

Improved Standards in Laser Diffraction

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ABSTRACT

Since the introduction of laser diffraction for particle size analysis in the beginning of the 1970's the verification of the complete laser diffraction system is a challenge. The first paper titled "Standards in laser diffraction" has addressed this subject already in 1992 at 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 metre. This material is still not available. Within the last 15 years several attempts have been made: spherical 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 large with respect to the observed reproducibility of this method. The group of non-spherical particles has shown its usability within the last 20 years of our experience as a well-suitable testing tool for the overall system's performance at very high precision, but with the lack of not being directly traceable to the standard metre. This article will give answers, how today the precision of standard reference materials can be improved, 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.

Keywords: Reference Material, Standard Material, Laser Diffraction, Particle Size

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 metre has become the dominating question since the last decade. In a first paper Röhle 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 $Q_3(\lg(x))$, covering more than one decade in size, traceable to the standard metre. 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 it is widely accepted that stable materials having 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 are 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 (Figure 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.

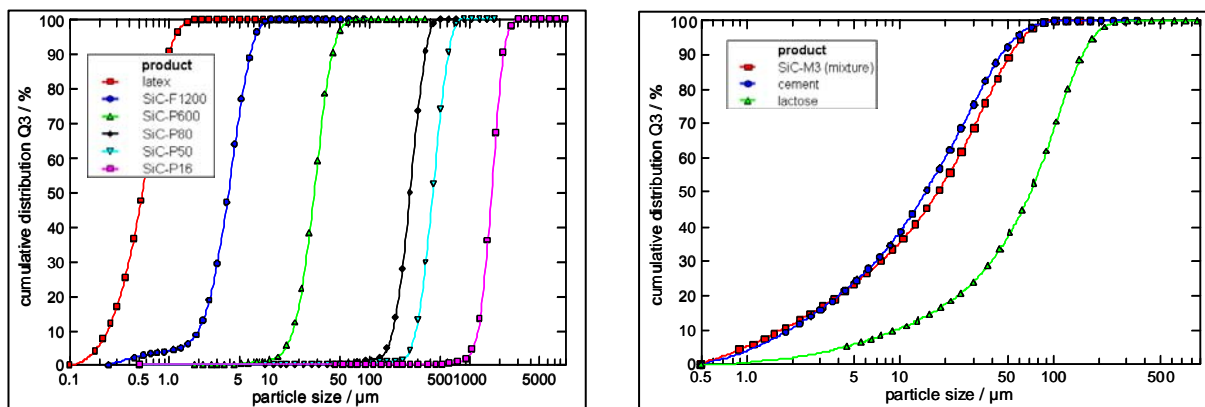


Figure 1. left: Example of RMs used for secondary tests of the HELOS LD instruments family with $x_{90}/x_{10} = 2$ to 3.5. right: Wide PSDs of some real materials compared with the RM SiC-M3 with $x_{90}/x_{10} > 10$

The width of the distribution 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 coming standard ISO/DIS 13320. Unfortunately this is much smaller than the width of many real products, as displayed in Figure 1b. 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 Figure 1b.

3 STANDARD REFERENCE MATERIALS

While non-spherical RMs check the LD instrument at conditions close to real operation, traceability to the standard metre is difficult and limited to applications using the same dispersing device for the LD and 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 mono-disperse 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. Many traceable monodisperse materials are commercially available. Unfortunately LD instruments and their inversion algorithms are optimised for (real) PSDs having a certain width. ISO/DIS 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 certification procedure becomes worse with increasing width of the PSD, the published specifications show in general unacceptable large error bars. How can we overcome this situation?

3.1 New Approach: Lattice Fence Distributions (LFDs)

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 upon 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 lattice-fence-like looking distribution $q_3(x)$ of the peaks of the individual SMMs. So $Q_3(\lg(x))$ would become a step distribution. LFDs with wide distribution widths are possible without significant reduction of accuracy.

The main questions are: is it possible to create such LFDs, how will the inversion procedure react on this type of distribution, and what accuracy can be finally obtained for a typical LD system?

3.2 The Spherical Monodisperse Material (SMM)

For the individual pickets of the LFD, stable, spherical SMMs are necessary with a well defined x_{50} and mass density ρ . Several materials have been investigated: glass beads and glassy carbon beads showed significant broken (non-spherical) fractions, ball mill beads (ZrO_2) showed unsatisfactory sphericity and the density of metal powders was too high for most of the wet loops, etc. The most promising candidate we have found was stabilised polystyrene, which does not swell in water. Special physical-chemical processes have been developed to get very narrow size distributions of nearly ideal spherical particles at a given size in the range from about 1 to 1000 μm , transparent or with a specific colour including black. The material itself provides the colour, no pigments are used.

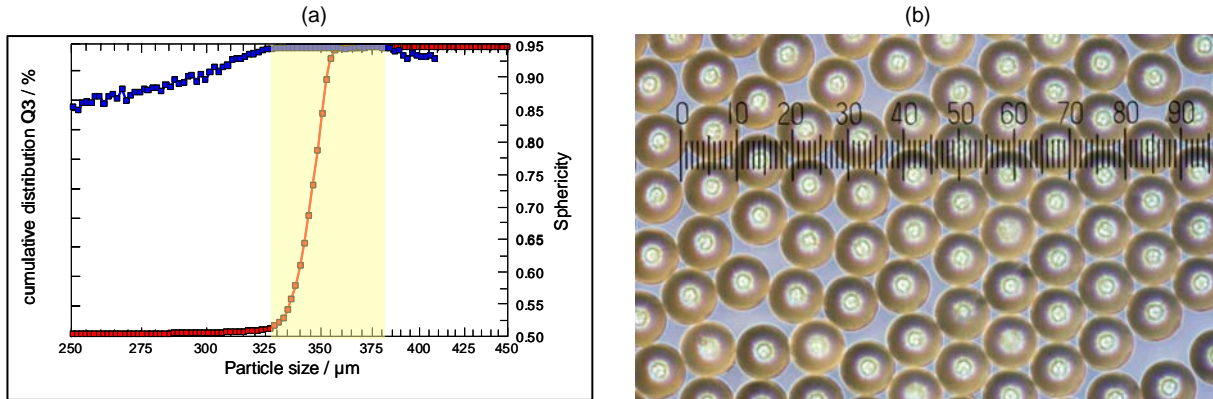


Figure 2. Monodisperse polystyrene beads, (a) Size distribution $x_{90}/x_{10} = 1.053$, and sphericity $\chi(x) = 0.95$ for $1\% < Q_3(\lg(x)) < 99.9\%$, (b) microscopic image.

The characterisation was performed in steps. 1) High-speed dynamic image analysis (DIA) was used to characterise large quantities of the particles in PSD, sphericity $\chi(x)$ and non-spherical fractions. Figure 2 shows the PSD of one SMM together with its sphericity. $\chi(x) = 0.95$ is at the sphericity limit of DIA for the resolution of the used instrument. 2) The absolute size was determined by two methods: a) microscopy of large hexagonal packed areas on a certified reticle by counting the number of particles fitting on a pattern of a defined length 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 4.554 m and fitted to an intensity distribution which was as calculated through application of 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 $> 30 \mu m$. Smaller particles will have to be investigated later. The density was determined to $1.05 \text{ g/cm}^3 \pm 0.5\%$.

So SRM using a LFD with overall errors of below about 1% in x and Q_3 should be possible.

3.3 Simulation Results for Lattice Fence Distributions (LFDs)

As the production of several SMMs with specific particle sizes is time-consuming and expensive, computer simulation was used to investigate the influence of the parameter choice to the expected results. Basing 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 LFDs and possible sources of error could be investigated. In a first step, the PSD of the SMM of Figure 2 was used to prove the correctness of the simulation method by comparing measured and calculated intensities. In a second step, LFDs were designed and simulated as mixtures using the measured PSD shape of the SMM of Figure 2.

The influence of the width of the LFD, 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 showed that in most cases the inversion procedure reacts quite good-natured to the input of the LFD, as shown in Figure 3.

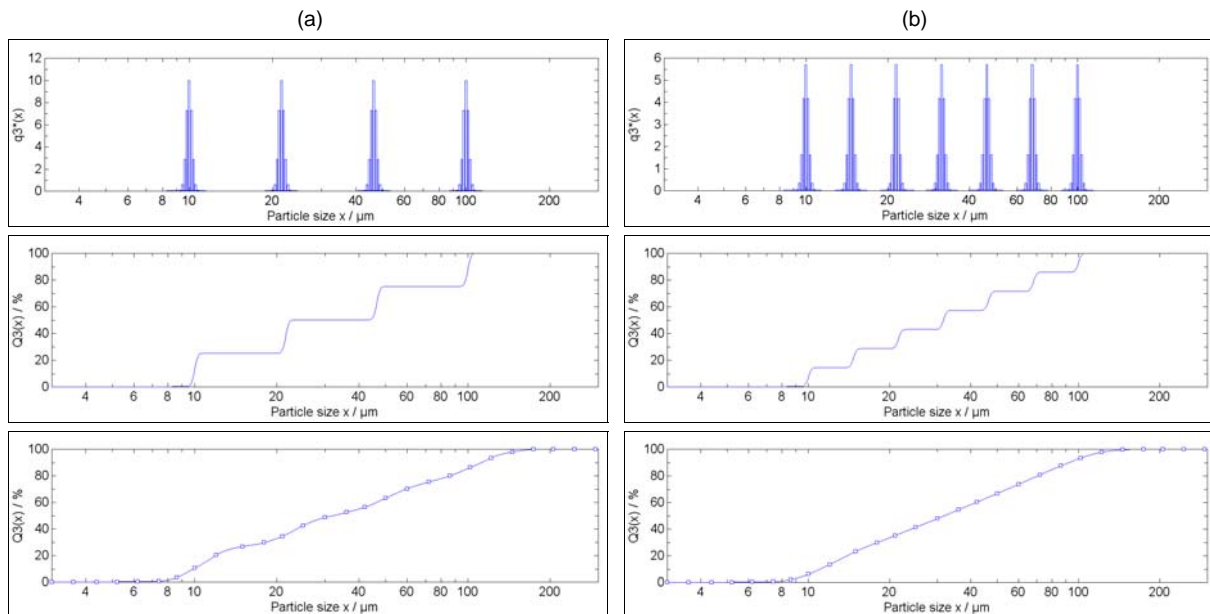


Figure 3. Simulated LFDs composed from 4 (a) and 7 (b) SMMs.
 Input LFD: top: $q_3^*(x)$, middle: $Q_3(\lg(x))$, bottom: HELOS LD result for measuring range R4 (0.5/1.8 – 350 μ m)

The inversion of a LFD covering one decade with four uniformly distributed SMMs shows a structure in the calculated PSD, while a LFD with seven SMMs cannot be resolved in this set-up any more and a linear $Q_3(x)$ distribution is reported. 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 x_{50} of the individual fractions, as shown in Figure 4. Here the displacement of one SMM leads to more distortion the inversion result.

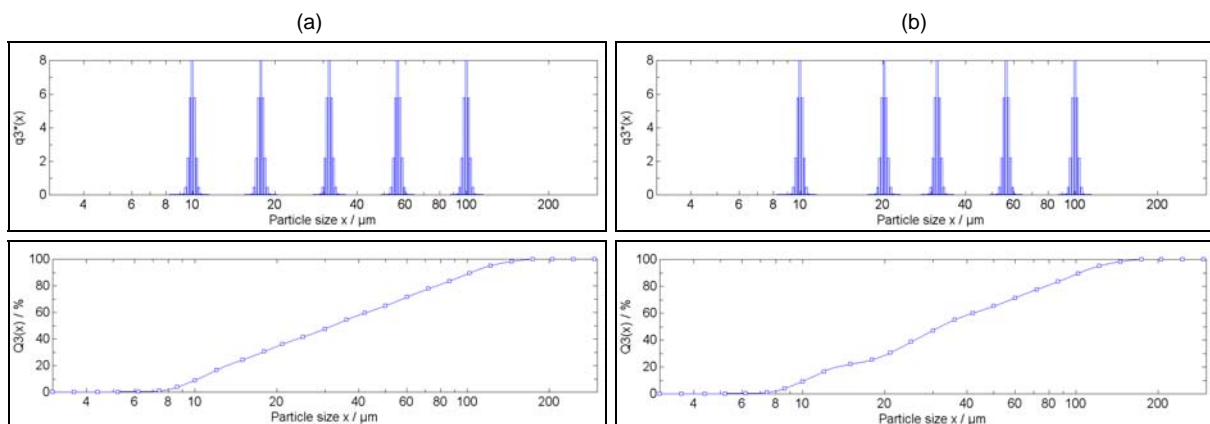


Figure 4. Influence of the distribution of the SMMs vs. size: (a) Equally spaced SMMs, (b) second SMM displaced.
 Top: simulated input LFDs, bottom: HELOS result for measuring range R4 (0.5/1.8 – 350 μ m)

Generally, the behaviour of a log-normal distributed $q_3^*(x)$ LFD was observed to be less critical than a LFD constant over $\lg(x)$, LFDs with smaller widths behave better than LFDs with a wider size range.

For a strong test a LFD 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 the achievable accuracy. Figure 5 shows that for this set-up the maximum difference in $Q_3(\lg(x))$ between the simulated input and the output from the inversion procedure is less than 1% for $[x_{10}, x_{90}]$.

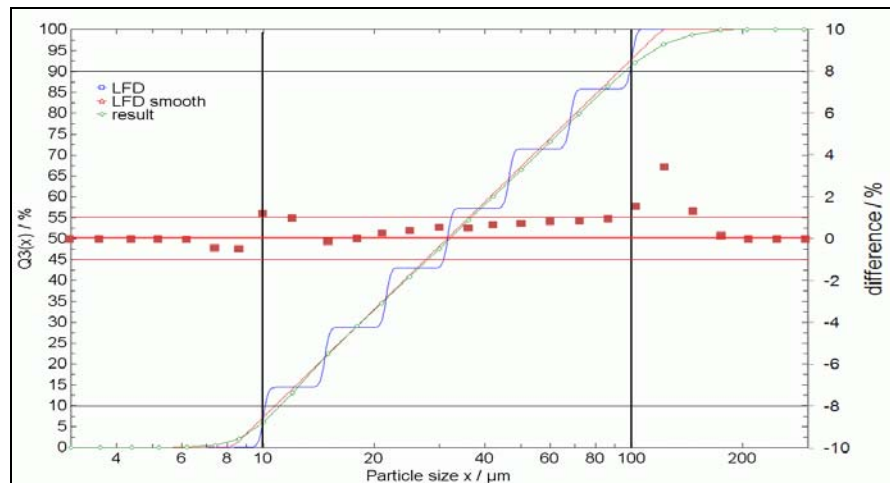


Figure 5. Comparison of the original LFD with seven SMMs over one decade with the result of a real LD instrument (HELOS). LFD: $Q_3(\lg(x))$ of the applied LFD; LFD smooth: $Q_3(x)$ interpolated to the centre of the size classes of the LD sensor; result: $Q_3(\lg(x))$ as output of the LD sensor (including the inversion procedure); squares: difference = LFD smooth minus result

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 complete check of all system components included – at reasonable low costs. 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 lattice fence distributions (LFD) 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 metre 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 $\pm 1\%$ 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 LFD.

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 LFD covering one decade is expected for the beginning of 2009. If the results of the simulation are confirmed, other size ranges and PSD widths will follow as well as the production of larger quantities.

5 REFERENCES

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