IMPROVED STANDARDS IN LASER DIFFRACTION

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ABSTRACT

A laser diffraction system is based on first principles. In a strict sense a calibration is not required, as the measured particle size is depending on fixed and usually precisely known instrument parameters - the wavelength of the light, the geometry of the detector and the focal length of the system. In practice the results are affected by the optical model and inversion procedure used, the dispersion, sample transport, velocity bias and segregation errors etc.. Usually the latter are dominating the errors of the sensor by far. So the verification of the complete laser diffraction system is the main challenge and was addressed with our first paper titled “Standards in laser diffraction” already in 1992 on the PARTEC in Nuremberg. The proposal was a “standard material” of well absorbing spherical particles with a wide size distribution linear in $Q_3(lg(x))$, covering more than one decade in size, traceable to the standard meter. This is still not available.

Within the last 15 years several attempts have been made instead: spherical (glass) beads standard materials of various compositions mainly testing the sensor to an absolute scale, and reference materials of non-spherical particles, testing the complete measuring system towards a reference result. Common to the first group of materials is that they are either only available as mono-disperse (wet) particles – difficult to be used in a particle sizing instrument usually optimised for detecting wide size distributions – or that the error bars in the specifications are very large with respect to the observed reproducibility of this method.

This article will give answers, how the precision of standard materials can be improved today, how they can be precisely traced to the standard metre and how they can be designed to test not only the sensor but the overall system’s performance at high precision. Special emphasis has been put on wide size distributions, as the characterisation of these distributions typically show large errors. They can be overcome with a specific distribution type, the "Picket Fence Distribution" (PFD, also denoted as "Lattice Fence Distribution", LFD) composed from a mixture of well traceable mono-disperse spherical reference materials, and results are shown for various compositions of PFDs. Possible theoretical limits for the precision of the quality control of laser diffraction systems are deducted from these investigations and compared with measured data from the new HELOS/R sensor family.

1 INTRODUCTION

Although laser diffraction (LD) for particle size analysis (PSA) is based on first principles and does not require calibration in a strict sense, many sources of error may affect the correctness of the results, such as the particle transport, the dispersion, the optical set-up, the data acquisition and the mathematical treatment, especially the inversion procedure. While the improvement of the reproducibility and the system-to-system comparability was the main issue for more than two decades after the introduction of LD for PSA, the traceability to the standard meter has become the dominating question since the last decade. In a first paper Röthele and Witt (1992) displayed the superiority of the use of powders over reticles and pin-holes. They proposed a “standard material” of well-absorbing spherical particles with a wide size distribution linear in Q3(lg(x)), covering more than one decade in size, traceable to the standard meter. This material is still not available. Currently two species of materials are in use: reference materials (RMs) and standard reference materials (SRMs).

2 REFERENCE MATERIALS

Today stable materials with material properties and particle size distributions (PSDs) close to the target distributions are the preferred choice for the daily verification of a system’s performance. These RMs are typically non-spherical and referenced relative to a specific system status or group of instruments. Since 1992 we have introduced a variety of RMs in the size range from 0.1 µm to above 1 mm (fig. 1). For the stable silicon carbides (SiC) relative standard deviations σ have been determined to $\sigma < 0.01\%$ for the same sample and about 0.3 % for different samples, making possible an improvement of the system-to-system comparability of the HELOS LD PSA systems to below 1 % (including sampling errors) by introducing RMs as the final check in our systems integration.

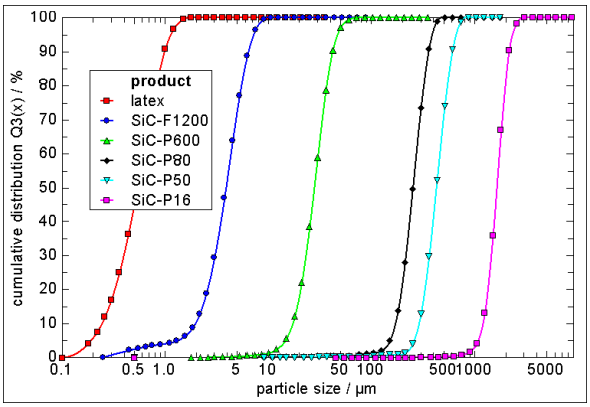

Fig. 1: Example of RMs used for secondary tests of the HELOS LD instruments family with x_{90}/x_{10}= 2 to 3.5.

The distribution width of these RMs defined by x_{90}/x_{10} is in the range of 2.05 to 3.5, which is compliant with the requirements of the new standard ISO 13320: 2009-10. This is much smaller than the width of most real products, as displayed in fig. 2. As LD instruments are challenged more by wider PSDs, the results of instruments for wide size distributions can differ, even when checks with more narrow PSDs have perfectly matched. So checks with wide PSDs are generally required to establish confidence in the proper operation of the instrument. We are using special RMs, e.g. SiC-M3 with a PSD close to cement PZ35 and x_{90}/x_{10} > 30, as shown in fig. 2.

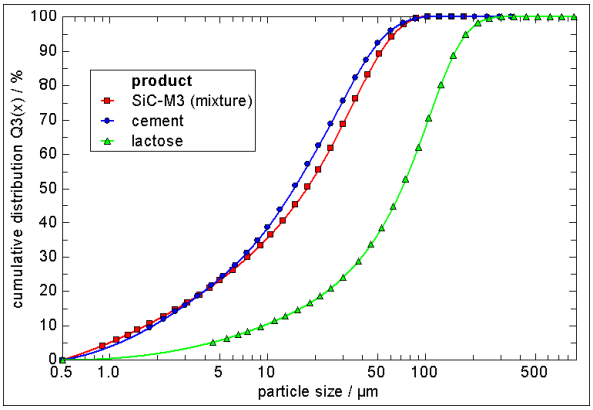

Fig. 2: Wide PSDs of some real materials compared with the RM SiC-M3 with x_{90}/x^{10} > 10.

3 STANDARD REFERENCE MATERIALS

While non-spherical RMs check the LD instrument at conditions close to real operation, traceability to the standard meter is difficult and limited to applications using the same dispersing device for the LD and a traceable method, e.g. dynamic image analysis (DIA) as shown by Köhler (2007). Even then systematic errors, e.g. of the disperser, remain undetected.

So, spherical monodisperse materials (SMMs) are the optimum choice for the primary check. As any segregation, velocity bias and inhomogeneous illumination effects are negligible, the sources of errors are reduced and the PSD can be measured at high precision. Unfortunately LD instruments and their inversion algorithms are optimized for (real) PSDs having a certain width. ISO 13320 requests standard reference materials with x_{90}/x_{10} of 1.5 to > 4 for instrument qualification. Materials of this type are available, but as the accuracy of the certification procedure becomes worse with increasing width of the PSD, the published specifications show in general inacceptable large error bars. How can we overcome this situation?

3.1 New Approach: Picket Fence Distributions (PFDs)

The idea is to compose a wide size distribution from a well defined mixture of precisely qualified SMMs. The accuracy of the resulting distribution is then only dependent on the accuracy of the SMMs, their mass density and the weighing process, all of which can be controlled precisely. Mixing SMMs with equally spaced particle sizes $lg(x_{50})$ would create a picket-fence-like looking distribution $q_3^*(x)$ of the peaks of the individual SMMs. So $Q_3(lg(x))$ would become a step distribution. PFDs with wide distribution widths are possible without significant reduction of accuracy. The main questions are: 1) is it possible to create such PFDs, 2) how will the inversion procedure react on this type of distribution, and 3) what accuracy can be finally obtained for a typical LD system?

3.2 The Spherical Monodisperse Material (SMM)

For the individual pickets of the PFD, stable, spherical SMMs are necessary with a well defined x50 and mass density ρ. Several materials have been investigated, e.g. resorcinol formaldehyde or ball mill beads (ZrO2). A currently very promising candidate is glassy carbon which does not swell in water.

The characterization was performed in steps. 1) High-speed dynamic image analysis (DIA) was used to characterize large quantities of the particles in PSD, aspect ratio χ(x) and non-spherical fractions. Fig. 3 shows the PSD of a SMM together with its aspect ratio. 2) The absolute size was determined by two methods: a) microscopy of particle-rows with a certified micro-ruler (fig. 4) and b) by LD. For the latter the SMM was brought in suspension and exposed to a convergent HeNe-Laser beam in a closed loop set-up. The scattered intensity distribution was measured in a distance of 3.970 m and fitted to an intensity distribution which was calculated through application of the Mie theory, with the size distribution measured by DIA as a starting point for the fitting

procedure. Thus errors resulting from lenses or the inversion procedures were avoided. The absolute values for the x_{50} could be specified to an accuracy better than 1 % for sizes > 30 µm. Smaller particles will have to be investigated subsequently.

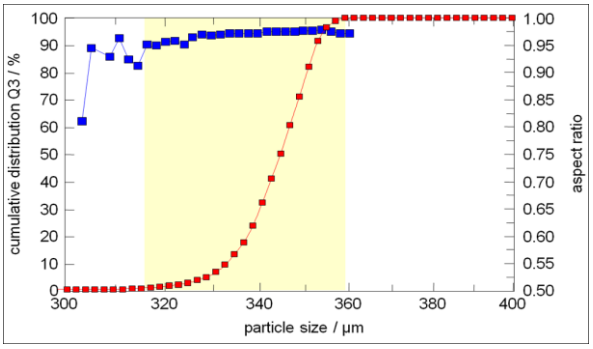

Fig. 3: Resorcinol formaldehyde beads, size distribution x_{90}/x_{10} = 1.06, and aspect ratio χ(x) = 0.95 (upper curve, yellow area) for 1% < Q_3(lg(x)) < 99.9%.

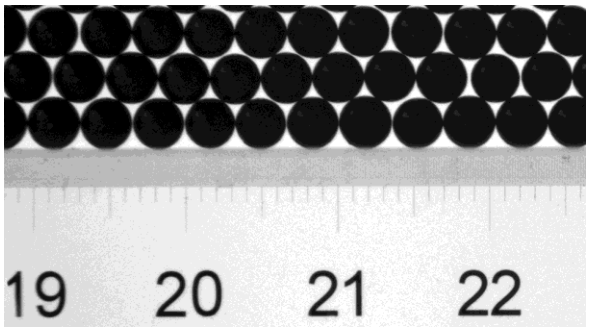

Fig. 4: Resorcinol formaldehyde beads, micro-ruler with particle-rows.

As a result SRM using a PFD with overall errors of below about 1% in x and Q3 should be possible.

3.3 Simulation Results for Picket Fence Distributions (PFDs)

Computer simulations were used to investigate the influence of the parameter choice to the expected results. Based on the precision Mie theory presented by Stübinger (2008) a special software was developed allowing for the calculation of the intensities for a given detector geometry and arbitrary PSDs. The intensities could be directly compared with the measurement or used as inputs to the evaluation software, e.g. of the HELOS LD sensor. In the latter case the PSD resulting from the inversion algorithm could be directly compared with the input PSD used for the simulation. So the influence of the design of the PFDs and possible sources of error could be investigated. In a first step, a concrete PSD of a SMM was used to prove the correctness of the simulation method by comparing measured and calculated intensities. In a second step, PFDs were designed and simulated as mixtures using the measured PSD shape of the SMM of fig. 3.

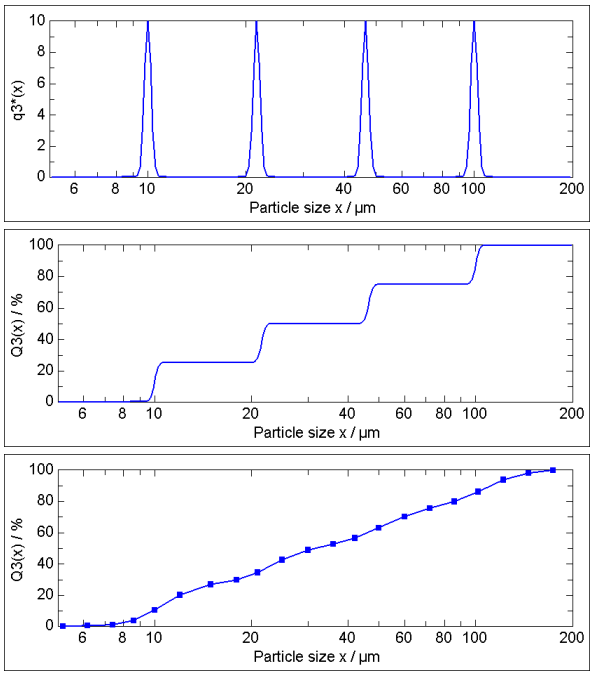

Fig. 5: Simulated PFDs composed from 4 SMMs. Input PFD: top: q_3*(x), middle: Q_3(lg(x)), bottom: HELOS LD result for measuring range R4 (0.5/1.8 – 350µm).

The inversion of a PFD covering one decade with four uniformly distributed SMMs (fig. 5) shows a structure in the calculated PSD, while a PFD with seven SMMs (fig. 6) cannot be resolved in this set-up any more and a linear Q_3(x) distribution is reported

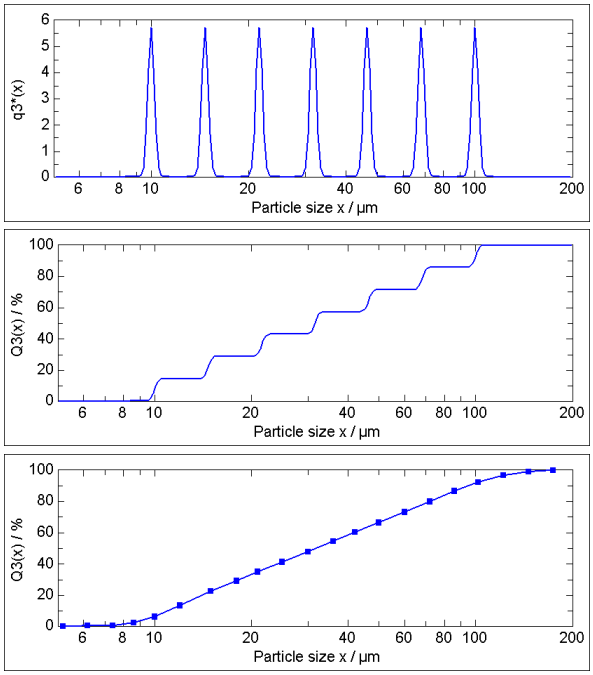

Fig. 6: Simulated PFDs composed from 7 SMMs. Input PFD: top: q_3*(x), middle: Q_3(lg(x)), bottom: HELOS LD result for measuring range R4 (0.5/1.8 – 350µm).

The influence of the width of the PFD, the number of SMMs, their distribution in x and the distribution type, e.g. log-normal, linear $Q_3(lg(x))$ etc. have been investigated. The simulations revealed that in most cases the inversion procedure reacts quite good-natured to the input of the PFD, as shown in fig. 5 and fig. 6.

The results are not sensitive to the width of the SMMs; small deviations have been observed. So the width of the SMMs can be made as small as possible, allowing for an optimum PSD determination of the individual SMMs. More critical is the selection of the x50 of the individual fractions. Here the displacement of one SMM leads to more distortion of the inversion result. Generally, the behavior of a log-normal distributed q3*(x) PFD was observed to be less critical than a PFD constant over lg(x), PFDs with smaller widths behave better than PFDs with a wider size range.

For a strong test a PFD covering one decade in size composed of seven equally spaced SMMs was found to compromise well between the requirements for a wide size range, a small number of SMMs and an achievable accuracy.

4 CONCLUSIONS & OUTLOOK

Highly stable reference materials such as the presented SiC have proven their excellent suitability for secondary checks over the last 20 years. They help to improve the system-to-system comparability to $\sigma < 1\%$ and provide a cost-efficient complete check of all system components included. For an optimum check wide sized distributions with $x_{90}/x_{10} \geq 10$ are preferred. For the primary validation of LD instruments spherical standard reference materials with wide PSDs should be used. The proposed PFD composed from mixtures of SMMs can overcome the limited accuracy of the currently existing materials with continuous PSDs, as the size of individual SMMs can be traced to the standard meter at high precision. For the LD sensor HELOS a minimum of seven uniformly over lg(x) distributed fractions was sufficient to simulate a linear $Q_3(lg(x))$ distribution covering one decade. The inversion procedure of this instrument was capable of reproducing $Q_3(lg(x))$ within ±1% using an errorless simulated scattered intensity pattern. This value defines the lowest possible error limit for this PSD and set-up. It will be interesting to detect how close one can get to this limit with the first real SRM basing on a PFD.

Outlook: The production of the first sets of SMM has started in the regime of some kilograms. The release of a fully certified SRM with a PFD covering one decade is expected in 2010. If the results of the simulation are confirmed, other size ranges and PSD widths will follow as well as the production of larger quantities.

REFERENCES

KÖHLER, U., LIST, J., WITT, W., (2007), Comparison of Laser Diffraction and Image Analysis under Identical Dispersing Conditions, PARTEC 2007, Nuremberg, Germany

RÖTHELE, S., WITT, W., (1992), Standards in Laser Diffraction, 50th European Symposium Particle Characterisation, Nuremberg, Germany

STÜBINGER, T., KÖHLER, U., WITT, W., (2008), 100 Years of Mie Scattering Theory: Expanded Size Range by Extreme Precision Calculations, PSA 2008, Stratford-upon-Avon, England