LASER DIFFRACTION FOR PARTICLE SIZE ANALYSIS AT ABSOLUTE PRECISION

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ABSTRACT

Since its introduction in the early seventies laser diffraction has developed to the dominating technique for particle size analysis. While reproducibility and comparability of this method was the main interest in the first three decades, today the requirements are mainly tending towards the absolute precision of the results with respect to the standard meter.

The new HELOS/R family of laser diffraction sensors is exactly addressing this requirement. After its introduction at POWTECH 2008 the sensor family has been presented completely at the ACHEMA 2009. Before, all components of the laser diffraction system had undergone a radical analysis and has been developed further to absolute precision: the light source, the beam generation, the Fourier optics, the multi-element detector, the electronics and data acquisition, and especially the inversion algorithm for the evaluation of particle size distribution from the intensity data. Special importance has been taken on the modelling of the optical setup and the verification of the optical models. The result is, that the existing laser diffraction sensors already show an excellent absolute accuracy.

For the HELOS/R series the goal was to improve the absolute accuracy to ±1% of the "truth". This guaranties an optimum comparability to other methods, e.g. dynamic image analysis.

The new completely renovated evaluation algorithms now offer the calculation of particle size distributions for the complete range from 0.1 µm to 3500 µm for the optical models Fraunhofer and Mie theory. For the first time the Mie theory has been verified over the complete size and refractive index range by precision analysis with more than 40 000 exactly calculated test data sets and extended to very coarse highly transparent particles. In addition the algorithms have been expanded to the exact measurement of extremely wide size distributions: Up to 217 independent intensity values of several measuring ranges can be acquired and converted to a single particle size distribution at high reproducibility. Statistical information of the raw data is used to optimize the inversion algorithm further. Dry and wet dispersion can be applied using the known and well established dispersers.

1 INTRODUCTION

Ideally a measuring device is both: accurate and precise. For a particle sizing system this means accurate with respect to the standard meter and precise in terms of reproducibility for the same and comparability for different instruments.

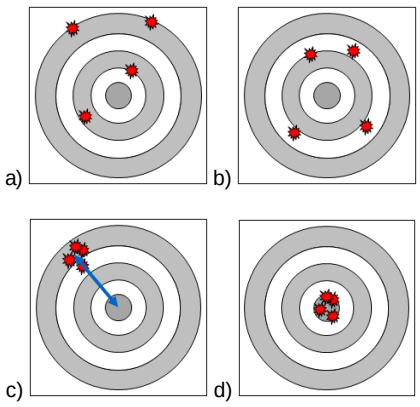

Fig. 1: a) Neither precise nor accurate, b) not precise but accurate mean value, c) precise but not accurate due to a bias, d) the goal: precise and accurate

Although a typical laser diffraction analyzer (LDA) consists of a few parts: the light source, the particle disperser, the Fourier optics, the multi-element detector, data acquisition electronics and the inversion algorithm on a computer, it was difficult on early LDAs to get reproducible results. So the main focus was precision (fig. 1c) for the first three decades after the introduction of this technology in the seventies.

The break-through was accomplished by testing the complete system of particle size analyzer and dispersing device with reference materials. For this purpose stable but not necessarily spherical powders have been precisely certified to a reference particle size distribution obtained as an average for a specific instrument family or type (Röthele 1992). Relative standard deviations for the x_{10}, x_{50} and x_{90} percentiles of less than 1 % could be achieved, even between different units of the same instrument type and in

combination with various dry or wet dispersers (Witt 1995). The LDA became a sensitive tool for particle size analysis in the laboratory and process environment and laser diffraction the dominating technique.

Today, LDAs of various vendors are often used to characterize specific products on a global scale. This is still handicapped by the unknown bias of the individual instruments. So today's focus is to keep or improve precision but to add accuracy with respect to the standard meter, and it is not surprising that the recently published ISO standard for LD (ISO 13320: 2009) is addressing this subject expressively.

2 INSTRUMENTATION

The recent development of a new LDA called HELOS/R was specially focused on these requirements. For this purpose, all components of the existing LDAs had undergone a radical analysis in terms of accuracy.

2.1 Optical Set-up and Data Acquisition

The measured particle size is linearly depending on the wavelength of the light source. Today semiconductor lasers are widely used as they are much smaller and less power consuming than HeNe-lasers. But their wavelength depends on the manufacturing process and varies with temperature. Furthermore the tiny resonator limits the stability of the output modes. This is why a HeNe-laser was used instead. The absolute wavelength is 632.8 nm (± 10-8/K). The error is negligible with respect to all other errors. In combination with a patented fiber optical mode filter an almost perfect plane wave is generated to illuminate the particles. This combination has already been proven to satisfy the requirements for particle size analysis (PSA) from 0.1 µm to 8 750 µm using a single wavelength (Heuer 1995).

The conversion of the angular distribution of the scattered intensity to the spatial intensity distribution on the detector location is done by a Fourier optics. ISO 13320 offers two choices, the standard and the inverse Fourier set-up.

The latter is often preferred as it only requires a single lens and separate detectors can be arranged over a wide range of angles. This set-up is handicapped by the fact that the distance of the particles to the detector defines the effective focal length, which is reciprocal to the measured particle size. So the position of the particles has to be precisely controlled. Narrow glass cuvettes are frequently used. They are critical optical devices which can influence the scattered light substantially.

So not only in terms of accuracy the standard set-up of the Fourier optics is advantageous. Here the particles are illuminated by a parallel laser beam, the position of the particles can be varied without influencing the result and even spatially extended aerosols can be measured.

Specially designed optical modules precisely image the diffraction pattern on the detector. Several optical modules can be mounted on a carousel to change a measuring range within seconds.

A single multielement-detector with semi-circular detector elements and auto-centring was given preference with respect to a multi-detector arrangement in combination with individually distributed detectors. The precision of semiconductors can be controlled down to some nanometers and the quantum efficiency of a single device is more homogeneous and needs less adaptation than discrete sensors.

The complete light path from the light source to the detector including all optical surfaces has been evaluated with the help of ray tracing and latest optical design software, resulting in optical models for each combination of measuring range and disperser. Also the exact position of the detector with respect to the lens was calculated from first principles.

The electronics used for the conversion of the photo-currents to digital numbers is permanently measuring 2000 intensity distributions per second at a very low noise level, with a linearity error of better than 10^{-5} and a wide dynamic range.

Figure 3: A gravity disperser is used to capture images of the same particle from different aspects. The 5 binary images are acquired in direct sequence at about 500 fps.

2.2 Evaluation

The evaluation software offers now two new modes: the parameter free FREE (Fraunhofer Enhanced Evaluation) mode and the Mie Evaluation Extended to MIEE which requires as input a complex refractive index of the material analyzed. The MIEE algorithm has been verified with a Mie validation data set, which has been established using the precision calculator CALC with more than 44 000 entries of different Mie parameters, optical parameters and scattering angles and covers particle sizes from 1 nm to 10 mm and 0.2 to 3.0 for the real part and 0; 10^{-5} to 8 for the imaginary part of the refractive index (Stübinger 2008).

Although each of the overlapping measuring ranges covers about 2½ decades in size, sufficient for most of the typical PSD, wider size distributions can be measured by combining a selection of overlapping measuring ranges to one single result for all evaluation modes. Up to 217 directly measured intensity values are available as input. The signal statistics is used to optimize the inversion procedure.

2.3 Realization

The HELOS/R series is housed in a small table top metal housing.

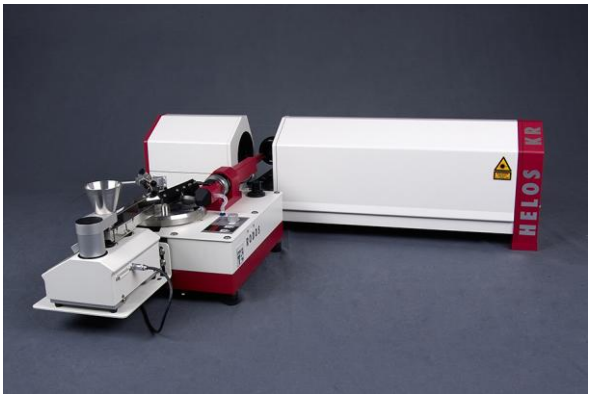

Fig. 2: HELOS/KR 0.1 µm to 8750 µm with dry disperser RODOS,

Fig.3: HELOS/BR 0.1 µm to 875 µm with dry and wet disperser OASIS combining RODOS & SUCELL

3 RESULTS

10 different instruments have been set-up to first principles (for the lenses used). Fig. 3 show that the FREE results for SiC samples agree within < 0.5% for x10 to x90.The result is independent of the measuring range (fig. 4), as long as it covers the distribution width. The MIEE results are almost identical for this sample.

The accuracy of the absolute scale was checked e.g. with spherical mono-disperse particles. The sphericity and size was investigated by the dynamic image analyzer QICPIC.

The absolute size was refined by fitting the simulated intensity distribution to the measured intensity distribution, by varying the complex refractive index and the distribution width of an assumed lognormal distribution for these monodisperse materials. Fig. 5 shows that the Mie intensity distribution with its several peaks allows for a determination of the absolute size x of better than 0.5%. This method is more sensitive than just the variation of the focal distance, which does not show changes over a variation of ± 1%. No inversion algorithm is involved, so the set-up can be aligned to absolute scale independent of the evaluation algorithm.

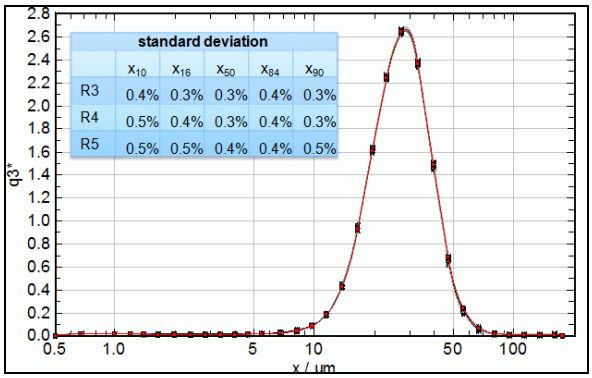

Fig. 3: Three different types of dry dispersers on 10 different instruments, 120 plots, σ<0.5%;

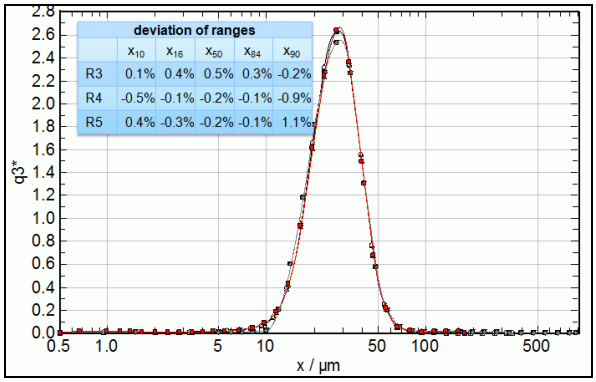

Fig. 4: Comparison of the results of different measuring ranges, σ ≅ 0.5% typ.

As the inversion procedures are optimized for distributions of certain widths, monodisperse material cannot be used for a direct verification. The recently introduced picket fence distributions (PFD, Witt 2008) will help to overcome this situation in the near future.

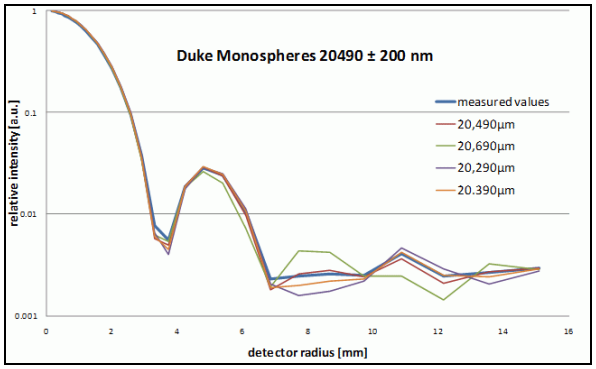

Fig. 5: Simulation parameters are deduced from the best fit to the measured data, → n = 1.585 + 0i in water with n = 1.330) and distribution width w = $0.7 \cdot 10^{-3}$

As the accuracy of these distributions is independent of the width of the distribution, they also serve as a test for the complete LDA including the dispersion device.

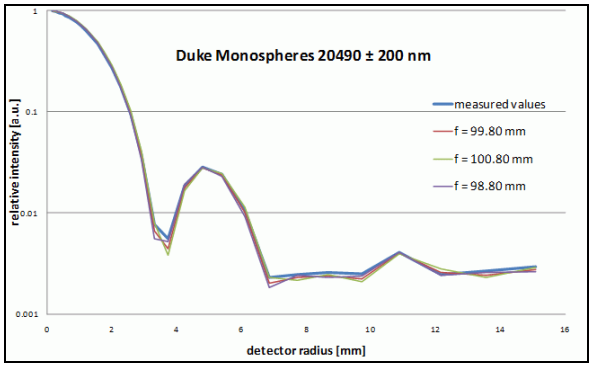

Fig. 6: Simulated variation of the focal distance within ± 1%

The output of a PSA is Q3(x) and not only x. So the accuracy of the quantity has been checked by various mixing series with typically 5% increments in mass. The results are influenced by the particle transport within the dispersing device. First results of mixtures of glass beads show agreement between the predicted and measured values to typically ± 2% for HELOS/R and the wet disperser QUIXEL.

4 CONCLUSIONS

The presented LDA has been optimized for precision and accuracy on an absolute scale. First results show that deviations in x of about ± 1% are achievable with respect to the standard meter and ± 2% in Q3. The presented instrument family offers enhanced Fraunhofer (FREE), extended Mie evaluation (MIEE) and the combination of measuring ranges. It covers a size range of 0.1 µm to 8750 µm and is fully compliant with ISO 13320: 2009. Validation packages are available as an option for pharmaceutical applications.

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