MICROTRAC MRB
PARTICLE CHARACTERIZATION

DIFFERENT MEASURING TECHNIQUES PROVIDE DIFFERENT RESULTS – BUT WHAT IS THE TRUTH?

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Particle characterization is a common analytical method for powders, granulates, suspensions and emulsions in many industries and applications, with sizes ranging from nanoparticles to pebbles. Various technologies and measuring instruments are used for this purpose, each of which is optimal for specific size ranges or specific material properties.

The diagram in Fig. 1 shows that the measuring ranges partially overlap. This leads to the question of which method is best suited for a particular application, and the measuring range of the device alone is not sufficient to answer this question. Another complicating factor is that different measurement methods often provide different results for the same sample. Interpreting and reconciling these differences can be challenging for users.

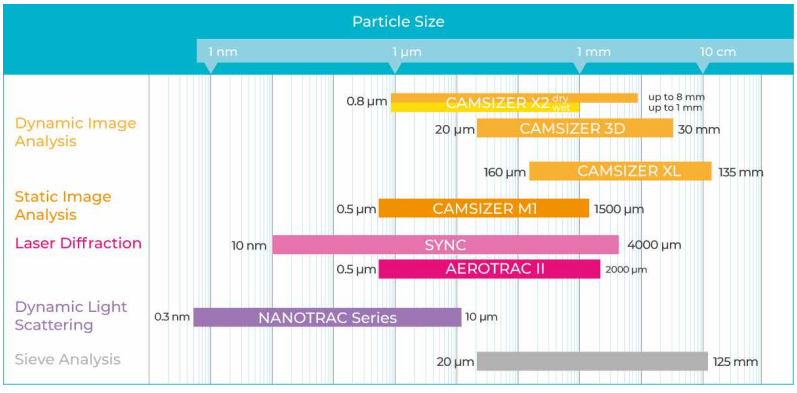

Fig. 1: Measuring ranges of different methods

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In this white paper, the common methods of particle analysis will first be presented and then compared with each other. These methods are:
- Dynamic image analysis (ISO 13322-2)
- Laser diffraction analysis (ISO 13320)
- Dynamic light scattering (ISO 22412)

Let's start, however, with analytical sieving. This simple, intuitive, and inexpensive technique is still the most widely used method for determining particle distributions. However, sieve analysis is relatively time and labor intensive, error prone, and limited in resolution and accuracy by the quality and quantity of available sieves. Retsch is the world's leading manufacturer of test sieves and sieving machines.

Sieve analysis: not as easy as it seems

In analytical sieving, several sieves with ascending mesh sizes are stacked on top of each other and the sample is placed on the top sieve. The sieve tower is clamped onto a sieving machine and set in motion, usually vibration, for a set time. During this process, the particles are distributed among the individual sieves (fractions) according to their size. Ideally, the particles pass with their smallest projection area through the smallest possible sieve mesh. In the model case of cube-shaped particles, this corresponds to the edge length of the cube. For lens-shaped particles, the size determined by sieving would be a value between the thickness and diameter of the lens, since the particle is oriented diagonally to the sieve mesh (Fig. 2). Sieve analysis is a method that measures particles in a preferred orientation and tends to determine the width.

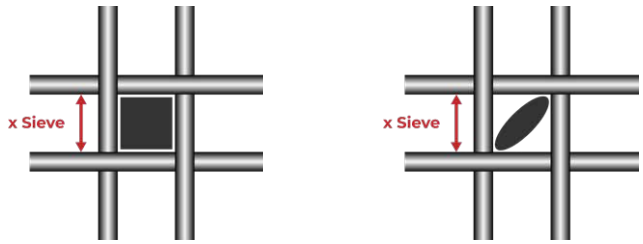


Fig. 2: Which dimension does the sieve analysis measure? For cube-shaped particles (left) the edge length, for oblate particles (right), which orient themselves diagonally, a value between thickness and diameter of the lens. Provided the particles have enough time to orient themselves and the movement is sufficiently strong.

The sieving process should be continued until the quantity on the sieves remains unchanged, i.e. until mass constancy. The sieves are then weighed and the amount of each fraction is converted into weight %, so that a mass-based distribution is obtained. The number and limits of the fractions are limited by the number of sieves used, or available. Usually, no more than eight size classes are determined, which corresponds to the capacity of common sieving machines. In this case, therefore, the size distribution contains only eight data points. The accuracy of the measured values depends, among other things, on how precisely the wire cloth sieves are manufactured. The requirements for wire cloth sieves are specified in the ISO 3310-1 standard. Among other things, this specifies for each mesh size how far the average real mesh size of a sieve may deviate from the nominal mesh size. In addition, the maximum permissible aperture size of a single mesh is specified, in each case for both weaving directions (warp and weft).

Therefore, all test sieves manufactured according to ISO 3310-1 are inspected by an optical method before delivery and a specified number of meshes are measured. The user can obtain a calibration certificate for each sieve, on which the real mesh sizes are indicated. According to the standard, for a sieve with a nominal aperture size of 1 mm (1000 µm), the permitted deviation of the mean mesh size from the nominal value is +/- 30 µm, with no single opening larger than 1127 µm. Even with an average real mesh size close to or smaller than the nominal aperture size, there are often enough relatively large meshes. This allows even large particles to find these meshes and pass through the sieve, given a sufficiently long sieving time. As a result, the effective aperture size of a sieve is usually larger than the nominal aperture size.

The data of the calibration certificate can be used to better determine the actual size of the particles. Especially with spherical particles and narrow distributions, the effect of the real mesh sizes on the result is noticeable, even with new, standard-compliant sieves. In the trial in Fig. 3, a sample with 40% < 63 µm is analyzed. Using a sieve with all meshes at the lower limit of tolerance (+/- 3.4µm), only 36% of the sample would pass the sieve. With a sieve that is completely at the upper limit, it would be 44%!

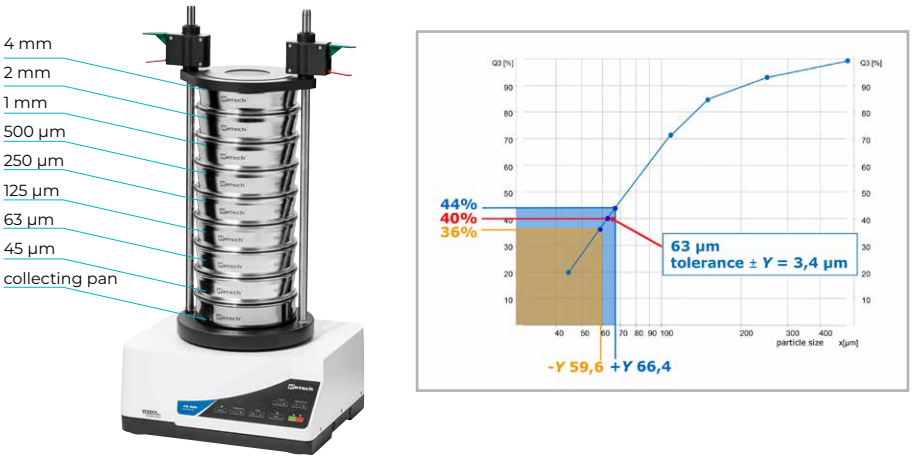


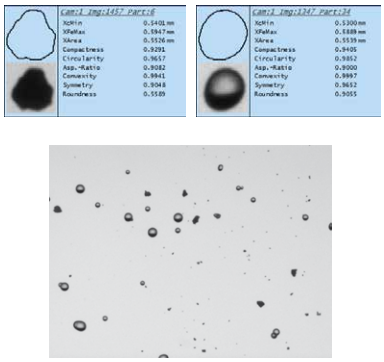
Fig. 3: Typical sieving tower (left). Influence of the real mesh sizes (right)

The analytical sieving process can hardly be automated and requires the user to perform many manual operations, making the method relatively time-consuming overall. The work steps are: Weighing in the sieves, sieving for about 10 minutes, backweighing, calculating the result and finally cleaning the sieves. The main sources of error are overloading of the sieves (clogging of the sieve meshes, too coarse result), old, worn or damaged sieves (too fine result), or errors in the transmission of measured values.

In addition to the dry set sieving method with wire cloth sieves described here, other special techniques are used for analytical sieving, such as air jet sieving, rotary sieving, tap sieving, and wet sieving. Many users of traditional sieve analysis are looking for alternative ways to characterize particles that are faster, easier and safer to perform, in addition to providing higher accuracy and more information. In many cases, dynamic image analysis, which will be presented in the next chapter, has proven its worth.

Dynamic Image Analysis (DIA): What you see is what you get

For particle characterization there are two techniques of image analysis. Static image analysis is basically a microscope which measures the sample placed on an object slide step by step. Although the quality of the images is very good and the optical resolution quite high, this method has some decisive drawbacks with regards to representing particle size distributions: the size range is limited, the procedure is rather time-consuming and the quantity of analyzed particles is often not sufficient to obtain a statistically sound statement about the entire sample. Consequently, static image analysis is mostly used for small sample volumes in the miligram range with narrow distributions. **Dynamic Image Analysis** (ISO 13322-2) has a much wider field of application. It involves a large quantity of particles which pass a camera system in a relatively short time (2 - 5 minutes) and are analyzed in real time. The graphic below shows the principle, using the CAMSIZER X2 as an example.



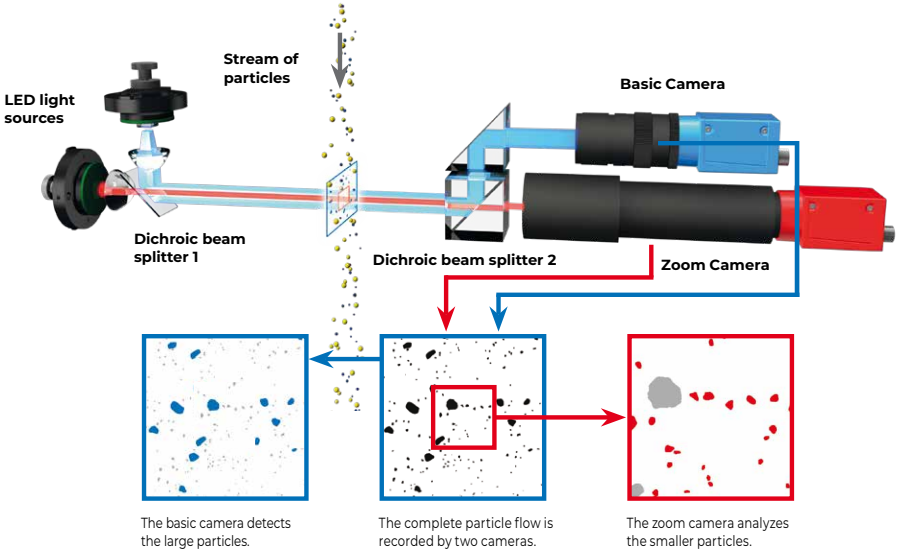


Fig. 4: Functional sketch of the CAMSIZER X2 dynamic image analyzer. Right: typical image taken during dynamic image analysis. A large number of size and shape parameters are determined for each individual particle.

The particles can be in free fall, in suspension in a liquid, or, if they tend to form agglomerates, dispersed (separated) by compressed air. Modern DIA systems evaluate several hundred images per second and capture many millions of individual particles within one measurement. Fast cameras, bright light sources, short exposure times and powerful software are the prerequisites for this.

This approach results in a number of advantages. Since each particle recorded is included in the result as a measured value, a **very high sensitivity is achieved for small amounts of oversize particles**. Furthermore, the high number of particle detections leads to very stable results with excellent reproducibility. Image analysis systems also offer size distributions with detailed resolution in **almost any number of measurement classes** and thus excellent possibilities for the analysis of mixtures. Furthermore, only imaging methods are capable of evaluating **particle shape**.

A possible disadvantage with image analyzers is the limited measuring range. The lower limit of such a measuring system is determined by the resolution of the camera. The theoretically smallest possible particle would cover exactly one pixel, but the size measurement in the range of the detection limit would still not be very accurate and significantly more pixels would be required for meaningful shape description. The upper limit is determined by the image size. Particle projections that touch the edge must be discarded. It is technically feasible to analyze particles of a size up to a maximum of 1/3 of the image diagonal in a meaningful way with dynamic image analysis.

In the devices of the CAMSIZER series, this disadvantage is compensated by the simultaneous use of two cameras with different imaging scales. The ZOOM camera analyzes fine particles with high accuracy, while the BASIC camera measures large particles that the ZOOM camera cannot detect in sufficient quantity. This realizes a dynamic range of a factor of 10,000 between the smallest and largest particle in one measurement, without the need for hardware adjustments by the user.

So there are good reasons to consider dynamic image analysis as an alternative to sieving. However, the results should be comparable so that all product specifications based on sieve analysis do not have to be changed, and data can still be compared with other laboratories where sieving continues.

Comparison of Dynamic Image Analysis with sieve analysis

Based on the particle projections, several size parameters as well as shape parameters can be determined with dynamic image analysis. Typical size parameters are width, length and diameter of the equivalent circle (see Fig. 5). Depending on the question, each of these size definitions can serve as the basis for the distribution curve. Thus, in image analysis, several results can be obtained from one measurement, e.g., a "width distribution," a "length distribution," and one based on the diameter of the equivalent circle of the particle projection (Fig. 5).

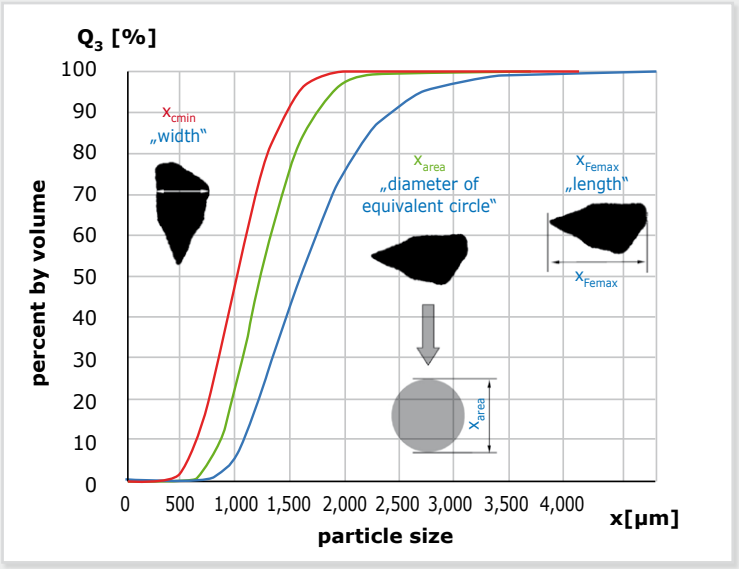


Fig. 5: Different size definitions in dynamic image analysis provide different results for non-spherical particles.

Since sieve analysis, as already described, tends to determine the width of the particles, the "width distribution" of image analysis is the parameter of choice when it comes to comparing the two methods. It must be noted, however, that in image analysis the particles are in absolutely random orientation whereas with sieving an orientation takes place. This effect is responsible for most of the differences between the two methods. However, since this difference is determined by the particle shape, it can be reliably compensated for with a material-specific correlation function. This will be illustrated by some examples.

For the cube-shaped model particles from Fig. 2, the edge length of the particle can be determined with image analysis, just as with sieving, but only if one face of the cube points towards the camera. For all other orientations, larger projection areas result, so that the size distribution of a real sample of cube-shaped particles would be coarser with image analysis compared to sieving. In this case, the distribution curves would be closer together in the fine area, since the smaller projection areas are represented here. Never can a cube-shaped particle be measured smaller with image analysis than with (ideal) sieving (Fig. 6 left).

For lens-shaped particles as in Fig. 2, certain orientations (side view) allow smaller values in image analysis and other orientations (circular cross-section) allow larger values than with sieving. It is often observed in oblate particles that the cumulative curves of sieving and image analysis cross, with image analysis being the broader distribution. These differences, determined by particle shape and orientation, are particularly pronounced for narrow distributions, and less pronounced for wide distributions (Fig. 6 right).

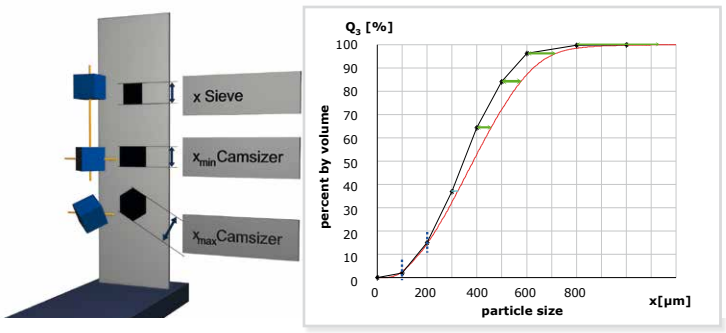


Fig. 6: Typical differences between dynamic image analysis (red) and sieve analysis (black) for approximately angular, cube-shaped material and more platy material.

Since the differences are characteristic for each grain shape, material-specific fitting functions can be created with little effort, achieving almost 100% comparability of results. This correlation then works for all samples with comparable shape, even with different distribution widths. This is clearly illustrated by the example in Fig. 7.

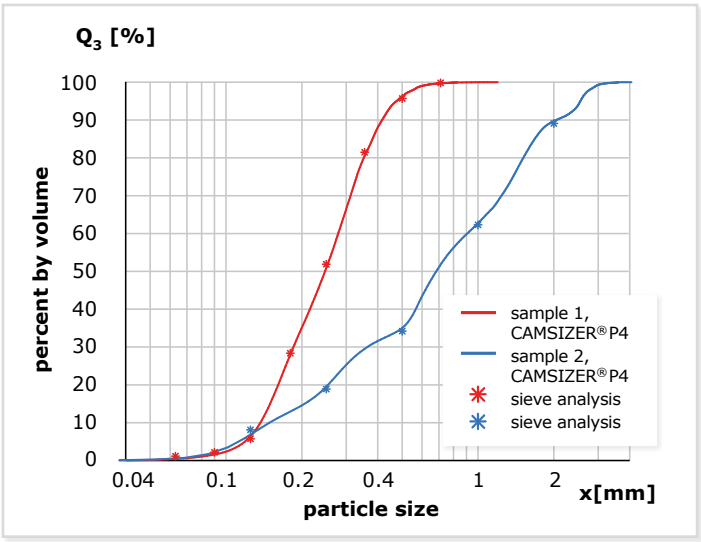


Fig. 7: Good comparability of image analysis and sieving results for wide and narrow distributions thanks to material-specific fitting function.

For nearly spherical particles, a no too large deviation between sieve analysis and imaging methods should be detectable and mostly the comparability is also very good. On closer inspection, however, a slight shift of the sieve curve towards finer values can be observed in some cases (Fig. 8), especially for very narrow distributions. These differences are due to the sieve tolerances, which have been previously discussed. Fig. 8 shows that at 710 µm image analysis and sieving are only about 15 µm apart, but this leads to about 6% difference in Q3 (passage value). The 15 µm difference can easily be explained by sieve tolerances and would be verified by the calibration certificate belonging to the sieve.

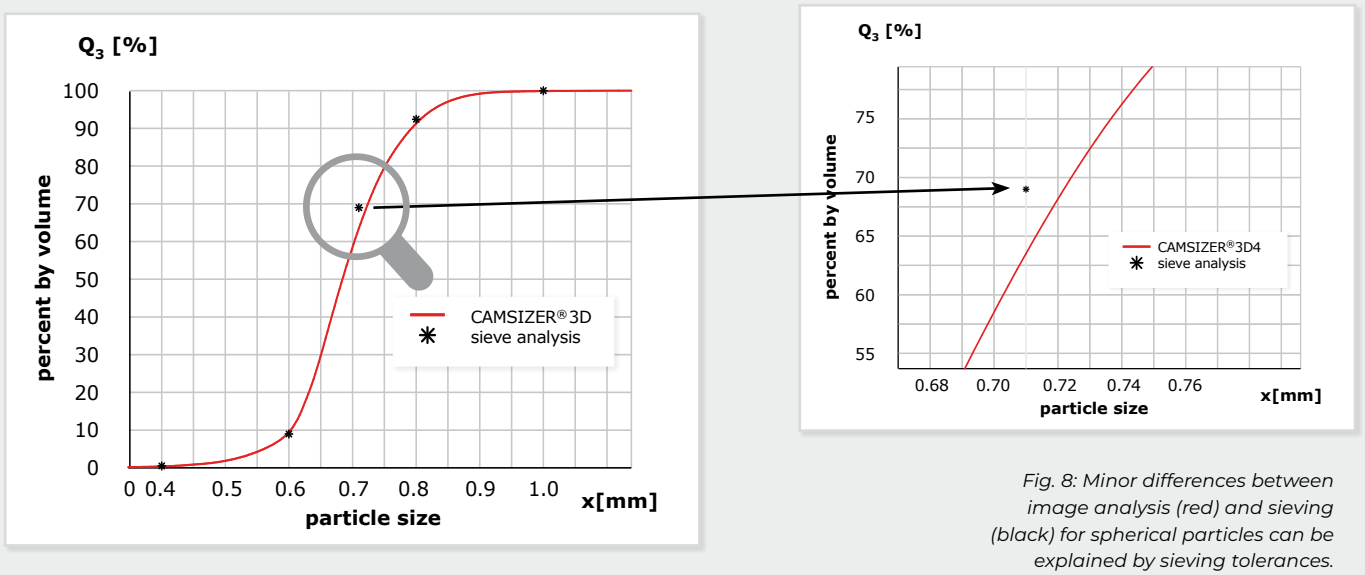


Fig. 8: Minor differences between image analysis (red) and sieving (black) for spherical particles can be explained by sieving tolerances.

Laser diffraction: a versatile method with a wide measuring range

Laser diffraction analysis, also called static light scattering, is, along with sieve analysis, the most common method for determining particle size distributions and the de facto standard for quality control in many industries. The method is based on the deflection of a laser beam by a particle collective dispersed in either a liquid or an air stream. The diffraction angles or scattering angles are characteristic of the particle size. To put it simple, one can say that large particles scatter the light to small angles, small particles cause large scattering angles.

While large particles still produce quite sharp intensity distributions with pronounced maxima and minima at defined angles, with smaller particles the scattered light pattern becomes increasingly diffuse and the total intensity also decreases. ISO 13320 describes this laser diffraction method in detail and comprehensively. The measuring principle and design of a modern laser analyzer is shown in Fig. 9 using the Microtrac SYNC as an example.

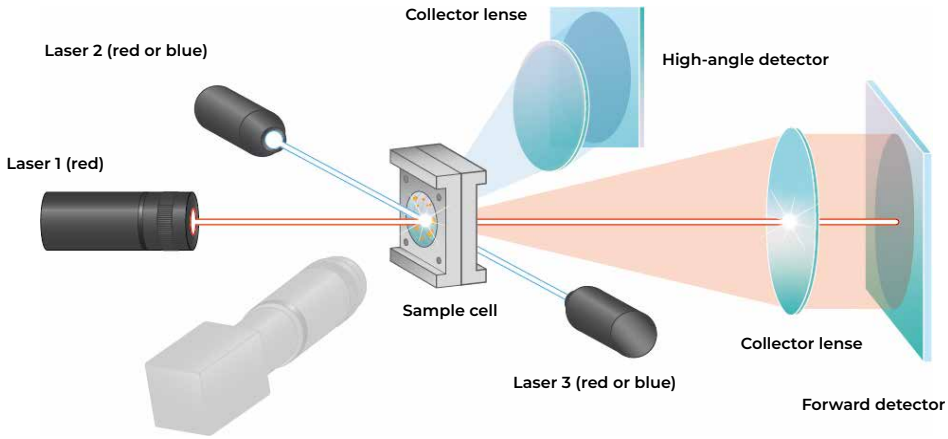


Fig. 9: Setup of the SYNC laser particle analyzer. The sample in the measuring cell is detected by three lasers from different angles. The resulting scattered light is recorded by two detector arrays over a total angular range of 0.02° to 163°.

Reasons for the popularity of laser diffraction are the enormous flexibility and the wide range of applications. The measurement range lies between 10 nm and 4 mm, which corresponds to a factor of 400,000 between the smallest and largest particle. This means that the dynamic range is larger than for all other methods presented. In practice, however, laser diffraction is typically used in a size range from about 30 nm to 1 mm. For very small particles, the scattering intensity is weak and the angular dependence of the signal is low. At the upper end of the measurement range, the very small diffraction angles of large particles become difficult to resolve metrologically. Another advantage of laser diffraction is the ability to measure wet and dry samples, with measurement times that are usually less than one minute. The entire process can be automated via SOPs and handling is so simple that analyses can be carried out after only a short training period.

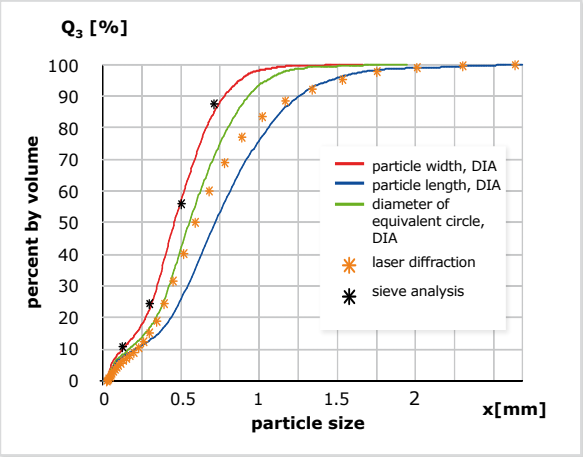
In laser diffraction, all measurement signals refer to the size of an equivalent sphere. The result is therefore an "equivalent sphere diameter" (ESD). In contrast to image analysis, the particle shape cannot be measured by laser diffraction. When interpreting the results, it must also be taken into account that the scattered light pattern is generated simultaneously by many particles of different sizes. Mathematical models are used to calculate a particle size distribution. This is therefore a so-called collective measurement method. This has both advantages and disadvantages: on the one hand, the measurement is very robust, easily repeatable and not susceptible to disturbing influences such as temperature fluctuations, vibration or even contamination and impurities, since the signal generated by it is subtracted with a zero measurement. On the other hand, laser diffraction is also relatively insensitive to small amounts of "oversize". For this reason, only percentiles between d10 and d90, and possibly d95, are usually specified. Also, the analysis of mixtures of particles of different sizes, whose modal values are close to each other, is often difficult with laser diffraction.

Many users are faced with the question of whether a laser diffraction instrument or an image analysis system would be more suitable for them. In the next section, we compare the two methods to provide decision support for specific individual cases.

Laser diffraction, image analysis or both?

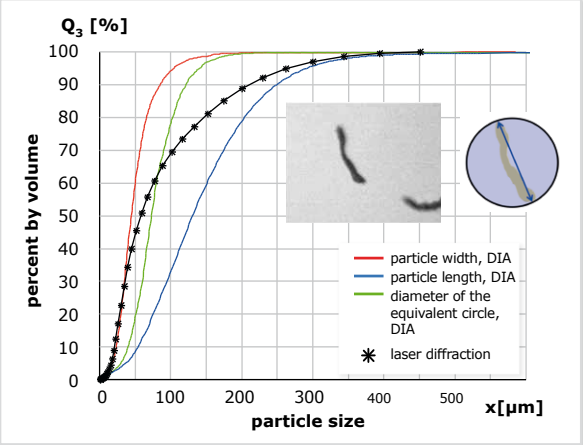
The measuring ranges of laser diffraction and dynamic image analysis partially overlap. In cases where particles smaller than 1 µm are to be measured, the situation is clear: laser diffraction must be used here. The same applies when particles are in the millimeter range: in this case, image analysis is the method of choice. However, many samples have size distributions in the range 1 µm - 1 mm and here both methods can be usefully employed. So how do the results differ when such a material is analyzed by both techniques? Fig. 10 shows size distributions from a sample of coffee powder measured by laser diffraction and image analysis. Image analysis shows distributions analogous to Fig. 5 based on width, length, and circle-equivalent diameter; laser diffraction provides only one distribution. Since spherical model particles are assumed here, the result correlates best with "diameter of area-equivalent circle" of image analysis. However, laser diffraction tends to deliver broader and broader distributions, since here also, for example, the length of the particles produces diffraction signals, which are then also included in the result. Furthermore, it is noticeable that the image analysis correlates better and better with the sieving, which is also represented by black dots in Fig. 10.

Fig. 10: Measurements of a sample of coffee powder with laser diffraction (orange), dynamic image analysis (red / green / blue) and sieve analysis (black).



The differences between laser and image analysis also depend on the particle shape. While a very good match is usually achieved with spherical particles, the results are further apart for extreme particle shapes. Nevertheless, the distribution curve of laser diffraction always runs between those of the size definition "width" and "length" of the image analysis, either closer to the width or the length, depending on the material. Fig. 11 shows this comparison for cellulose fibers, i.e. very elongated particles. The laser curve is closer to the width measurement of the image analysis, because statistically more scattered light reaches the detectors from this side of the fibers.

Fig. 11: Measurement of a sample of cellulose fibers with the CAMSIZER X2 (image analysis): Particle width (red), particle length (blue), circle equivalent diameter (green) and laser diffraction (black). The laser result is a mixture of length and width and shows a continuous transition. DIA can determine length and width separately.



When comparing the two techniques, one finds that the disadvantages of one method are the advantages of the other and vice versa. Therefore, it makes sense to combine both methods in one measuring device. This is the case with the Microtrac SYNC, which is primarily a laser diffraction instrument, but with a built-in stroboscopic light source and camera for dynamic image analysis. The same sample feed, measuring cell and optical bench are used for both measurements, so the same particles are evaluated. This makes the particle shape accessible, which provides valuable additional information for many applications and also helps to use laser diffraction to interpret specific distributions of irregular particles such as those of the cellulose fibers in Fig. 11. The image analysis option also significantly improves sensitivity to oversize particles, which is limited to about 2% by volume with pure laser diffraction, and improves accuracy, especially for large particles. This is done via a patented BLEND algorithm, which merges the image analysis data and laser data into one result, if required (Fig. 12).

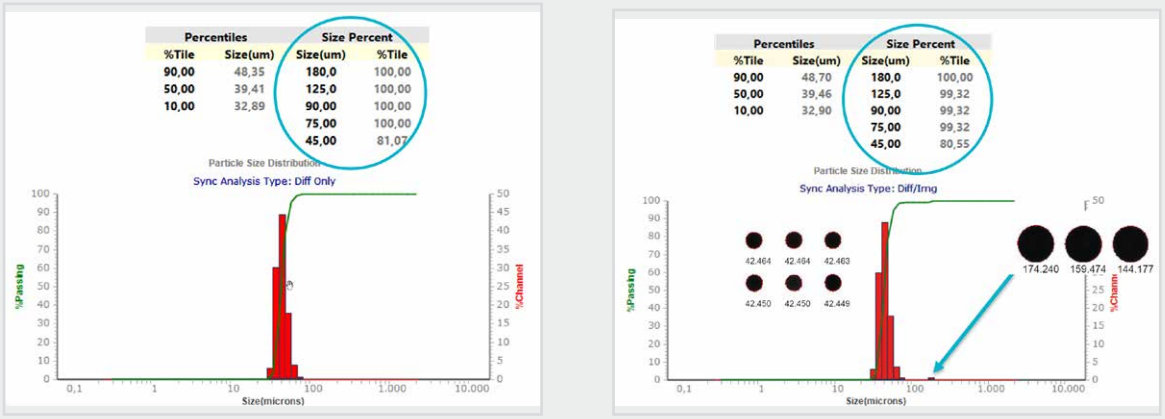
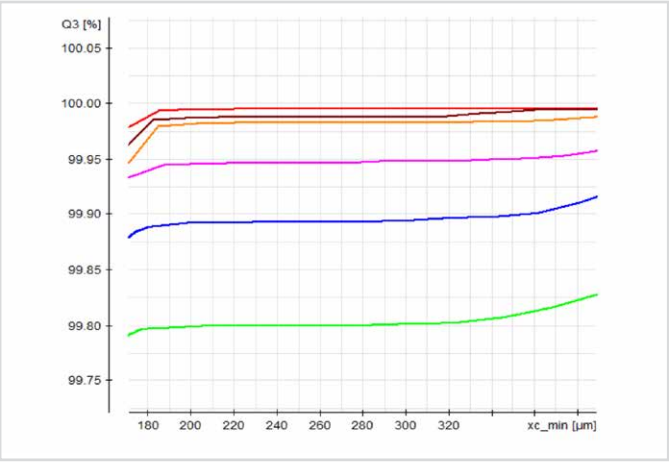


Fig. 12: Oversize detection. Oversize grains were added to a sample of metal powder in a controlled manner. Left: Laser diffraction alone cannot detect oversize contained in the sample. Combining this with image analysis in Microtrac SYNC detects and displays 0.5% oversize. Bottom: a pure image analysis instrument like the CAMSIZER X2 can still correctly measure oversize particles even in low concentrations like 0.005 %.

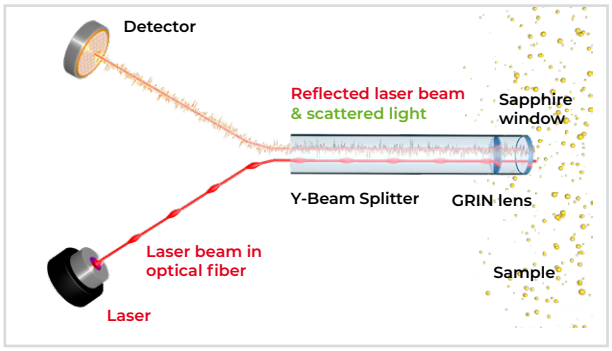
% oversize >200 µm added	% oversize >200 µm detected by CAMSIZER X2	Difference
0.005%	0.005%	0.000%
0.010%	0.013%	0.003%
0.020%	0.019%	0.001%
0.050%	0.054%	0.004%
0.100%	0.107%	0.007%
0.200%	0.201%	0.001%
1,000%	0.936%	0.064%



However, to take full advantage of image analysis, it is recommended to use a pure image analysis system such as the CAMSIZER X2. This device is fully optimized for image analysis, which is reflected in the significantly higher image acquisition rate alone: SYNC: 22-60 frames per second, CAMSIZER X2: 320 frames per second. This results in excellent measurement statistics and thus better accuracy and reproducibility, especially for wide distributions. Furthermore, the sensitivity for oversize or other unwanted particles (e.g. fused spheres in metal powders, Fig. 12) is once again significantly higher and the comparison to test sieving can be made almost without problems.

Dynamic Light Scattering (DLS): Nano particle analysis and more

Dynamic light scattering (DLS, ISO 22412) is an established and precise measurement technique for characterizing particle sizes in suspensions and emulsions. It is based on the Brownian motion of particles: this states that smaller particles move faster, while larger ones move slower in a liquid. The light scattered by particles contains information on the diffusion velocity and thus on the size distribution. The relationship of diffusion constant, temperature, viscosity and hydrodynamic particle diameter is defined in the Stokes-Einstein relationship (Fig. 13). Dynamic light scattering allows the analysis of particles in suspensions and emulsions in a size range from 0.3 nm to 10,000 nm. The operating principle of a DLS analyzer is shown in Fig. 13. The setup shown here is so-called heterodyne detection, which is used in all DLS instruments from Microtrac. The scattered light is recorded in 180° backscatter direction. It contains information about the movement speed of the scattering particles in the form of small fluctuations in intensity. By superimposing a reference beam, these fluctuations are measured and evaluated via a Fast Fourier Transform. The resulting frequency-power spectrum contains all information about the particle size distribution. The hardware is integrated into a probe that can measure in-situ by immersion in a wide variety of containers and different volumes.



$$D = \frac{kT}{3\pi\eta d_p}$$

k = Boltzmann constant; **T** = Temperature; **η** = Viscosity

Fig. 13: Operating principle of dynamic light scattering in Microtrac analyzers and the Stokes-Einstein relationship underlying the method.

Dynamic light scattering is a technique that is particularly suitable for the analysis and characterization of nanoparticles. Further advantages are the measurements of both highly concentrated and highly diluted samples as well as the possibility of determining zeta potential and concentration, which is integrated in many analyzers.

Laser Diffraction or Dynamic Light Scattering

Laser diffraction and DLS also have overlapping measurement ranges, and again, laser diffraction is the more versatile method. For dry measurement DLS is not suitable and for particles above 1 µm only to a limited extent. However, a major advantage of DLS is that it covers a wider concentration range, ideally between a few ppm and up to 40% by volume. In many cases, this is a clear advantage, because dilution can lead to a change in the size distribution, for example due to agglomerate formation. In laser diffraction, the particle concentration is adjusted, according to the sample material, based on the laser transmission and the strength of the detector signal. The particle concentration usually lies in the range of approx. 0.1 vol.%.

Considering the measurement results, it is important to note that DLS is a hydrodynamic diameter and that the size distributions are intensity-based. This means that the included particle sizes are weighted according to their contribution to the total intensity. Since large particles are more scattering than small particles, the intensity-based distribution is larger than the volume distribution of laser diffraction. However, DLS data can be reliably converted to volume distributions using Mie theory, so that reasonable comparability between the two methods can be established if all constraints are met, as illustrated by the example of a sample of barium sulfate in Fig. 14. Although it is possible to obtain reasonable results below 100 nm with laser diffraction, in terms of accuracy DLS has advantages in this size range. Above 100 nm, laser diffraction is more suitable compared to DLS with increasing particle size.

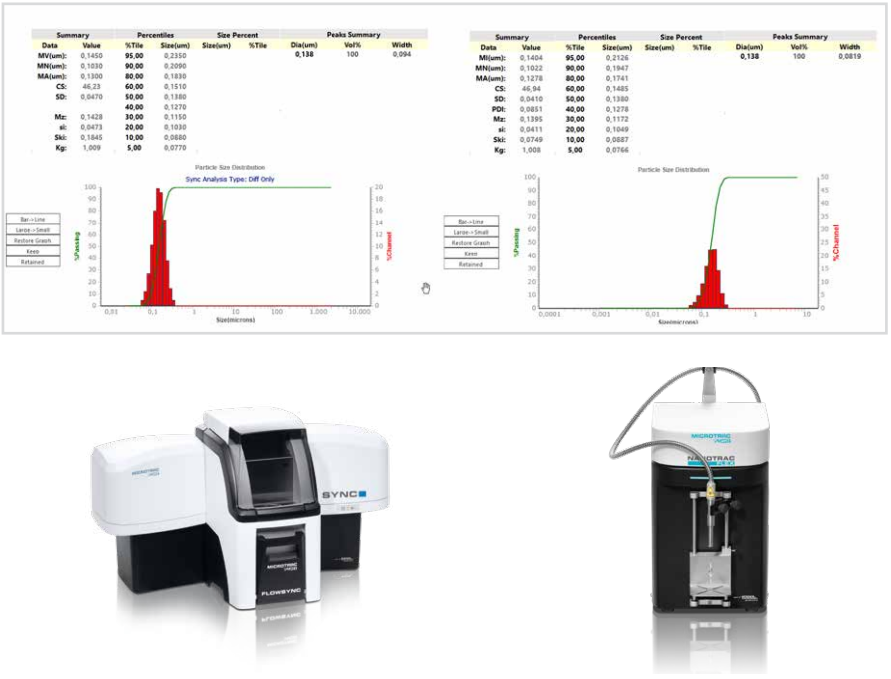


Fig. 14: Size distribution of a barium sulfate suspension measured with laser diffraction (Microtrac SYNC) and DLS (Nanotrac Flex). The matching of the measured values is excellent, the median is 138 nm.

Conclusion

For particle characterization, different techniques are available depending on the size range and the problem, some of which are only comparable with each other under certain conditions. The tables compare the methods that overlap in terms of the measurement range.

Table 1: Comparison sieve analysis and dynamic image analysis

	Sieve Analysis	Image Analysis
Particle model	comparison with apertures, equivalent diameter	direct length/width measurement; diameter calculation from the projection surface; different size models
Measuring range	20 µm – 125 mm (wire mesh sieves)	from 1 µm (CAMSIZER® X2) to 135 mm CAMSIZER® XL
Particle shape analysis	no	yes
Detection of oversized grains	each particle	CAMSIZER® 3D: each particle CAMSIZER® X2: < 0.1 % Vol.
Resolution	poor	very high
Dissolution of multimodalities	poor	excellent
Repeatability and lab-to-lab comparison	limited	very good
Comparability of results	identical results possible	
Process time	up to 30 min incl. cleaning	2-5 min per measurement

Table 2: Comparison laser diffraction and dynamic image analysis

	Laser Diffraction	Image Analysis
Particle model	Equivalent sphere diameter (ESD)	direct length/width measurement; diameter calculation from the projection surface; different size models
Measuring range	10 nm – 4 mm	>1 µm
Particle shape analysis	no	yes
Detection of oversized grains	> 2 % Vol.	CAMSIZER® 3D: each particle CAMSIZER® X2: < 0.005 % Vol.
Comparability of results	usually good for "equivalent circle diameter", laser diffraction tends to have broader distributions	
Dissolution of multimodalities	3 modes max., standard 70 channels (140 max.)	virtually unlimited
Process time	<1 min per measurement	2-5 min per measurement
Comparability to sieve analysis	poor	identical results possible

Table 3: Comparison laser diffraction and dynamic light scattering

	Laser Diffraction	Dynamic Light Scattering
Particle model	Equivalent sphere diameter (ESD)	hydrodynamic diameter, sphere model
Measuring range	10 nm – 4 mm, strong in the range >100 nm	> 0.3 nm - 10,000 µm, strong in the range <500 nm
Particle shape analysis	no	no
Detection of oversized grains	> 2 % Vol.	good for intensity-based distributions
Comparability of results	often larger with DLS due to intensity, hydrodynamic diameter, usually good comparability for volume distributions	
Process time	<1 min per measurement	2 min max. per measurement
Concentration range	low concentration, diluted samples approx. 0.1 Vol. %	highly diluted and highly concentrated samples
Dry measurement	yes	no