Laser Diffraction: Millennium-Link for Particle Size Analysis

Although the effect of particles interacting with light was described by Fraunhofer already early in the last century [1] the idea of measuring particle size distributions with this physical principle could be realised only after reliable lasers were developed providing a light source and microcomputers became powerful enough to calculate the size distribution from the light intensity distribution detected by a semiconductor-detector.

In the early seventies the first instruments for particle size analysis (PSA) with means of laser diffraction (LD) covered a measuring range from coarser than 1 micron up to 200 microns. Until the middle of the eighties only wet dispersion was available. Knowledge of the shape of the sample distribution was required or preassumed.

In the mid-eighties a different attitude towards particle size analysis entered the market with capable dry dispersion [2]. LD systems no longer required the sample to be prepared according to the measuring system but offered the ability to be adapted to the needs of the products. Furthermore no longer additional information about the distribution shape was required [3].

Parameter-free analysis as well as dry and wet dispersing modules which adapt the instrument to the sample should be standard today. Latest technology covers a measuring range from below 0.1 µm up to 1 cm.

Set up for PSA with LD

The classical set-up for the particle-light-interaction is shown in fig. 1. The basic physical principle is light scattering at the edges of particles. After focussing the light in the centre of a multielement-detector the scattering effect leads to signals on the non-central elements of the detector. The optical set-up is referred to as Fourier-optics [4].

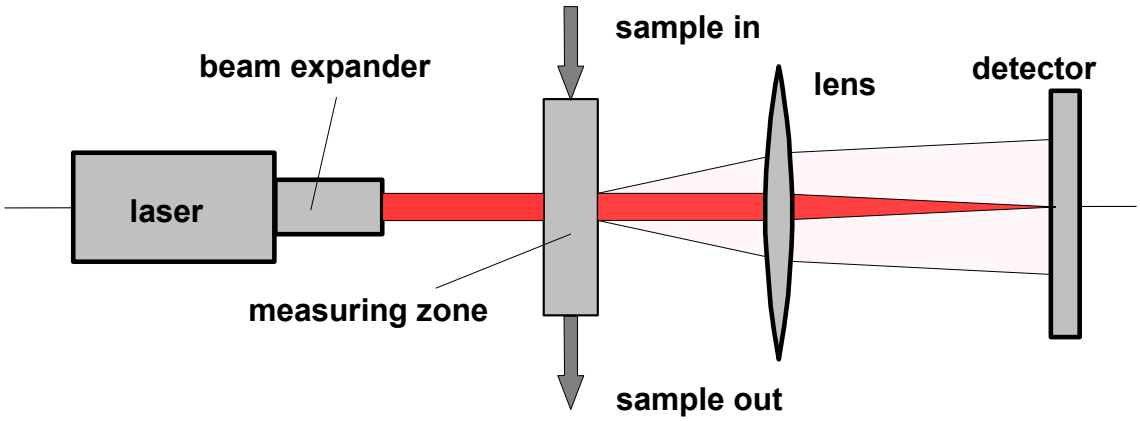

Fig. 1 Set up for generation of diffraction patterns in a PSA system

After widening, the monochromatic wave of laser light enters the measuring zone. The passing and the scattered light are focussed by a lens system. Generally the smaller the particles are the larger are the resulting diffraction angles. Hence the focal length determines the measuring range. Diffraction at small angles, however, can only be recognised by the system if the scattered light is not focussed to the central elements where all the unscattered light is collected.

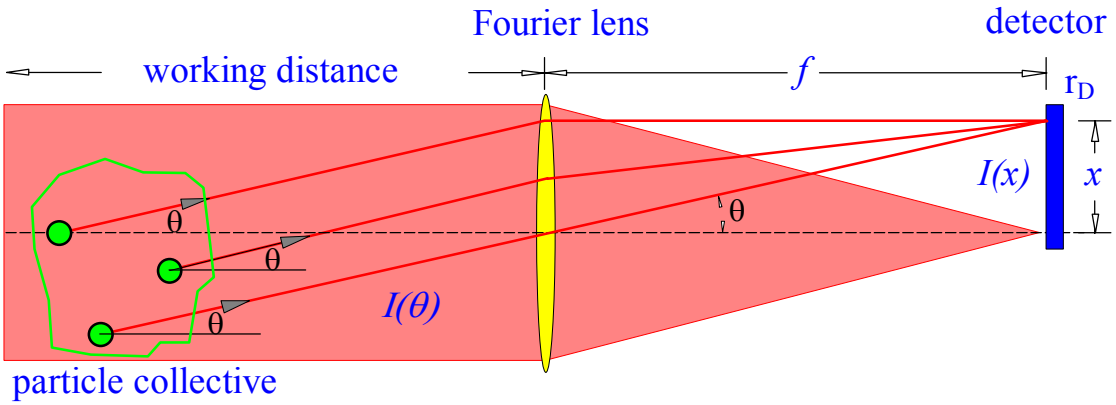

Fig. 2 Particle size analysis in the parallel laser beam. (Sketch simplifies diffraction pattern)

The particle flow behind the focussing lens can be a modification, known as reverse Fourier set up. In this case the distance of the measuring zone from the detector determines the measuring range. The disadvantage is that a measuring zone has a certain depth and therefore the measuring instrument has to cope with particles closer or more distant to the detector as shown in fig. 3. Particles of the same size at different positions in the measuring zone produce diffraction effects at different diameters i.e. a blurred diffraction pattern with an additional inaccuracy usually of several percent.

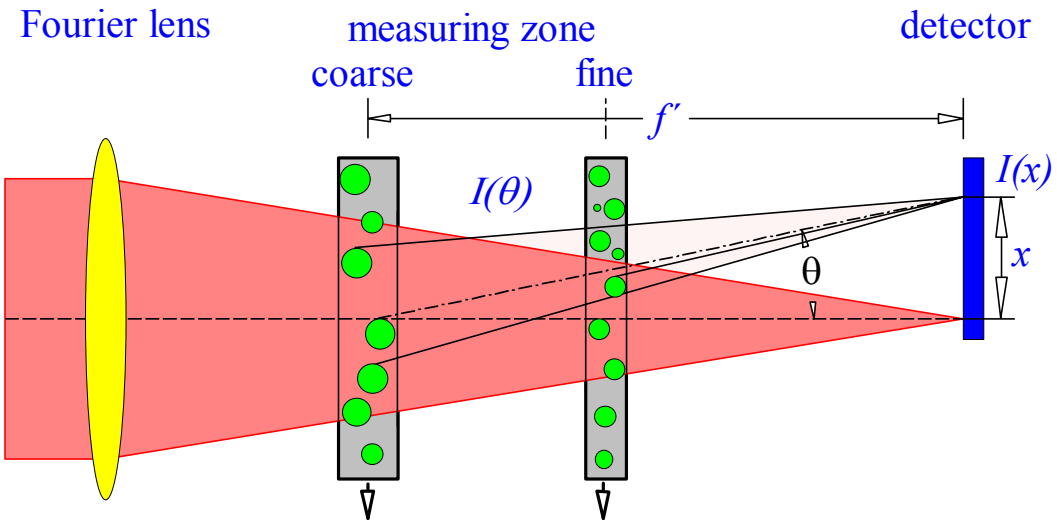

Fig. 3 Measuring zone behind the lens: Size and distance of particles to detector determine diameter of diffraction pattern.

The result gained with laser diffraction is the size distribution of equivalent spherical particles. I.e. the result refers to a distribution of spherical particles that interact with the laser

light in the same way as the sample. Therefore differences can occur in comparison to sieving, sedimentation or other PSA techniques.

Mixing up methods

In addition to sieving and sedimentation several other optical principles can be applied for PSA. Back light scattering, light extinction and image processing are methods to gain information about particle size. Each of them has its own advantages, disadvantages and limitations. So why not combine different methods to overcome restrictions and improve results?

Although several attempts have been made to do so, combination of results is limited already when measured with one principle. The reason is that there are different possible ways of combining. Can the results be added after multiplication with a weighting factor? In case, are the characteristics of different detectors known precisely? Can the mass fraction serve as weight although volume and not mass is the measurement basis? If a sample is measured with different methods, can “the truth” be approximated with the mean value? Are necessary parameters like reflectivity, shape factors and others known precisely?

A combination of methods requires proper answers to these questions. A system determined answer excludes user influence but will be arbitrary. How can for example a sieve result be combined with a laser diffraction measurement? First the class limits must be (made) the same. In a second step a solution for shape influence has to be found as laser diffraction reflects equivalent spherical particles but sieving is sensitive mainly to the smallest projection area only. And finally the calculation of results with weighting and handling of overlapping and non-overlapping measuring ranges has to be performed.

Thus a combination of different measurements or even different methods cannot be recommended for the sake of approvable results. The more unknown parameters appear and the more influence the operator has on the analyses, the less reliable results will be. Therefore one must be extremely careful with combination of different analysis principles, even with combination of results of different detectors in one measurement.

Current technology

The approved standard light source is a **Helium-Neon-laser** with 632.8 nm wavelength. Semiconductor lasers have a shorter lifetime and produce an elliptical beam and a large wavefront distortion. As the quality of the results is directly related to the quality of light, instruments should employ those types of lasers that refer to the demanded quality of accuracy.

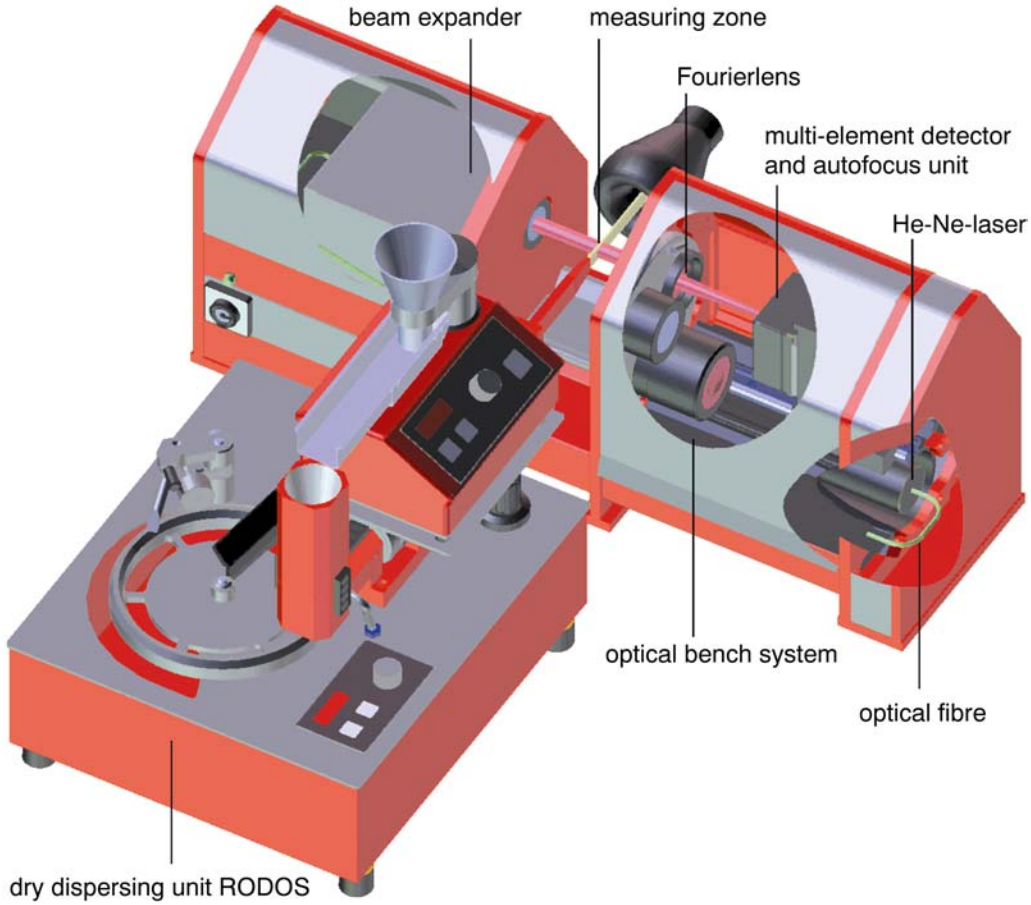

Fig. 4 Sympatec HELOS LD instrument with dry dispersing system RODOS; 0.1 µm to 8750 µm

The optical set up performs the Fourier transformation of the light that produces results symmetric to the centre point, but dependent on the orientation of the transformed pattern. Hence integration over a half circle is necessary to collect the complete information. The best performing detector therefore is a multi-element detector with concentric semicircular or circular elements.

The **detector** is the most sophisticated element of a LD instrument. It should have a number of discrete non-overlapping sensitive elements of precise geometry without gaps between their areas and a reflectivity of zero. The detection of coarse particles requires very small detector elements and an exact alignment of the highly intensive central beam to the centre of the detector. If the centre consists of at least three sector fields, dynamic centring is possible even during data acquisition.

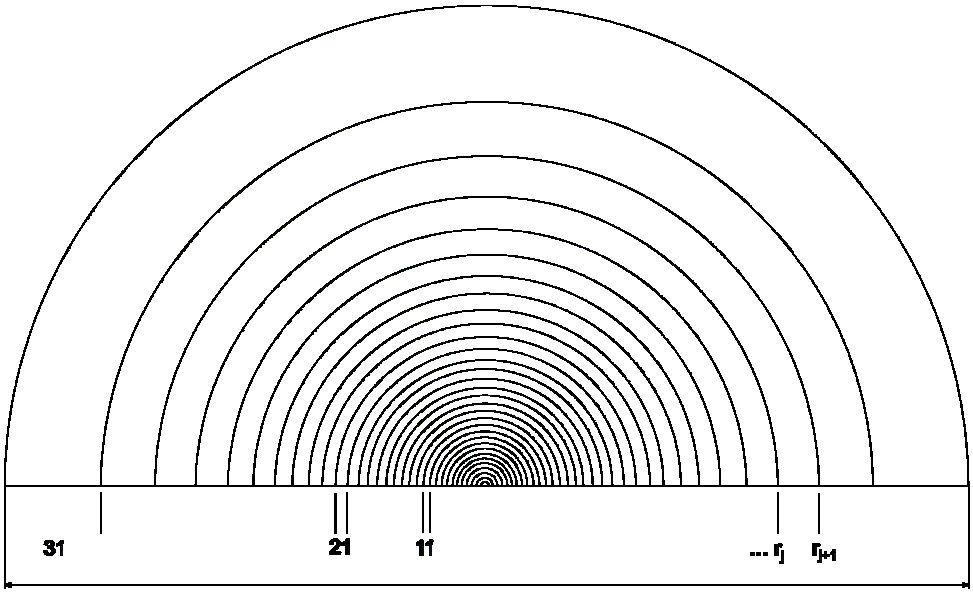

Fig. 5 Approved detector layout of 31 semicircular elements. Optimised for logarithmic scaled size distribution.

The **resolution** of the system, i.e. the number of classes, should be the same as the number of independent detector elements, i.e. the number of elements in the same distance from the centre. An artificially increased resolution cannot increase the sensitivity because there is no more information in the acquired data. A common detector has about 32 elements ensuring a high signal-to-noise ratio and a reliable reflection of the shape and especially of the coarse tail of a measured distribution [5].

The **mathematical evaluation** should be parameter-free, stable and sensitive. Being parameter-free is important for the quality of results and for comparability purposes, as user influence is excluded. Applying Fraunhofer diffraction model this means that the calculation of the particle size distribution out of the light intensity distribution is the solution of a Fredholm integral equation, for instance with the Philipps-Twomey approach. A higher resolution has to be paid for with higher mathematical instability resulting in higher smoothing – reducing and not increasing the measured information. Typically a coarse fraction of less than one percent can be detected by sensitive instruments.

An analysis with a modern LD system lasts a few seconds in average, if the dispersion is adapted to the sample. With automated sample dosing and dispersing as well as measurement system rinsing and cleaning the **duration** of a standard application has been reduced to the range of a minute or even less.

It can be stated that today the measurement technology is much more accurate than the sample preparation can be. Therefore the formerly unknown grade of **reproducibility and reliability** brought to particle size analysis has also opened new fields of application. However, attention must be paid to the **system-to-system comparability**. With up-to-date LD technology a standard deviation of less than 2 % between different systems can be expected. This for the first time allows for reliable comparisons of results of systems all over the world. Even results of off-line laser diffraction systems, for instance in a laboratory, are directly comparable with

in-line measurements in the production line – at least when adequate sampling and dispersing is integrated.

Important for the customer is that he can participate in new developments by upgrading his instrument. One way to achieve this is a modular design with dispersing modules, optical modules and a standard personal computer allowing for software updates.

Limits and limitations

Today's laser diffraction instruments can be applied for particles up to the centimetre range. Mechanical stability with long focal lengths necessary for measurement of large particles can be guaranteed with optical modules similar to camera lens systems. Therefore mainly samples and applications limit a further enhancement.

The wavelength of laser light determines the lower limit [6]. Scattering angles occurring at very small particles are so large that the working conditions are quite restricted. Single lenses with a focal length of 50 mm and an opening diameter large enough (allowing the entry of scattered light) are not available, because the focus would be inside the lens. Therefore optical modules are applied. A lens system with a focal length of 20 mm and a diameter of 50 mm can cope with scattering angles of 0.1 µm particles only with a working distance of 20 mm, i.e. the measuring zone has to be in a distance of about 19 mm from the lens system surface, to be sure to collect all scattered light. Information of smaller particles is collected only partially or not at all.

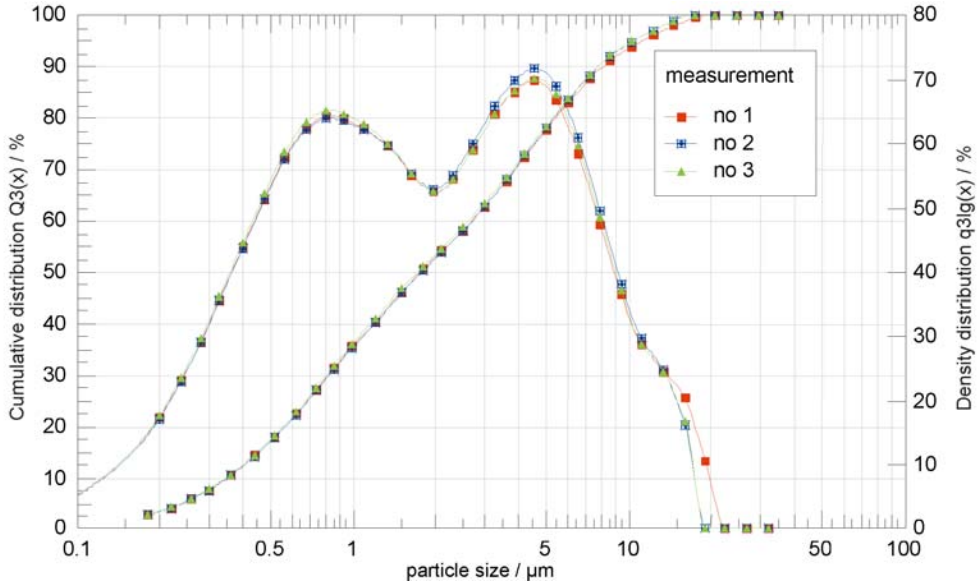

Fig. 6 Reproducibility of dry measurements at the fine edge of the measuring range

With light of a shorter wavelength the scattering angles would be reduced. Even light, however, with half the wavelength of the He-Ne-laser would only reduce the lower limit to half of the actual one but the instrument would have to cope with less reliable laser, lenses and detector technology and therefore lower accuracy.

Submicron – Fraunhofer vs. Mie

Below one micron application of Fraunhofer diffraction theory is not covering all effects of the laser light [7]. Besides scattering there is reflection, absorption and refraction. All these effects are described by Mie theory generally making it the preferable evaluation theory for particle size analysis with laser diffraction near or in the submicron area.

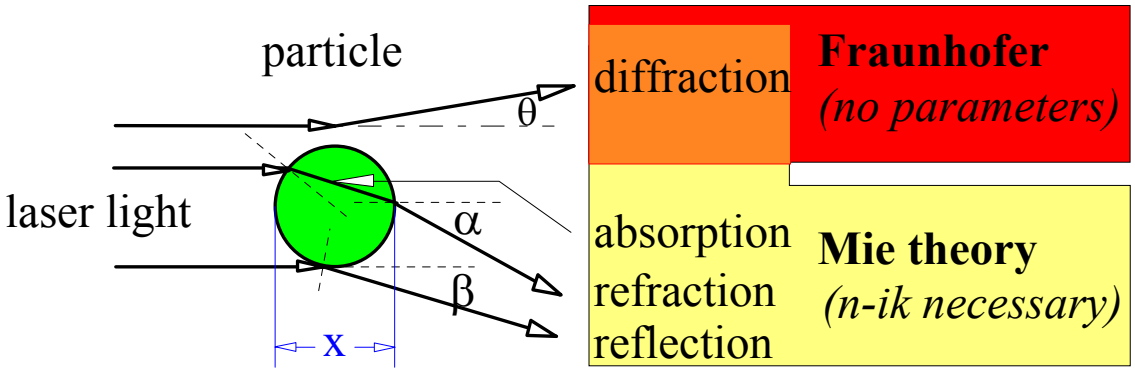

Fig. 7 Physics of light-particle-interaction

But there are severe restrictions coming with the Mie theory. First of all the particles have to be isotropic and spherical with a smooth surface. If this precondition is fulfilled a material dependent complex Mie parameter has to be known, consisting of refractive index and absorption coefficient. And finally no Mie-based measuring system can deal with a mixture of different components.

If the Mie parameter is not known exactly virtually any result can be generated. Extended experiments with different Mie parameters have shown that a wide range of results can be calculated from the same light intensity distribution on the detector. Small changes have huge effects on the results. Monomodal distributions can be made to bimodal ones, coarse fractions may vanish or appear and a fine tail may be reduced or created.

The extension of Fraunhofer diffraction theory also into the submicron range may not give the real “truth” but excludes this possible influence of normal lack of information. The results are of the same magnitude as Mie-calculated ones. The relation between coarse and fine particles may be slightly shifted, but differences, trends and comparisons are monitored very clearly. So if the Mie parameter is unknown or the preconditions are not completely fulfilled the application of parameter-free Fraunhofer theory is favourable.

Validation

More and more important is the verification of results and the validation of analytical devices [8]. Therefore modern PSA suppliers have to fulfil several quality assurance regulations.

The whole development of a system has to be documented: mechanics, electronics and software. The documentation proves a structured approach and lists parts and serial numbers. So any problem can be traced back and solved quickly. The customer wants to rely not only on the measurement results but also on the quality of the analyser.

The second step for this is the certification of each system. Each component, the sensor as well as the dispersing unit, must fulfil the specifications regarding optical properties and performance. Only if all results are within the limits and also reference materials have been measured correctly can the certificate be awarded. This certification process must be repeatable and as reproducible as the measurement results.

As **reference materials** several materials were tested: quartz, latex, silicon carbide (SiC), silicon dioxide (SiO_2) and others. Ideally, reference materials for laser diffraction should be spherical. For wet dispersing systems, in addition, a value for the particle density near to the density of the dispersion fluid is required to avoid sedimentation in the suspension. In dry dispersing systems, comminution or electrostatic charging of the particles must be avoided. Long-term stability of the material is demanded and the price must be reasonable as dry dispersion uses also larger quantities for increased statistics.

As an alternative to reference materials, reticles are sometimes suggested. Reticles are optically inactive plates with well-defined particle size distributions on them transferred e.g. from a high-precision photographic original by a photochemical process. Some properties, however, are unsatisfactory: The influence of the dispersing unit is not under supervision at all, with larger particles the number of illuminated particles is rather small and the stationary distribution may cause weighting errors as the laser beam often is of higher intensity in the centre than at the edge.

As a de facto standard only SiC and SiO_2 have been established as reliable reference materials, but the development towards high-quality reference materials will continue.

Today's applications

With the technology the field of applications grew. Today there is a growing variety of dispersing units and system options. In addition to fine and coarse dry and water- and solvent-based wet dispersing systems devices for metered dose inhalers (MDI) and sprays are available, automatic sampling is provided and even real in-line application of laser diffraction is in place.

Fig. 8 Current off-line technology (i.e. lab-applications) for wet dispersion (Sympatec HELOS/BF with QUIXEL)

E.g. for cement industry dry measurement is a well-established application nowadays. An automated system can analyse up to 100 samples per hour allowing for an exact monitoring of the production process. These types of analyses today are improved by real in-line measuring systems that are integrated into the production pipeline. Because of in-line sampling and guaranteed system-to-system-comparability this approach avoids sophisticated and expensive sample transportation but fulfils the demands for qualitative results.

The challenges of pharmaceutical sprays and inhaler powders are, that not only the particle size distribution of the whole shot is to be measured but also the changes of the particle size during the shot. The analyser measures the particle size every half millisecond, i.e. 2000 times in a second, providing a detailed view on the changes in the aerosol and the possibility to improve the outlet of the spray or powder in order to maximise the pharmaceutical effect.

Latest measuring systems are completely supported and adjustable from a database-controlled software [9]. Handling is easy and results are presented in a way that the important figures or the details of interest are visible immediately. With network and database support sophisticated analysis, remote system control and even fully automatic process control with means of a programmable logical control (PLC) is available.

Application is possible in hazardous areas and systems are able to fulfil good manufacturing practice (GMP) standard. Pharmaceutics and chemistry are the current main application fields, followed by metal powders, minerals and raw earth materials, toner, pigments and cement, food, e.g. coffee and chocolate, and many others. And the field is growing because of speed,

reliability, applicable size range and formerly unknown reproducibility and comparability of LD particle size analysis.

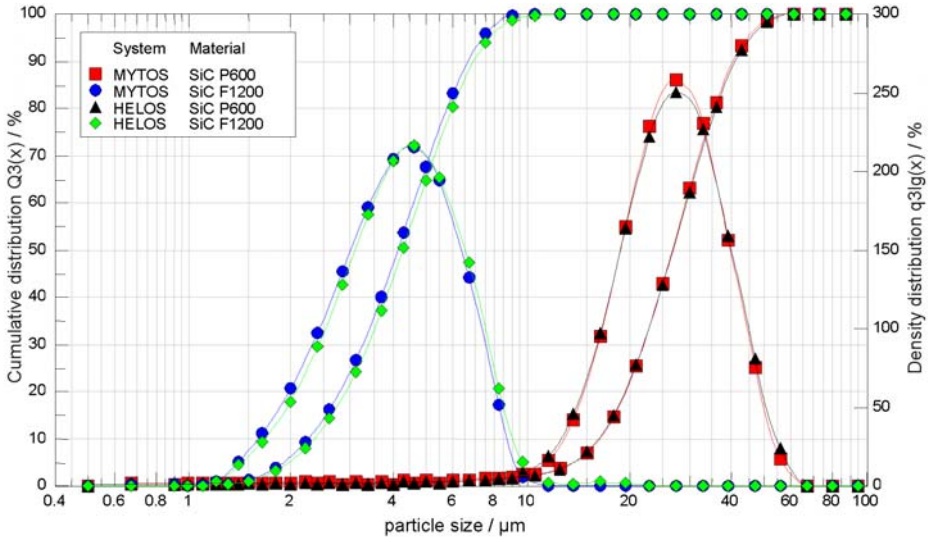

Fig. 9 System-to-system comparability: off-line HELOS & RODOS and in-line MYTOS & TWISTER

On-line and in-line applications are ready today [10]. To gain information about the particle size not only the analyser has to be of superior quality. Also the sampling and sample handling is crucial for good results. Sampling must be representative to make sure that the analyser measures not just an arbitrary particle size distribution but the true one of the process. Sample transportation and dispersion enable the analyser to measure single particles without agglomerates, losses and dilution.

The new millennium will bring the new ISO standard 13320 for particle size analysis with laser diffraction and a movement towards high-quality analysers that are even simpler to use but more reliable and comparable.

Summary

Based on the classical set up of laser diffraction instruments some currently discussed questions of particle size analysis are examined. It is shown that highest accuracy can only be achieved by high quality components and a measuring principle that sticks close to the physical background. Combination of different methods or simplification of the applied technology decreases the quality and approvability of results.

Although Mie in theory allows for more precise analysis of light scattering effects practically it is limited to very few applications in comparison to parameter-free Fraunhofer evaluation because of preconditions.

Modern validation and quality standards for PSA instruments are presented as well as an overview over state of the art LD-technology.

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