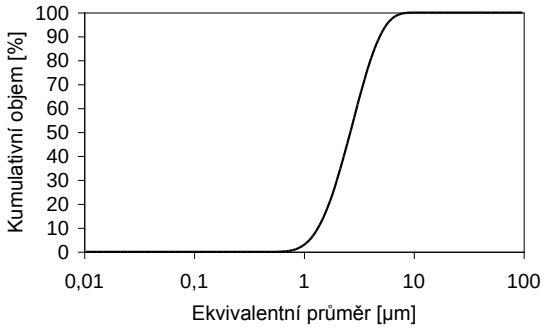
1.2. Particle size distribution

Particle systems are usually polydisperse (not monodisperse), which means that the particles have different sizes. These systems are characterized by distribution functions, which provide information about the amounts (e.g. number or volume) of particles with different sizes in the system.

Graphical representations of distributions are the granulometric curves, i.e. frequency curves - ***f(x)***, which show the ratio of particle amount belonging into a certain size class, or cumulative curves – ***F(x)***, which show the percentage of smaller (or larger) particles than a given size (e.g. equivalent diameter) **x**. Cumulative curves can be obtained by integration of frequency curves and frequency curves can be obtained by derivation of cumulative curves. The information is in both cases the same.



Frequency curve



Cumulative curve

Distributions with one maximum in the frequency curve (i.e. one inflection point in the cumulative curve) is called monomodal. Analogously, distributions with two maxima are bimodal, with three trimodal, or with many of them polymodal. The particle size corresponding to the maximum of the frequency curve is the **mode** (D_m), around which the frequency (e.g. number or volume) of particles is highest. The size corresponding to 50 % in the cumulative curve is called **median** (D_{50}), meaning that 50 % (e.g. in number or volume) of particles are smaller and 50 % of particles are larger than this size. However, a complete information about particle size distribution is provided only by the whole distribution curve (frequency or cumulative curve).

In general, there are distribution curves weighted with respect to the number of particles (f_0), length (f_1), area (f_2) and volume (f_3). From the practical point of view, only number-weighted curves (obtained e.g. via image analysis) and volume-weighted curves (obtained e.g. via laser diffraction), which are similar to mass weighted ones (obtained e.g. via sieve analysis or sedimentation) when the density of particles is identical, are important. It has to be emphasized that the comparison between number-weighted and volume-weighted distributions required a recalculation of one of the two types of distribution (which is trivial for spherical particles, but not complicated for non-spherical particles as long as the shape is size-invariant).

1.3. Anisometric particles

Isometric particles are those with approximately same dimensions in each direction, e.g. spheres or regular polyhedra. Anisometric particles, on the other hand, do not have similar dimensions in each direction; those are for example needle shaped particles, platelets, long cylinders, etc.

Comparison of particle size measurements obtained via different methods leads to the conclusion, that only in the case of isometric particles are the results relatively similar (after considering the differences in instrumentation and methodology), whereas the results for anisometric particle systems show systematic deviation, which is the more significant the more anisotropic particle systems are.

A universally acknowledged approach for the quantitative description of particle shape does not exist. From the pragmatic point of view, it seems to be the most reasonable approach choosing some model shape (rotary cylinder, spheroid, etc.) and describing the particle shape via one number – the "**shape factor**". The practical of measurement of the shape factor is dependent on the particular problem.

For example, if there are distributions measured via sedimentation and laser diffraction of platelets available, it is possible to calculate the "LS shape factor":

$$R = \pi \left(\frac{D_i^L}{D_i^S} \right)^2 ,$$

where D_i^L is the value of diameter corresponding to quantile i measured via laser diffraction and D_i^S is the analogous value of diameter measured via sedimentation. Such a shape factor describes to some extent a "mean" shape (or "average" aspect ratio) of the size fractions of a particle system. The shape of particles does not have to be similar in every size fraction; therefore, it can be useful to display the data into **SSD** ("**shape size dependence**") **plot**.

1.4. Measurement techniques

For the measurement of particle size distributions, there is a variety of methods. The choice of a suitable method is dependent on many factors, e.g. the particle size, measurement time, accuracy of measurement, etc. The most widespread methods are sieve analysis, sedimentation methods, image analysis, dynamic light scattering and laser diffraction. The sedimentation method is a traditional method of particle size analysis. Its advantages are a simple measurement principle instrumentation, easy measurement and straightforward interpretation of results. The disadvantages are relatively long measurement time, narrow range of measurable particle size and high sensitivity to preparation of sample and agglomeration. Too large particles cause turbulent flow and small particles are influenced by Brownian motion. Therefore, the range of measurement is between 1-100 μm (from 0.1 μm in the case of centrifugal methods).

1.4.1. Sedimentation methods

In polydisperse particle system (particles in suspension), the large particles settle faster than the small ones (due to gravitational force).

A standard instrument for sedimentation analysis is the Andreasen apparatus (graduated cylinder and pipette with three-way valve). After standardized preparation (deagglomeration, shaking, ultrasonication, boiling and cooling) of the suspension, it is placed into the Andreasen apparatus and the particles start to settle. In certain time intervals, a small amount (in the case of 600 ml large and more than 20 cm high cylinder approximately 10 ml) of suspension is removed (from near the bottom of the cylinder). It is then dried and weighed to establish the cumulative amount of all size fractions, which were at the moment in the suspension (and not in the sediment on the bottom of cylinder). The suspension samples should be removed from the cylinder in geometric time intervals; in the case of particles around 1 μm this can even take a few days.

Other instruments for sedimentation analysis are the sedimentation balance (which detects the increase of weight corresponding to the size fractions in the sediment) or the photo- or x-ray sedimentograph (where the concentration is determined dynamically from the extinction of the radiation). These can reduce the measuring time up to few minutes.

Necessary conditions, which have to be met to accomplishing reliable results are: no interaction between particles (dilute suspensions) and slow laminar flow (so-called creeping flow, i.e. Reynolds numbers must be smaller than approximately 1; it is therefore crucial to eliminate large particles before the measurement – usually via sieving through a 63 μm sieve).

The data analysis is usually done using the Stokes relation for spheres resulting in Stokes diameter D_S (equivalent sphere diameter):

$$D_S = \sqrt{\frac{18\,\eta h}{(\rho_S - \rho_L) g t}},$$

where η is the viscosity (of the liquid medium without particles), ρ_S the density of solid particles, ρ_L the density of liquid medium (without particles), g the gravitational acceleration, h the height of the sedimentation column above the point where the sample was removed and t the sedimentation time.

The velocity can be calculated as $v = h/t$ only in the steady state, i.e. when the acceleration phase is finished and the velocity is constant. This state is usually attained after a few seconds. The Stokes relation can be derived from the equilibrium of forces,

$$F_B - F_G + F_R = 0,$$

where F_B is the buoyancy acting on the particle in liquid medium,

$$F_B = \frac{4}{3}\pi r^3 \rho_L g,$$

F_G the gravitational force acting on the particle,

$$F_G = \frac{4}{3}\pi r^3 \rho_S g,$$

and F_R the repulsion force (friction) acting on the particle in the viscous liquid medium,

$$F_R = 6\pi\eta r v,$$

where v is the relative velocity of the particle and liquid medium and $r = D_S/2$ is the equivalent particle radius. Besides the aforementioned conditions, Stokes relation is valid only when all particles are spherical. This condition is in real systems usually not fulfilled; therefore, the Stokes diameters are the diameters of spheres with the same sedimentation velocity as real irregular (or anisometric) particles. The Stokes diameters measured via sedimentation are therefore typical examples of equivalent diameters.

The Stokes relation can be modified for the case of anisometric particles, in particular flat platelets or oblate spheroids. The modified Stokes relation can be used for the reinterpretation of results and based on this, when other results (i.e. laser diffraction or image analysis results) are available, the shape of particles can be quantified.

The results of sedimentation methods are mass-weighted size distributions. When all of the particles have the same density, these results are identical with volume-weighted distributions (i.e. F_3 distributions).

1.4.2. Laser diffraction

Laser diffraction is nowadays the most widespread method for particle size analysis. Even though the scattering and diffraction principles are known for more than 100 years (Mie theory was published in 1908), the instruments for particle size measurements were constructed after the invention of the laser (approximately 1960). Additionally, for using this method, suitable computers are required (1970s – 1980s). Modern instruments are fast and flexible with the measuring range from a few nm up to a few mm. The sample preparation is easy and measurement reproducibility is high. This is the reason why this method is replacing other methods of particle size measurement in the majority of industries.

Instrument and sample preparation

Laser diffraction is an ensemble method, i.e. a large number of particles is illuminated at the same time. The diffraction pattern scanned by the photodetector is a superposition of the interference patterns of all particles. The concentration of particles has to be low enough, so that the particles do not overlap and multiple scattering is negligible. On the other hand, the concentration has to be high enough to obtain a reasonable signal-to-noise ratio.

A typical instrument for particle size measurement via laser diffraction consists of a laser, a flow-through optical cell, a sample reservoir (which can be ultrasonicated during the measurement) and a photodetector, which transforms the optical signal (angle dependence of light intensity) into an electrical signal, which is evaluated by the computer. The geometry of the photodetector can be crucial for particle shape measurement (based on the deviation of the diffraction pattern from circular symmetry) or for investigating the orientation of anisometric particles (e.g. short fibers); however, this is still a subject of current research. The distance between the laser, optical cell and photodetector, as well as the placement and resolution of photodetector determines the range of measurement. The Fourier optics (with Fourier lens between optical cell and photodetector, see **Figure 1**) or inverse Fourier optics (using convergent laser beam and with Fourier lens between laser and optical cell, **Figure 1**) makes the light to be focussed on a certain segment of the photodetector, regardless on the exact position of the particle in the illuminated volume.

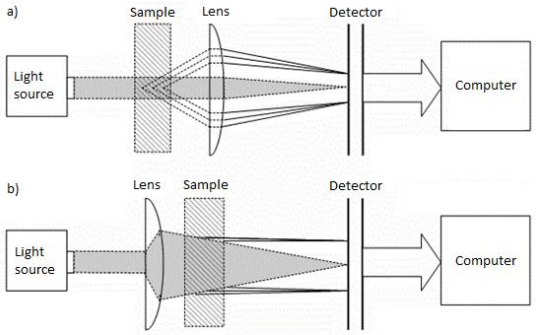


Figure 1: Scheme of Fourier (a) and inverse Fourier optics (b); Hříbalová S., Bachelor thesis, UCT Prague (2017).

The content of the reservoir is stirred and at the same time ultrasonicated during the measurement (one of the advantages of laser diffraction in contrast to other methods is the possibility of ultrasonication during the measurement). During the measurement, the suspension is constantly flowing through the optical cell (the velocity has to be high enough, so that the particles do not settle inside the instrument). Some instruments are able to measure dry powders using a "dry dispersion unit". The dry powder is, in this case, transported by a stream of compressed air through the optical cell. The sample preparation has to be adjusted to the type and size of particles, but in general, the requirements for the sample preparation are significantly less demanding than for sedimentation and other methods. However, in the case of submicron particles (and especially nanoparticles), strong agglomeration has to be expected and deflocculants or other tools might be necessary for achieving deagglomeration (if it is possible at all).

Data evaluation

The standard method for data evaluation is based on the Fraunhofer approximation. For polydisperse powders, the data evaluation is based on the deconvolution of diffraction pattern using the following integral equation:

$$I \propto I_0 \int_0^{\infty} \left(\frac{J_1(\alpha \sin\theta)}{\alpha \sin\theta} \right)^2 f(D) dD,$$

where $f(D)$ is the particle size distribution to be found. It is an "inverse problem", which is from the mathematical point of view ill-posed and ill-conditioned. The algorithm used for the solution of this problem is in commercial instruments usually proprietary. When the particles are not large enough for the Fraunhofer approximation to be valid ($D \ll \lambda$), Mie theory has to be used (especially for particles smaller than 1 μm), i.e. the complex refractive index of material is required for the calculation.

Primary results of laser diffraction are volume-weighted size distributions, which can be transformed into other types of distributions (e.g. number-weighted) only under certain conditions concerning the particle shape (size-invariance). For each type of distribution (of the same system), the statistical characteristics (i.e. median, modus, quantiles, etc.) as well the mean values are different.

2. Tasks

- Measurement of the particle size distribution via the Andreasen sedimentation method (see Appendix).
- Measurement of the particle size distribution via laser diffraction (Fritsch Analysette 22 NanoTec).
- Compare the results measured via laser diffraction and sedimentation analysis, discuss the differences with respect to the particle shape (known or presumed).
- Based on the values of both results (from cumulative curves), calculate the LS shape factors for quantiles *i* = 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100. Display the resulting values in a table and in a SSD graph (dependence of R on the sedimentation equivalent diameter).

- The **laboratory report** should be submitted in MS Word file within week via email (hribalos@vscht.cz) and should contain:
    - Introduction – short description of measurement principle
    - Experimental – overview of experimental procedure and description of measurement
    - Results and discussion – all of the measured data, results of calculations and SSD graph with corresponding table
    - Conclusions

- The final grade takes into account the test results, quality of the work, quality of the report and its timely submission

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4. Appendix

Andreasen sedimentation method

Workflow:

Mix 7 – 10 g of sample with a small amount of distilled water. Add 150 ml of distilled water of known temperature. Stir the suspension with a glass stirrer and place the suspension in a beaker into an ultrasonicated container and turn the ultrasonics on for 5 min. Add the deflocculant (e.g. tetrasodium pyrophosphate or ammonia) to prevent agglomeration. The amount of deflocculant is approximately 0 – 4 % with respect to the dry matter.

Stir the stabilized suspension and leave it for 5 min with an hourglass on the top. Ultrasonicate the suspension in the same way again. In some cases, it is necessary to filter the suspension through a 0.063 mm sieve; after filtration, wash the sieve with distilled water, dry it and express the amount of dry matter in %. Pour the suspension into the Andreasen cylinder, fill it approximately 1 cm below the upper mark, put the pipette in and increase the level of suspension to the 20 cm mark with the valve open, so that the levels of suspension in the pipette and the cylinder are the same. Before the measurement, draw the suspension into the pipette two times, so that the adhesion on the dry walls is reduced. Then close the valve and hole in the cap and shake the suspension in the cylinder for approximately 1 minute. Put the instrument on the desk and remove three samples right away (directly after shaking). The time corresponding to the last of these three (reference) sample is t = 0.

Open the valve and draw the sample (the drawing of the 10 ml sample should take approximately 20-30 s). It is crucial not to draw a larger amount of sample, because backflow from the pipette would disturb the sedimentation. The drawn amount is (after turning the valve) poured into a previously weighed bowl. After drying at 105 °C in an laboratory drier, weigh the bowls on analytical balance. Halloysite and montmorillonite samples should be dried at 60 °C.

From the first three samples, the one with largest weight is considered to be the ultimate reference sample and its weight is equated to 100 %.

The first "non-reference" sample is drawn after 2 minutes (which corresponds to 44 μm particles 2600 kg/m^3, 20 °C and sedimentation height 20 cm). It is recommended to take at least 7 samples corresponding to 40, 30, 20, 6, 4 and 2 μm. The last particle size with usual level drop (when pipetting approximately 3 mm) corresponds approximately to 14 h.

Evaluation:

From the equation: $\frac{1}{6}\pi\, d^3\, (\rho_s - \rho_l)g = 3\pi\eta d\, v$, after substituting the sedimentation velocity with $v = h/t$, the sedimentation time can be expressed for a certain size (diameter) of particle and vice versa as:

$$t = \frac{18\eta h}{d^2(\rho_l - \rho_s)g}$$

$$d = \sqrt{\frac{18\eta h}{t(\rho_s - \rho_l)g}}$$

d	particle diameter [m]
ρ_s	particle density [kg/m^3]
ρ_l	liquid medium density [kg/m^3]
g	gravitational acceleration [m/s^2]
η	viscosity of the liquid medium [Pas]
t	sedimentation time [s]

Display the results as a curve – y-axis with percentage, x-axis particle diameter in micrometers.

Example of table:

Number of sample	Time (min)	Column height (mm)	Dry matter in sample (g)	Mass fraction in suspension at given time (-)
1	0	Irrel.	0.5432	100
2	0	Irrel.	0.5442	100
3	0	Irrel.	0.5422	100
4	2	200	0.5321	97.8
5	5	196	0.5210	95.7
6	10	192	0.5111	93.9
7	40	…	…	…
8	120	…	…	…
9	180	…	…	…
10	300	…	…	…